

investigation. I do not therefore either affirm or deny his conclusions. I do affirm that they are supported by a rope of argument to the strength of which the one strand which I have tested contributes nothing. It is difficult to believe in discontinuities which their discoverer himself abandons in the heat of argument by showing that his original solution may be replaced by another in which three may be entire curves and parts of two others replaced by two only.

XX. *On the Theory of Surface Forces.—II. Compressible Fluids.* By Lord RAYLEIGH, *Sec. R.S.**

IN the first part of the paper published under the above title (Phil. Mag., Oct. and Dec. 1890) the theory of Young and Laplace was considered, and further developed in certain directions. The two leading assumptions of this theory are (1) that the range of the cohesive forces, though very small in comparison with the dimensions of ordinary bodies, is nevertheless large in comparison with molecular distances, so that matter may be treated as continuous; and (2) that the fluids considered are incompressible. So far as I am aware, there is at present no reason to suppose that the applicability of the results to actual matter is greatly prejudiced by imperfect fulfilment of (1); but, on the other hand, the assumption of incompressibility is a somewhat violent one, even in the cases of liquids, and altogether precludes the application of the theory to gases and vapours. In the present communication an attempt is made to extend the theory to compressible fluids, and especially to the case of a liquid in contact with its own vapour, retaining the first assumption of continuity, or rather of ultimate homogeneity. There will not be two opinions as to the advantage of the extension to compressible fluids; but some may perhaps be inclined to ask whether it is worth while to spend labour upon a theory which ignores the accumulated evidence before us in favour of molecular structure. To this the answer is that molecular theories are extremely difficult, and that the phenomenon of a change of state from vapour to liquid is of such extreme importance as to be worthy of all the light that can be thrown upon it. We shall see, I think, that a sufficient account can be given without introducing the consideration of molecules, which on this view belongs to another stage of the theory.

If p denote the ordinary hydrostatical pressure at any point in the interior of a self-attracting fluid, ρ the density, and V the potential, the equation of equilibrium is

* Communicated by the Author.

$$dp = \rho dV. \quad \dots \dots \dots (1)$$

If, as we shall here suppose, the matter be arranged in plane strata, the expression for the potential at any point is

$$V = 2\pi \int_{-\infty}^{+\infty} \rho' \psi(z) dz, \quad \dots \dots \dots (2)$$

where ρ' is the density at a distance z from the point in question. Expanding in series, we may write

$$\rho' = \rho + z \frac{d\rho}{dz} + \frac{z^2}{1 \cdot 2} \frac{d^2\rho}{dz^2} + \dots,$$

so that

$$V = 2K \cdot \rho + 2L \frac{d^2\rho}{dz^2} + \dots, \quad \dots \dots \dots (3)$$

where

$$K = 2\pi \int_0^\infty \psi(z) dz, \quad L = \pi \int_0^\infty z^2 \psi(z) dz. \quad \dots \dots \dots (4)$$

The integrals involving odd powers of z disappear in virtue of the relation $\psi(-z) = \psi(z)$.

We may use (3) to form an expression for the pressure applicable to regions of *uniform* density (and potential). Thus, integrating (1) from a place where $\rho = \rho_1$ to one where $\rho = \rho_2$, we have

$$\begin{aligned} p_2 - p_1 &= \int \rho dV = [\rho V] - \int V d\rho \\ &= 2K(\rho_2^2 - \rho_1^2) - \int d\rho \{ 2K\rho + 2L \frac{d^2\rho}{dz^2} + \dots \} \\ &= K(\rho_2^2 - \rho_1^2) - \int d\rho \{ 2L \frac{d^2\rho}{dz^2} + \dots \}. \end{aligned}$$

