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COURSE IN MATHEMATICAL PHYSICS

CAPILLARITY

Lectures taught during the second semester of 1888-1889

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FIRST CHAPTER

LAPLACE'S THEORY

1. Basis for the theory. – Laplace assumed that two molecules of a liquid exert an attraction upon each other that is directed along the line that connects them, is proportional to their masses, and depends upon the distance that separates them according to an unknown law.

That attraction will then have the expression:

$$mm' f(r),$$

in which m and m' are the masses of the molecules, r is the distance between them, and $f(r)$ is an unknown function of that distance.

However, those hypotheses are not sufficient. Indeed, Clairaut stated them fifteen years before Laplace, but he could still not deduce the explanation for capillary phenomena from them. Laplace also assumed that the attractive force decreases rapidly when the distance between the molecules increases, and that it will become negligible once that distance exceeds a very small value that one calls the *radius of molecular activity*. In other words, Laplace supposed that the function:

$$\varphi(r) = \int_r^\infty f(r)\,dr$$

is roughly zero when r is greater than the radius of molecular activity.

As a result of the initial hypotheses, the molecular forces will admit a potential:

$$V = \sum m\,\varphi(r),$$

so the partial derivatives $\frac{\partial V}{\partial x}, \frac{\partial V}{\partial y}, \frac{\partial V}{\partial z}$ will represent the components along the three axes of the attractive force that is exerted upon a unit mass that is located at the point x, y, z and is due to the action of molecules of mass m.

If the set of those molecules forms a volume then the expression for the potential will become:

$$V = \iiint \rho\,d\tau\,\varphi(r),$$

in which $d\tau$ denotes a volume element, ρ denotes the density of that element, and the integration is extended over the volume in question.

A new hypothesis by Laplace permits one to simplify that expression. Indeed, Laplace assumed that the density was constant. That hypothesis is not legitimate, because it is probable that the density at a point that is situated at a distance from the surface of the liquid that is less than the radius of molecular activity will not have the same value that it has at another point whose distance to the surface is larger than that radius. Despite its inaccuracy, that hypothesis will lead to the expression:

$$V = \rho \iiint d\tau \, \varphi(r) \, ,$$

and if we take the density of the liquid considered to be unity then we will get:

$$V = \iiint d\tau \, \varphi(r) \, .$$

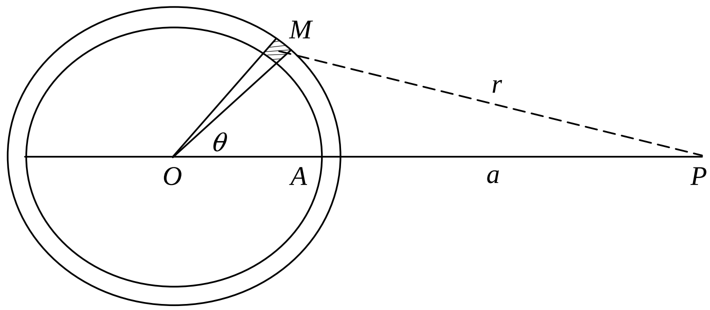

Figure 1.

2. Potential of an infinitely-thin spherical shell. – Let ρ and $\rho + d\rho$ be the radii of the two spheres that bound the shell, and let a be the distance from the common center O (Fig. 1) of those spheres at the point P where we would like to know the value of the potential. Take the plane of the figure to be an arbitrary plane that contains PO and draw two radii in that plane that make angles of θ and $\theta + d\theta$ with OP. The element M, thus-determined, will have an area of $\rho \, d\theta \, d\rho$, and the volume that it generates when one rotates it around PO will have the value:

$$2\pi\rho \sin \theta \, \rho \, d\theta \, d\rho \, .$$

All of the elements of that volume are at the same distance r from the point P, so the potential at that point that is due to the volume will be:

$$dV = 2\pi\rho^2 \sin \theta \, \rho \, d\theta \, d\rho \; \varphi(r).$$

Consequently, the potential of the spherical shell will have the value:

$$V = 2\pi\rho^2 \int_0^r \varphi(r) \; \sin \theta \, \rho \, d\theta \, d\rho.$$

However, the triangle POM provides the relation:

$$r^2 = \rho^2 + a^2 - 2a\rho \cos \theta,$$

so

$$r \, dr = a\rho \sin \theta \, d\theta.$$

We can then write:

$$V = 2\pi \frac{\rho}{a} d\rho \int_{r_0}^{r_1} r\,\varphi(r)\,dr\,,$$

in which r_0 denotes the distance PA, and r_1 denotes the distance PB.