In the latter integral each term vanishes. For example,

$$\int \frac{d^2\rho}{dz^2} d\rho = \frac{1}{2} \int d \left(\frac{d\rho}{dz} \right)^2 = \frac{1}{2} \left(\frac{d\rho}{dz} \right)_2^2 - \frac{1}{2} \left(\frac{d\rho}{dz} \right)_1^2,$$

and at the limits all the differential coefficients of ρ vanish by supposition. Thus, in the application to regions of uniform density—uniform, that is, through a space exceeding the range of the attractive forces,

$$p_2 - p_1 = K(\rho_2^2 - \rho_1^2); \quad \dots \dots \dots (5)$$

or, as we may also write it,

$$p = \varpi + K\rho^2, \quad \dots \dots \dots (6)$$

where ϖ is a constant, denoting what the value of p would be in a region where $\rho = 0$. We may regard ϖ as the *external* pressure operative upon the fluid. Equation (5) may also be

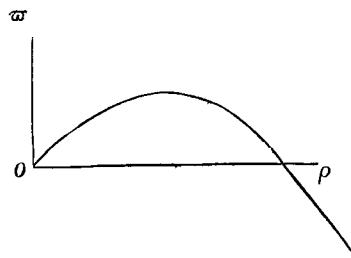
obtained, less analytically, by the argument employed upon a former occasion*, and still more simply perhaps by consideration of the forces operative upon the entire mass of fluid included between the two strata in question regarded as a rigid body. It is very important to remember that *it ceases to apply at places where ρ is varying*, and that unless the strata are plane it requires correction even in its application to regions of uniform density.

In the case of a uniform medium, (6) gives the relation between the external pressure ϖ , measured in experiments, and the total internal pressure p , found by adding to the former the intrinsic pressure $K\rho^2$. By the constitution of the medium, independently of the self-attracting property, there is a relation between p and ρ , and thence, by (6), between ϖ and ρ . If we suppose that the medium, freed from self-attraction, would obey Boyle's law, $p=k\rho$, and

$$\varpi = k\rho - K\rho^2. \quad \dots \dots \dots (7)$$

According to (7), when ρ is very small, ϖ varies as ρ . As ρ increases, ϖ increases with it, until $\rho = k/2K$, when ϖ reaches a maximum. Beyond this point ϖ diminishes as ρ increases, and this without limit. The curve which represents the relationship of ϖ and ρ

Fig. 1.



is a parabola; and it is evident that all beyond the vertex represents unstable conditions. For at any point on this portion the pressure diminishes as ρ increases. If, therefore, the original uniformity were slightly disturbed, without change of total volume, one part of the fluid becoming denser and the other rarer than before, the latter would tend still further to expand and the former to contract. And according to our equations the collapse would have no limit.

Points on the parabola between O and the vertex represent conditions which are stable so far as the interior of the fluid is concerned, but it may be necessary to consider the action of the walls upon the fluid situated in their neighbourhood. The simplest case is when the containing vessel, which may be a cylinder and piston, exercises no attraction upon the fluid. The fluid may then be compressed up to the vertex of

* "On Laplace's Theory of Capillarity," Phil. Mag. Oct. 1833.

the parabola without losing its uniformity or becoming unstable. If, however, there be sufficient attraction between the walls of the vessel and the fluid, instability leading to total collapse will set in before the vertex is reached.

It will be seen that condensation to a denser state is easily explained, without any reference to molecules, as a direct consequence of self-attraction in a medium otherwise obeying Boyle's law. The objection that may be raised at this point is rather that the explanation is too good, inasmuch as it points to indefinite collapse, instead of to a high, but finite, contraction in the condensed part.

A simple and well-known modification provides an escape from a conclusion which follows inevitably from a rigorous application of Boyle's law. A provision is required to prevent extreme collapse, and this we may find in the assumption that a constant must be subtracted from the volume in order to obtain the quantity to which the pressure is proportional. In this case it is usual and convenient to express the relation by the volume v of the unit mass, rather than by the density. We have

$$p(v-b) = \text{constant},$$

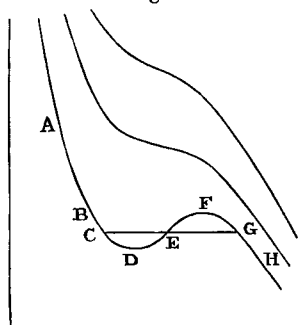
$$\text{or} \quad (\varpi + K/v^2)(v-b) = \text{constant}, \quad . . . \quad (8)$$

the well-known equation of Van der Waals. Here b is the smallest volume to which the fluid can be compressed; and under this law the collapse of the fluid is arrested at a certain stage, equilibrium being attained when the values of ϖ are again equal for the condensed and uncondensed parts of the fluid.

According to (8), there are three values of v corresponding to a given ϖ . Below the critical temperature the three values are real, and the isothermal curve assumes the form A B C D E F G H (fig. 2) suggested by Prof. James Thomson. The part D F is unrealizable for a fluid in mass, being essentially unstable; but the parts A D, F H represent stable conditions, so far as the interior of the homogeneous fluid is concerned. The line C G represents the (external) pressure at which the vapour can exist in contact with the liquid in mass, and the isothermal found by experiment is usually said to be H G E C B A. This statement can hardly be defended.

If a vapour be compressed from H through G, it can only

Fig. 2.



travel along the straight line from G towards E under very peculiar conditions. Apart from the action of the walls of the containing vessel, and of suspended nuclei, the path from G to F must be followed. The path from G to E implies that the vapour at G is in contact with the liquid in mass. This is by supposition not the case; and the passage in question could only be the result of foreign matter whose properties happened to coincide with those of the liquid. If the walls attract the vapour less than the vapour attracts itself, they cannot promote condensation, and the path H G F must be pursued. In the contrary case condensation must begin before G is reached, although it may be to only a limited extent. Probably the latter is the state of things usually met with in practice. So soon as the walls are covered with a certain thickness of liquid, the path coincides with a portion of G E C, and the angle at G is only slightly rounded off.

Similar considerations apply at the other end of the straight course. If the liquid be expanded through C, it will not, in general, pass along C E, but will continue to pursue the curve C D, and will even attain the limit D, if the attraction of the walls upon the liquid be not less than that of the liquid upon itself. In the contrary case separation will suddenly occur at a point upon the wall, a bubble of vapour will be formed, and a point on the straight line C E will be attained. It is thus scarcely conceivable that a fluid should follow the broken course A B C E G H without some rounding of the corners, or else of overshooting the points C, G, with subsequent precipitation upon the line C E G.

A very important question is the position of the line C G. Maxwell* showed that inasmuch as the area of the curve represents work performed at a constant temperature, it must be the same for the complete course as for the broken one. The line C G is therefore so situated as to cut off equal areas above and below.

This discussion is of course quite independent of the precise form of the relation between p and v . All that is necessary is such a modification of Boyle's law at great densities as will secure the fluid against indefinite collapse under the influence of its self-attraction.

We will now pass to the question of the transition from liquid to vapour, still supposing the strata to be plane. This is a problem considered by Maxwell in his article upon "Capillary Action" in the *Encyclopædia Britannica* †; but

* 'Nature,' vol. xi. p. 358, 1875; Reprint, vol. ii. p. 418.

† Reprint, vol. ii. p. 560.

his solution appears to me to be vitiated by more than one oversight. By differentiation of (6) he obtains (with A written for K)

$$dp = 2A\rho d\rho,$$

and thence, by (1),

$$2A\rho d\rho = \rho dV;$$

so that

$$V = 2A\rho + \text{constant}.$$

In the subsequent argument the identity of A with K is overlooked; and the whole process is vitiated by the illegitimate differentiation of (6), which is only applicable at places where ρ is not varying. The final result, which appears to be arrived at without any assumption as to the physical connexion between p and ρ , is thus devoid of significance.