Set:

$$\int_r^{+\infty} r\,\varphi(r)\,dr = \psi(r)\,.$$

The function ψ thus-defined will have a value that is roughly zero for any value of r that is greater than the radius of molecular activity, since the function $\varphi(r)$ will be almost zero for those values, by hypothesis.

Introduce that function ψ into the expression for V. We will have:

$$\int_{r_0}^{r_1} r\,\varphi(r)\,dr = \int_{r_0}^{\infty} r\,\varphi(r)\,dr + \int_{\infty}^{r_1} r\,\varphi(r)\,dr = \psi(r_1) - \psi(r_0).$$

However, if ρ is finite then the distance r_1 will be necessarily greater than the radius of molecular activity. Consequently, $\psi(r_1)$ will be negligible, and we will have simply:

$$V = 2\pi \frac{\rho}{a} d\rho\ \psi(r_0), \tag{1}$$

and that quantity will itself become negligible when r_0 becomes finite.

The figure was traced under the hypothesis that the point P was exterior to the spherical shell. However, the argument applies just the same to the case in which the point P is interior. The only difference is that r_0 , whose value is $a - \rho$ in the first case, will become $\rho - a$ in the second.

3. Potential of a solid sphere. – First consider the case in which the point P is exterior to the sphere.

If the point is at a finite distance from the surface then the attractive forces that are exerted on a mass that is placed at that point by all of the molecules of the sphere will be negligible; consequently, the potential will be roughly zero.

Suppose that the point P is at a very small distance ε from the surface. Decompose the sphere into concentric spherical shells of thickness $d\rho$; each of then will contribute a potential to P of:

$$dV = 2\pi \frac{\rho}{a} d\rho\ \psi(a - \rho).$$

Consequently, the potential of the entire sphere will be:

$$V = \int_0^R 2\pi \frac{\rho}{a} d\rho\ \psi(a - \rho),$$

in which R is the radius of the sphere.

If we set:

$$a - \rho = z$$

then that potential will become:

$$V = \int_0^R 2\pi \frac{x-a}{a} \psi(z)\, dz = \int_\varepsilon^a 2\pi \psi(z)\, dz - \frac{1}{a}\int_\varepsilon^a 2\pi z\, \psi(z)\, dz\,.$$

However, since a is finite and the function $\psi(z)$ is roughly zero for any finite value of the variable, one will have, approximately:

$$\int_a^\infty 2\pi \psi(z)\, dz = 0, \qquad \int_a^\infty 2\pi z\, \psi(z)\, dz = 0,$$

and as a result:

$$\int_\varepsilon^a 2\pi \psi(z)\, dz = \int_\varepsilon^\infty 2\pi \psi(z)\, dz + \int_\infty^a 2\pi \psi(z)\, dz = \int_\varepsilon^\infty 2\pi \psi(z)\, dz = \theta(\varepsilon),$$

$$\int_\varepsilon^a 2\pi z\, \psi(z)\, dz = \int_\varepsilon^\infty 2\pi z\, \psi(z)\, dz + \int_\infty^a 2\pi z\, \psi(z)\, dz = \int_\varepsilon^\infty 2\pi z\, \psi(z)\, dz = \theta_1(\varepsilon).$$

We then have that the potential at P is:

$$V = \theta(\varepsilon) - \frac{1}{a}\theta_1(\varepsilon).$$

We ignore the form of those functions θ and θ_1, since φ and ψ are unknowns. Nonetheless, we see that θ and θ_1 are roughly zero for any finite value of ε, since ψ enjoys that property. We can add that θ_1 is much smaller than θ, because for small values of z (which are the only ones to consider, from the preceding), the differential element $2\pi z\ \psi(z)\ dz$ will be smaller than $2\pi z\ \psi(z)\ dz$.

The latter property will permit one to modify the expression for V. Indeed, when ε is very small, a will differ only slightly from R. Since θ_1 will be very small with respect to θ then, we would not change the value of V appreciably if we were to replace the coefficient $1 / a$ of θ_1 with the factor $1 / R$. We would then have:

$$V = \theta(\varepsilon) - \frac{1}{R}\theta_1(\varepsilon). \tag{2}$$

4. – We now pass on to the case in which the point P is interior to the sphere.

When the distance from the point on the surface of the sphere is finite, the action that is exerted upon P by a molecule that is exterior to the sphere is negligible, since the distance from that molecule to the point P will then be greater than the radius of molecular activity. We can then replace the sphere with another sphere of the same material that has an infinite radius and a center at P without changing the value of the potential at P. Decompose that sphere into concentric spherical shells of radius r and thickness dr. The potential at P that is due to one of those shells will be:

$$dV = 4\pi r^2\, dr\ \varphi(r).$$

As a result, the potential of the entire sphere will be:

$$V = \int_0^\infty 4\pi r^2\, dr\, \varphi(r)\,.$$

That integral is a constant A. The potential of solid sphere at an interior point that is situated at a finite distance from its surface will then be a constant.

Now suppose that the point is at an extremely small distance ε from the surface. Upon decomposing the sphere into infinitely-thin concentric shells, the point P will be exterior to one of them and interior to another. The potential of each of them is represented by formula (1), in which r_0 must be replaced with $a - \rho$ or $\rho - a$, according to whether P is exterior or interior to the shell considered, resp. The potential of the entire sphere will then be:

$$V = \int_0^{R-\varepsilon} 2\pi \frac{\rho}{a}\, d\rho\ \psi(a-\rho) + \int_{R-\varepsilon}^{R} 2\pi \frac{\rho}{a}\, d\rho\ \psi(\rho - a).$$

Consider the first integral. Upon setting $z = a - \rho$, it will become:

$$\int_a^0 2\pi \frac{z-a}{a} \psi(z)\, dz \ = \int_0^a 2\pi\, \psi(z)\, dz - \frac{1}{a}\int_0^a 2\pi\, \psi(z)\, dz\,.$$

Since a is finite and the function ψ is roughly zero for any finite value of the variable, one can replace the upper limits a of the integrals in the right-hand side with infinity. As a result, those integrals will be constants, and the same thing will be true for the expression for V.

When one sets $\rho - a = z$, the second integral in that expression will become:

$$\int_0^\varepsilon 2\pi \frac{z+a}{a} \psi(z)\, dz \ = \int_0^\varepsilon 2\pi\, \psi(z)\, dz + \frac{1}{a}\int_0^\varepsilon 2\pi z\, \psi(z)\, dz\,.$$

The two integrals on the right-hand side are the ones that we considered in the case where P was exterior to the sphere. Consequently, any two of them will be functions of ε. If we introduce a constant that represents the value of the first integral into one of those functions of V then we can write the expression for that potential as:

$$V = \theta(\varepsilon) - \frac{1}{a}\, \theta_1(\varepsilon)\,.$$

It is obvious that those functions are not identical to the ones that entered into the expression (2). If we compare the preceding expression for V with the value $V = A$ of the potential for an interior point at a finite distance from the surface then we will see that $\theta_1(\varepsilon)$ must tend to A, and $\theta_1(\varepsilon)$ will tend to zero when ε becomes finite.

The latter property of the function $\theta_1(\varepsilon)$ permits one to replace $1 / a$ with the factor $1/R$, which differs from it only slightly when ε is small. One will then come back to the expression for the potential that was obtained for an exterior point, but θ and θ_1 will not denote the same functions in those two cases.

In summary:

1. If the point is exterior and at a finite distance then:

$$V = 0.$$

2. If the point is at a very small distance from the surface then:

$$V = \theta(\varepsilon) - \frac{1}{R}\theta_1(\varepsilon)$$

and the functions θ and θ_1 will not be the same when the point is interior or exterior.

3. If the point is interior and at a finite distance then:

$$V = A.$$

5. Potential of a volume of revolution. – Let us first show that the potential at a point P that is located on the axis at a very small distance from the surface that bounds the volume will increase or decrease with the radius of curvature of the neighboring summit.

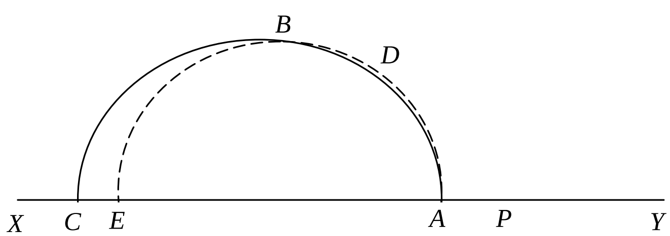

Figure 2.