Let us integrate (1) from a place in the vapour round which the density has the uniform value ρ_1 to a place in the liquid where the uniform density is ρ_2 . Thus,

$$\int_{(1)}^{(2)} \frac{dp}{\rho} = V_2 - V_1 = 2K(\rho_2 - \rho_1), \dots \dots (9)$$

by (3). The external pressure is uniform throughout, and may be denoted by ϖ' ; and by (6),

$$\varpi' = p_1 - K\rho_1^2 = p_2 - K\rho_2^2. \dots \dots (10)$$

At places where ρ is varying, that is in the transitional layer, ϖ , as given by (6), does not represent the external pressure; but we will still regard it as defined analytically by (6). Thus

$$\int_{(1)}^{(2)} \frac{dp}{\rho} = \int_{(1)}^{(2)} \frac{1}{\rho} \left(\frac{d\varpi}{d\rho} + 2K\rho \right) d\rho = \int_{(1)}^{(2)} \frac{1}{\rho} \frac{d\varpi}{d\rho} d\rho + 2K(\rho_2 - \rho_1), \dots (11)$$

By comparison of (9) and (11),

$$\int_{(1)}^{(2)} \frac{1}{\rho} \frac{d\varpi}{d\rho} d\rho = 0; \dots \dots (12)$$

or on integration by parts,

$$\left[\frac{\varpi}{\rho} \right]_{(1)}^{(2)} + \int_{(1)}^{(2)} \frac{\varpi}{\rho^2} d\rho = 0.$$

The values of ϖ at the limits are the same, and have been denoted by ϖ' . Hence

$$\int_{(1)}^{(2)} \frac{\varpi - \varpi'}{\rho^2} d\rho = 0. \dots \dots (13)$$

Since $dp/\rho^2 \propto dv$, this equation, obtained by purely hydrostatical methods applied to the liquid and vapour and the layer of transition between them, has precisely the same significance as Maxwell's theorem upon the position of the line C G in J. Thomson's diagram. In that theorem ϖ represents the external pressure that would be exerted by the fluid in various states of uniform density, some of which are not realizable. In the subject of the present investigation all the densities intermediate between those of the vapour and liquid actually occur; but, except at the extremities, ϖ no longer represents external pressure.

The explanation of the stable existence in the transitional layer of certain densities which would be unstable in mass, depends of course upon the fact that in the transitional layer the complete self-attraction due to the density is not developed in consequence of the rapid variation of density in the neighbourhood.

The distribution of density in the transitional layer, and the tension of the surface, can only be calculated upon the basis of a knowledge of the physical constitution of the fluid as expressed by the relation between p and ρ , and by the law of self-attraction. Poisson's contention that the surface-tension cannot be found upon the supposition of an abrupt transition from the liquid to its vapour is evidently justified; and since the thickness of the layer of transition is necessarily of the order of the range of the attraction, it follows that the correction for gradual transition is not likely to be small. A complete calculation of a particular case would be of interest, even on rather forced suppositions; but the mathematical difficulties are considerable. An approximate investigation might be conducted as follows:—

From (1) and (3),

$$\int \frac{dp}{\rho} = V = \rho \cdot 2K + \frac{d^2\rho}{dz^2} 2L + \dots$$

If we neglect the terms in $d^4\rho/dz^4$, &c., this becomes

$$2L \frac{d^2\rho}{dz^2} = \int \frac{dp}{\rho} - 2K \cdot \rho = f(\rho) - 2K \cdot \rho, \quad \dots \quad (14)$$

where $f(\rho) = \int dp/\rho$ is a function of ρ given by the constitution of the medium.

Equation (14) may now be integrated by quadratures.

$$L \left(\frac{d\rho}{dz} \right)^2 = \int f(\rho) d\rho - K\rho^2,$$

and

$$z = L^{\frac{1}{2}} \int \{ \int f(\rho) d\rho - K\rho^2 \}^{-\frac{1}{2}} d\rho. \dots (15)$$

It is possible that a graphical process would be found suitable. Equation (14) determines the curvature at any point of the curve representing the relation between ρ and z in terms of the coordinates and the slope.

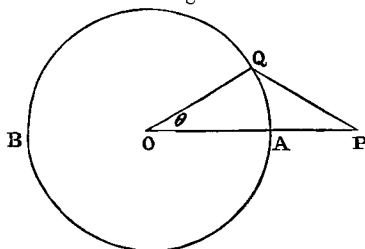
When the relation between ρ and z is known, the calculation of the surface-tension is a matter of quadratures. Probably the simplest way of considering the question is to regard the free surface as spherical (liquid within and vapour without), and to calculate the difference of pressures.

We have from (1),

$$p_2 - p_1 = [\rho V] - \int_{(1)}^{(2)} V d\rho = 2K(\rho_2^2 - \rho_1^2) - \int_{(1)}^{(2)} V \frac{d\rho}{dz} dz, \dots (16)$$

z being measured outwards along the radius. The question is thus reduced to the determination of V at the various points

Fig. 3.



of the layer of transition, for all of which $z = R$ approximately. Let P (fig. 3) be a point at which V is to be estimated, so that $OP = z$, and let AQB be a spherical shell of radius $z - \zeta$, of thickness $d\zeta$, and of density ρ' . We have first to estimate the potential dV of this shell at P.

The element of mass at Q is

$$\rho' \cdot 2\pi \sin \theta d\theta (z - \zeta)^2 d\zeta.$$

If, as before, $\phi(f)$ express the ultimate law of attraction, and

$$\Pi(f) = \int_f^{\infty} \phi(f) df,$$

we have to multiply the above element of mass by $\Pi(f)$. Now

$$f^2 = PQ^2 = z^2 + (z - \zeta)^2 - 2z(z - \zeta) \cos \theta,$$

so that

$$-d \cos \theta = \frac{f df}{z(z - \zeta)}.$$

The element of the potential is therefore

$$\frac{2\pi\rho'(z-\xi)d\xi}{z} \cdot \Pi(f) f df.$$

In the integration the limits of f are AP and BP. The former is denoted by ζ , and the latter may be identified with ∞ , since z or R is supposed to be a very large multiple of the range of the forces. Accordingly for the potential at P of the whole shell, we have

$$dV = \frac{2\pi\rho'(z-\xi)d\xi\psi(\xi)}{z}, \dots \dots (17)$$

where, as usual,

$$\psi(\xi) = \int_{\xi}^{\infty} \Pi(f) f df. \dots \dots (18)$$

To find the whole potential at P, (17) must be integrated with respect to ξ from $-\infty$ to $+\infty$, ρ' being treated as a function of ξ . As we need only consider P near the layer of transition, z in (17) may be identified with R .

If the transition is continuous, we may expand ρ' in the series

$$\rho' = \rho - \zeta \frac{d\rho}{dz} + \frac{\zeta^2}{1 \cdot 2} \frac{d^2\rho}{dz^2} - \dots;$$

and then at the point P,

$$\begin{aligned} V &= 2\pi \int_{-\infty}^{+\infty} \left(\rho + \frac{\zeta^2}{1 \cdot 2} \frac{d^2\rho}{dz^2} + \dots \right) \zeta \psi(\xi) d\xi \\ &+ \frac{2\pi}{R} \int_{-\infty}^{+\infty} \left(\zeta \frac{d\rho}{dz} + \frac{\zeta^3}{1 \cdot 2 \cdot 3} \frac{d^3\rho}{dz^3} + \dots \right) \zeta \psi(\xi) d\xi \\ &= 2K \cdot \rho + 2L \frac{d^2\rho}{dz^2} + 2M \frac{d^4\rho}{dz^4} + 2N \frac{d^6\rho}{dz^6} + \dots \\ &+ \frac{2}{R} \left\{ 2L \frac{d\rho}{dz} + 4M \frac{d^3\rho}{dz^3} + 6N \frac{d^5\rho}{dz^5} + \dots \right\}, \dots \dots (19) \end{aligned}$$