Let ABC (Fig. 2) be the meridian section of the volume considered. Deform that curve in such a manner that the radius of curvature at A decreases, and let $ADBE$ the new form. The potential of the volume that is generated by the surface $ADBE$ will be equal to the potential of the volume that is generated by ABC plus that of volume that is generated by ABD and minus that of the volume that is generated by BCE. The point P is supposed to be at a very small distance from A, so it will have a finite distance from the molecules of the latter volume, and as a result, the corresponding potential will be negligible. The potential of the volume that is generated by *BDA* will be positive if one meanwhile supposes that the force between two molecules is attractive. Consequently, the volume that is generated by the surface *ADBE* will contribute a potential at *P* that is greater than that of the original volume.

Having said that, trace out two spheres that are tangent at *A* to the volume considered and whose radii are R' and R''. Let V' and V'' be the potentials of those spheres at the point *P*, while *V* is the potential of the volume considered at the same point, which can be interior or exterior to that volume. If the radius of curvature at *A* of the surface generated by *ABC* is found between R' and R'' then, from the preceding, one will have:

$$V' < V < V''$$

or

$$\theta(\varepsilon) - \frac{1}{R'}\theta_1(\varepsilon) < V < \theta(\varepsilon) - \frac{1}{R''}\theta_1(\varepsilon).$$

Upon making R' and R'' tend to the radius of curvature *R*, one will have:

$$V = \theta(\varepsilon) - \frac{1}{R}\theta_1(\varepsilon), \tag{3}$$

in the limit.

The potential then depends upon only the distance from the point on the surface to the volume considered and the radius of curvature at the summit.

We have assumed that the forces between two molecules are always attractive. Reality does not impose that restriction, and one will arrive at the same expression for the potential by supposing that those forces can be attractive or repulsive according to the situation. Indeed, if the force is repulsive then the sign of φ must be changed; as a result, the most general expression for φ will be:

$$\varphi(r) = \varphi_1(r) - \varphi_2(r),$$

in which $\varphi_1(r)$ and $\varphi_2(r)$ are two functions that are always positive. The potential at a point will then be:

$$V = \iiint \varphi(r)\,d\tau = \iiint \varphi_1(r)\,d\tau - \iiint \varphi_2(r)\,d\tau .$$

However, the preceding arguments are still applicable to the integrals on the right-hand side, since φ_1 and φ_2 are always positive. Hence, each of them can be put into the form $\theta(\varepsilon) - \frac{1}{R}\theta_1(\varepsilon)$. The same thing will be true for their difference – viz., *V*.

Take a spindle that is bounded by two planes that pass through the axis of the volume of revolution and define a certain angle between them. Another spindle with the same angle will have the same potential at *P* because upon rotating the latter spindle through a convenient angle, one can make it coincide with the first one. It results from this that the potential of a spindle is proportional to the dihedral angle that is formed by the planes that bound it. Consequently, the potential of a spindle of angle *a* will have the expression:

$$V = \frac{\alpha}{2\pi}\left[\theta(\varepsilon) - \frac{1}{R}\theta_1(\varepsilon)\right]. \tag{4}$$

6. Potential of an arbitrary volume. – We look for the potential of a volume that is bounded by an arbitrary surface Σ at a point *P* that is either interior or exterior, but very close to that surface.

Take the *z*-axis to be the normal to the surface that passes through *P*. Take the *x* and *y* axes to be the axes of the indicatrix of the foot *A* of the normal. The equation of the surface with respect to that system of axes will be:

$$z = ax^2 + by^2 + \ldots,$$

and the radius of curvature at *A* of its intersection with a normal plane Π that makes an angle φ with the *x*-axis will be given by the relation:

$$\frac{1}{R} = 2\,(a \cos^2 \varphi + b \sin^2 \varphi).$$

Consider the spindle *F* with an angle $d\varphi$ that is bounded by the plane Π and an infinitely-close plane. That spindle will differ infinitely little from the spindle that makes the same angle with the surface of revolution that is generated by rotating the intersection of the surface Σ with the plane Π. The potentials of those spindles can then coincide. Consequently, from formula (4), the potential of *F* will be:

$$dV = \frac{d\varphi}{2\pi}\left[\theta(\varepsilon) - \frac{1}{R}\theta_1(\varepsilon)\right].$$

The potential of the volume that is bounded by the surface Σ will then be:

$$V = \int_0^{2\pi} \frac{d\varphi}{2\pi}\left[\theta(\varepsilon) - \frac{1}{R}\theta_1(\varepsilon)\right],$$

or upon replacing 1 / *R* with its value:

$$V = \frac{\theta(\varepsilon)}{2\pi}\int_0^{2\pi} d\varphi - \frac{a\,\theta_1(\varepsilon)}{\pi}\int_0^{2\pi} \cos^2\varphi\, d\varphi - \frac{b\,\theta_1(\varepsilon)}{\pi}\int_0^{2\pi} \sin^2\varphi\, d\varphi\ ,$$

and upon performing the integrations:

$$V = \theta(\varepsilon) - a\ \theta_1 - b\ \theta_1\ .$$

However, if we set $\varphi = 0$ in the expression for $1 / R$ and then $\varphi = \pi / 2$ then we will get:

$$\frac{1}{R_1} = 2a, \qquad \frac{1}{R_2} = 2b$$

for the principal curvatures.

Consequently, we can write:

$$V = \theta(\varepsilon) - \frac{\theta_1(\varepsilon)}{2}\left(\frac{1}{R_1} + \frac{1}{R_2}\right), \tag{3}$$

which is a formula that shows that the potential at a point depends upon only the distance from that point to the surface and the mean curvature at the pole.

7. Equations of equilibrium for a fluid. – In order to find the laws of capillarity, all that remains is to apply the general principles of hydrostatics.

Recall that if one lets p denote the pressure at a point x, y, z, while X, Y, Z are the components of the external forces that are exerted upon a unit mass that is placed at that point then one will obtain the fundamental equations:

$$\frac{dp}{dx} = X, \qquad \frac{dp}{dy} = Y, \qquad \frac{dp}{dz} = Z,$$

upon writing that a volume element is in equilibrium under the influence of the forces that act upon it.

In the particular case that we are concerned with, there are two types of external forces: capillary forces and forces that act at an appreciable distance. We just saw that the first ones admit a potential V. In general, the second ones likewise admit a potential, which we denote by W.

The preceding equations will then become:

$$\frac{dp}{dx} = \frac{dV}{dx} + \frac{dW}{dx},$$

$$\frac{dp}{dy} = \frac{dV}{dy} + \frac{dW}{dy},$$

$$\frac{dp}{dz} = \frac{dV}{dz} + \frac{dW}{dz}.$$

We deduce from this that:

$$p = V + W + \text{const.},$$

or upon replacing V with the value (5):

$$p = \theta(\varepsilon) - \frac{\theta_1(\varepsilon)}{2}\left(\frac{1}{R_1} + \frac{1}{R_2}\right) + W + \text{const.} \tag{6}$$

8. Equation of the free surface of a liquid. – That equation is deduced from the preceding one immediately.

One has $\varepsilon = 0$ for a point on the surface. As a result, the pressure p_0 at that point will be:

$$p_0 = \theta(0) - \frac{\theta_1(0)}{2}\left(\frac{1}{R_1} + \frac{1}{R_2}\right) + W + \text{const.}$$

However, $\theta(0)$ is a constant, so p_0 will also have the same value at any point on the free surface, and one will have simply:

$$\frac{\theta_1(0)}{2}\left(\frac{1}{R_1} + \frac{1}{R_2}\right) = W + \text{const.} \tag{7}$$

When the forces that act at an appreciable distance reduce to gravity, one will have $Y = X = 0$, $Z = g$ if one takes the z-axis to be vertical and directed downwards and the xy-plane to be a horizontal plane. As a result, one will then have:

$$W = gz$$

in that case, and the free-surface equation will become:

$$\frac{\theta_1(0)}{2}\left(\frac{1}{R_1} + \frac{1}{R_2}\right) = gz + \text{const.} \tag{8}$$

9. Capillary ascension and depression. – When a capillary tube is submerged vertically in water, the liquid will go up in the tube until it is above its level in the vessel. When it is submerged in mercury, the free surface in the tube will be below the free surface in the vessel. The preceding equation will permit us to find the form of the meniscus in both cases.