where (as in Maxwell's "Capillary Action")

$$\begin{aligned} K &= \pi \int_{-\infty}^{+\infty} \psi(\xi) d\xi, & L &= \frac{1}{2} \pi \int_{-\infty}^{+\infty} \zeta^2 \psi(\xi) d\xi, \\ M &= \frac{\pi}{4!} \int_{-\infty}^{+\infty} \zeta^4 \psi(\xi) d\xi, & N &= \frac{\pi}{6!} \int_{-\infty}^{+\infty} \zeta^6 \psi(\xi) d\xi \dots (20) \end{aligned}$$

When (19) is multiplied by $d\rho/dz$ and integrated across the whole layer of transition, we get for the part independent of R ,

$$2K \int_{(1)}^{(2)} \rho \frac{d\rho}{dz} dz = K(\rho_2^2 - \rho_1^2)$$

simply, all the other terms in L, M, \dots vanishing. Hence by (16), with integration by parts,

$$p_2 - p_1 = K(\rho_2^2 - \rho_1^2) - \frac{2}{R} \left\{ 2L \int_{(1)}^{(2)} \left(\frac{d\rho}{dz}\right)^2 dz - 4M \int_{(1)}^{(2)} \left(\frac{d^2\rho}{dz^2}\right)^2 dz + 6N \int_{(1)}^{(2)} \left(\frac{d^3\rho}{dz^3}\right)^2 dz - \dots \right\} \dots (21)$$

The first term upon the right in (21) is the same as when the strata are plane. The second gives the capillary tension (T), and we conclude that when the transition is continuous

$$T = 2L \int_{(2)}^{(1)} \left(\frac{d\rho}{dz}\right)^2 dz - 4M \int_{(2)}^{(1)} \left(\frac{d^2\rho}{dz^2}\right)^2 dz + \dots \dots (22)$$

From these results we see that "the existence of a capillary force is connected with suddenness of transition from one medium to another, and that it may disappear altogether when the transition is sufficiently gradual"*.

The series (22) would probably suffice for the calculation of surface-tension between liquid and vapour when once the law connecting ρ and z is known. It is possible, however, that its convergence would be inadequate, and in this respect it must certainly fail to give the result for an abrupt transition. In the latter case, where the whole variation of density occurs at one place, (16) becomes

$$p_2 - p_1 = 2K(\rho_2^2 - \rho_1^2) - (\rho_2 - \rho_1)V, \dots \dots (23)$$

V relating to the place in question. And by (17)

$$V = \int_{-\infty}^{+\infty} 2\pi\rho'(1 - \xi/R)\psi(\xi)d\xi = 2\pi(\rho_2 + \rho_1) \int_0^\infty \psi(\xi)d\xi - \frac{2\pi}{R}(\rho_2 - \rho_1) \int_0^\infty \xi\psi(\xi)d\xi.$$

Thus

$$p_2 - p_1 = K(\rho_2^2 - \rho_1^2) + 2T/R, \dots \dots (24)$$

* "On Laplace's Theory of Capillarity," Phil. Mag. October 1883.

if

$$T = \pi \int_0^\infty \zeta_1 \psi(\zeta) d\zeta \cdot (\rho_2 - \rho_1)^2, \dots \dots (25)$$

where (25) agrees with the value of the tension found for this case by Laplace.