Take the xy-plane to be the horizontal plane that forms the free surface of the liquid outside the tube. For a point of that plane, one will have $R_1 = R_2 = \infty$ and $z = 0$. Hence, the constant in equation (8) will be equal to 0, and one will have simply:

$$\frac{\theta_1(0)}{2}\left(\frac{1}{R_1} + \frac{1}{R_2}\right) = gz.$$

If we suppose that the capillary tube is cylindrical then the free surface inside the tube will be one of revolution, and one will have $R_1 = R_2$ at the summit of that surface. One will then have:

$$\frac{\theta_1(0)}{R_1} = gz.$$

When there is ascension in the liquid, the z of the summit will be negative. As a result, R_1 must be negative, since θ_1 is positive when the forces are attractive. The center of curvature will then be on the negative side of the z-axis, and the meniscus will be concave.

When there is depression, the z of the summit will be positive. The radius of curvature at that summit must be positive, and the meniscus will then be convex.

We then see how Laplace's theory permits us to predict the form of the meniscus when one knows whether there is ascension or depression, or conversely, to predict whether there will be ascension or depression when one knows the form of the meniscus. Nonetheless, the problem is only half-solved because we have ignored the problem of explaining why certain liquids go up in a capillary tube, while other ones go down. Laplace attempted to give an explanation in two subsequent works. In the first paper ([1]), he arrived at an explanation that was plausible, but based upon a hypothesis. In another paper ([2]), the conclusions to which he arrived were rigorous only in the case where the tube was cylindrical, and the method was very complicated moreover. We shall nevertheless summarize those two papers.

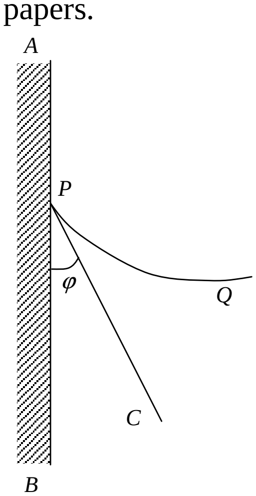

Figure 3.

10. Contact angle. Its variation. – Consider the free surface of a liquid in the neighborhood of a wall. Draw a plane through one of the points of the contact curve with the surface and the wall that is normal to that curve. It will cut the surface and the wall

([1]) *Œuvres complètes de Laplace*, t. IV, Supplement to Book X of his *Traité de mécanique céleste*, pp. 394.

([2]) *Œuvres complètes de Laplace*, 2nd supplement to Book X, pp. 419.

along two lines whose tangents at the point of contact will form a certain angle φ. That is the *contact angle* at the point considered.

In his first paper, Laplace assume without proof that this angle is constant, so it would have the same value at any point of the contact curve between the wall and the surface of the liquid. In order to explain the variation of that angle with the nature of the liquid and that of the wall, Laplace supposed that the solid molecules were attracted to the liquid molecules and that this attraction differed from the one that two liquid molecules exerted upon each other by only a constant factor.

Let us apply that hypothesis to the search for the equilibrium condition for a liquid molecule P (Fig. 3) that is located on the contact curve of a vertical wall AB and the free surface PQ.

In order for that molecule to be in equilibrium, it is necessary that the resultant of the forces that act upon it must be normal to the free surface, because in the contrary case, the molecule would slide under the action of the tangential component.

Now, those forces are:

1. The attraction F that is due to the molecules of the wall, which is an attraction that will be perpendicular to AB and directed towards the interior of the wall, by reason of symmetry.

2. The attraction F' that is due to the liquid molecules that are located in the dihedron BPC, which is an attraction that is obviously directed along the bisector of the angle BPC.

3. The attraction F_1' of the molecules that are found between the plane PC and the free surface, which is an attraction that must be added to F if the contact angle is acute and subtracted if the angle is obtuse.

4. The weight, whose value is g, since the mass of the attracted molecule is taken to be unity.

Upon expressing the idea that the sum of the projections of those forces onto the tangent PC should be zero, one will get the relation:

$$- F \sin \varphi + F' \cos \frac{\varphi}{2} + Q + g \cos \varphi = 0,$$

in which Q denotes the projection of the force F_1', which must be taken with the + sign in the case that is depicted in the figure and with the – sign when the angle φ is obtuse.