In the application to a sphere of liquid surrounded by an atmosphere of vapour, equations (9), (11), (12) remain unchanged, in spite of the curvature of the surface. If ω'' denote the external pressure acting upon the vapour,

$$p_1 = \omega'' + K\rho_1^2, \dots \dots (26)$$

$$p_2 = \omega'' + K\rho_2^2 + 2T/R. \dots \dots (27)$$

The symbol ω is still regarded as defined algebraically by (6), so that

$$\omega_1 = \omega'', \quad \omega_2 = \omega'' + 2T/R. \dots \dots (28)$$

Integrating (12) by parts, we find

$$\frac{\omega_2}{\rho_2} - \frac{\omega_1}{\rho_1} + \int_{(1)}^{(2)} \frac{\omega}{\rho^2} d\rho = 0;$$

or by (28),

$$\int_{(1)}^{(2)} \frac{\omega - \omega''}{\rho^2} d\rho + \frac{2T}{R\rho^2} = 0. \dots \dots (29)$$

In this equation ω is a known function of ρ . If we compare it with (13), where ω' represents the external pressure of the vapour in contact with a *plane* surface of liquid, we shall be able to estimate the effect of the curvature. It is to be observed that the limits of integration are not the same in the two cases. If we retain ρ_1, ρ_2 for the plane surface, and for the curved surface write $\rho_1 + \delta\rho_1, \rho_2 + \delta\rho_2$, we have from (29)

$$\frac{\omega_2 - \omega''}{\rho_2^2} \delta\rho_2 - \frac{\omega_1 - \omega''}{\rho_1^2} \delta\rho_1 + \int_{\rho_1}^{\rho_2} \frac{\omega - \omega''}{\rho^2} d\rho + \frac{2T}{R(\rho_2 + \delta\rho_2)} = 0;$$

or by (28),

$$\int_{\rho_1}^{\rho_2} \frac{\omega - \omega''}{\rho^2} d\rho + \frac{2T}{R\rho_2} = 0. \dots \dots (30)$$

The limits of integration are now the same as in (13), so that by subtraction

$$(\omega' - \omega'') \left(\frac{1}{\rho_2} - \frac{1}{\rho_1} \right) = \frac{2T}{R\rho_2},$$

or

$$\omega'' = \omega' + \frac{2T\rho_1}{\rho_2 - \rho_1}. \dots \dots (31)$$

This is the value for the excess of vapour-pressure in equilibrium with a convex surface that is given in Maxwell's "Heat" as a deduction from Sir W. Thomson's principle.

The application of this principle may be extended in another direction. When liquid rises in a capillary tube open above, the more attenuated vapour at the upper level is in equilibrium with the concave surface, and the more dense vapour below is in equilibrium with the plane surface of the liquid. But, as was pointed out in the former paper, the rise of liquid is not limited to the height of the meniscus. Above that point the walls of the tube are coated with a layer of fluid, of gradually diminishing thickness, less than the range of forces, and extending to an immense height. *At every point the layer of fluid must be in equilibrium with the vapour to be found at the same level.* The data scarcely exist for anything like a precise estimate of the effect to be expected, but the argument suffices to show that a solid body brought into contact with vapour at a density which may be much below the so-called point of saturation will cover itself with a layer of fluid, and that this layer may be retained in some degree even in what passes for a good vacuum. The fluid composing the layer, though denser than the surrounding atmosphere of vapour, cannot properly be described as either liquid or gaseous.

In our atmosphere fresh surfaces, *e. g.* of split mica or of mercury, attract to themselves at once a coating of moisture. In a few hours this is replaced, or supplemented, by a layer of grease, which gives rise to a large variety of curious phenomena. In the case of mica the fresh surface conducts electricity, while an old surface, in which presumably the moisture has been replaced by grease, insulates well.

XXI. *Some Experiments with a Platinum Pyrometer on the Melting-points of Gold and Silver.* By H. L. CALLENDAR, M.A., Fellow of Trinity College, Cambridge*.

[Plate V.]

IN a paper which appeared in the Philosophical Magazine for July 1891 I alluded to some experiments I had made with a platinum pyrometer on the melting-point of silver, and stated that the readings of these instruments were constant to a tenth of a degree at temperatures above 1000° C.

Through the kindness of Prof. Roberts-Austen I have recently had an opportunity of making some further experi-

* Communicated by the Author.