Let us calculate F and F'. In order to do that, we decompose the dihedron BPC into infinitely-small dihedral angles $d\psi$, in which ψ is the angle that one of the faces of that small dihedron makes with the bisecting plane of the dihedron BPC. The attraction that two dihedra with the same angle exert upon the molecule P will be equal, because when we rotate one of them around its edge through a convenient angle, we will get the other one. As a result, the attraction of each of the elementary dihedron will be proportional to

$d\psi$; with Laplace, denote it by $\rho' d\psi$. The projection of that attraction onto the bisector of BPC will be $\rho' d\psi \cos\psi$, and we will get the attraction of the dihedron BPC upon integrating between the limits of ψ – i.e.:

$$-\frac{\varphi}{2} \quad \text{and} \quad +\frac{\varphi}{2};$$

hence:

$$F' = \rho' \int_{-\varphi/2}^{+\varphi/2} \cos\psi \, d\psi = 2\rho' \sin\frac{\varphi}{2}.$$

In order to get F, it suffices to set $\varphi = 2\pi$ in that expression and to replace ρ' with the value ρ of that quantity that relates to the action of the solid on the liquid. Consequently:

$$F = 2\rho.$$

If we replace F' and F with those values in the equilibrium relation then it will become:

$$-2\pi \sin\varphi + 2\rho' \sin\frac{\varphi}{2} \cos\frac{\varphi}{2} + Q + g \cos\varphi = 0,$$

or

$$(\rho' - 2\rho) \sin\varphi + Q + g \cos\varphi = 0. \tag{9}$$

When the contact angle is acute, $\sin\varphi$, $\cos\varphi$, and Q will be positive; consequently, the latter equality can be satisfied only if:

$$\rho' - 2\rho < 0 \quad \text{or} \quad 2\rho > \rho'.$$

If the contact angle is obtuse then Q must be taken to be negative, as we have pointed out. Since $\cos\varphi$ is negative then, while $\sin\varphi$ is positive, the condition (9) will lead to:

$$\rho' - 2\rho > 0 \quad \text{or} \quad 2\rho < \rho'.$$

Finally, if the contact angle is a right angle then one will have:

$$\sin\varphi = 1, \qquad Q = 0, \qquad \cos\varphi = 0,$$

and as a result:

$$\rho' = 2\rho.$$

The value of the contact angle, and as a result, the depression and ascension of the liquid in capillary tubes will then depend upon the intensities ρ and ρ' of the attractions that are exerted upon a liquid molecule by a dihedron on the solid that forms the wall and an equal dihedron on the liquid itself.

11. – Laplace likewise considered two particular cases: viz., the one in which $\rho = \rho'$ and the one in which $\rho = 0$.

Supposing that ρ and ρ' are equal amounts to assuming that the tube is composed of the liquid that it contains and the molecules are subjected to forces of cohesion that do not modify the capillary forces. We shall show that under those conditions, the contact angle will be zero and that the separation surface in a cylindrical tube will be a hemisphere if one can nonetheless neglect the weight of the liquid.

Imagine that the weightless liquid fills up all of the space that is exterior to a sphere whose center is *O* (Fig. 4). The liquid will then be in equilibrium because by reason of symmetry, the attractive forces that act upon a molecule will pass through the center *O*, and as a result they will be normal to the surface of the sphere.

Draw a cylinder that is tangent to the sphere and solidify the liquid that is exterior to that cylinder; i.e., introduce forces of cohesion between the molecules of the liquid that do not modify the attractive capillary forces. Equilibrium will not be perturbed.

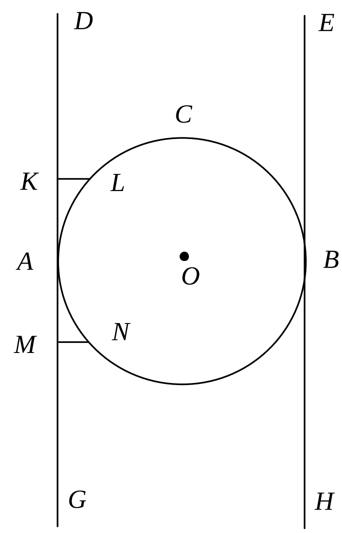

Figure 4.

That will no longer be the case if we remove the liquid that occupies the space *DACBE*, because the action of that liquid on the liquid that occupies the space *GANBH* is negligible. Indeed, the only molecules of the first volume that can react with the molecules of the second one are the ones that are situated at a distance from the circle *AB* that is less than the radius of molecular activity. Those molecules are situated in the volume that is generated by the rotation of the curvilinear triangle *KAL* around the axis of the cylinder. Now, that volume is a third-order infinitesimal, since *AK* is infinitely small. One can then neglect the action of that volume.

All that remains then is the liquid *GANBH*, which is in equilibrium and whose free surface is a hemisphere. However, from the remark that was made previously, the liquid exists under the same conditions that are found in a tube that is composed of a material such that $\rho = \rho'$. The contact angle will then be indeed zero in this case.

The case in which $\rho = 0$ (which does not correspond to anything in physical reality, moreover) leads to a value of π for the contact angle.

Indeed, consider a sphere of weightless liquid; it is in equilibrium. Draw a cylinder that is tangent to that sphere and fills up the space that is found outside of the cylinder, as well as the space *DABCE* of the material for which $\rho = 0$. Equilibrium persists, since the matter that was added has no effect on the molecules of the liquid. If we fill up the space *GANBH* with the liquid then we will not destroy the equilibrium, because the molecules of the added liquid that act upon the molecules of the sphere are solely the ones that are located in the small volume that is generated by the rotation of the curvilinear triangle *MAN*, and since that volume is a third-order infinitesimal, its action can be neglected.

We then see that when a liquid is in equilibrium in a cylindrical tube that is composed of a material that does not act upon its molecules, the free surface will take the form of a convex hemisphere *ACB*. Consequently, the contact angle will be equal to π.

In summary, Laplace succeeded in explaining the various forms of the surface of the meniscus by an attraction of greater or lesser magnitude between the solid and liquid molecules, but he assumed that the contact angle was constant. In his second paper, he returned to that explanation, but also adopted the latter hypothesis, whose exactness was proved only by Gauss. Nevertheless, we shall analyze that paper, which contains some new results.

12. – Expression for the liquid volume that is raised in a cylindrical tube of arbitrary section. – Consider a cylindrical tube whose cross-section is arbitrary and is submerged in a liquid.

Take the *xy*-plane to be the horizontal plane of the free surface of the liquid outside of the tube, and take the *z*-axis to be normal to that plane and point downwards.

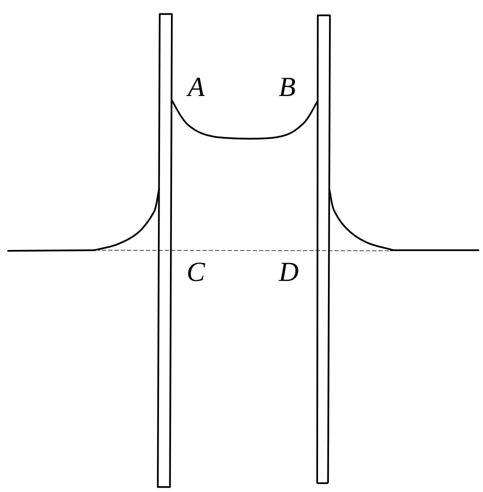

Figure 5.

The volume *U* of the liquid *ABCD* (Fig. 5) that is found in the tube above the *xy*-plane has the expression:

$$U = -\iint z\,dx\,dy\,,$$

in which *z* is the ordinate of a point on the free surface and the integration extends over the cross-section of the tube.

Now, we have found (9) that the equation of the free surface with respect to this system of axes is:

$$gz = \frac{\theta_1(0)}{2}\left(\frac{1}{R_1}+\frac{1}{R_2}\right);$$

consequently, we will get:

$$gU = -\iint \frac{\theta_1(0)}{2}\left(\frac{1}{R_1}+\frac{1}{R_2}\right) dx\,dy.$$

Let l, m be the direction cosines of the normal at a point on the free surface. The radii of principal curvature that pass through that point satisfy the equations:

$$\frac{dl}{dx}dx+\frac{dl}{dy}dy = -\frac{1}{R}dx,$$

$$\frac{dm}{dx}dx+\frac{dm}{dy}dy = -\frac{1}{R}dy,$$

in which dx, dy are proportional to the direction cosines of the tangent to the line of curvature. One can write the latter equations as:

$$\left(\frac{dl}{dx}-\frac{1}{R}\right)dx+\frac{dl}{dy}dy = 0,$$

$$\frac{dm}{dx}dx+\left(\frac{dm}{dy}-\frac{1}{R}\right)dy = 0,$$

resp., and one will deduce that:

$$\left(\frac{dl}{dx}+\frac{1}{R}\right)\left(\frac{dm}{dy}+\frac{1}{R}\right)-\frac{dl}{dy}\frac{dm}{dx} = 0,$$

or

$$\left(\frac{1}{R}\right)^2+\frac{1}{R}\left(\frac{dl}{dx}+\frac{dm}{dy}\right)+\frac{dl}{dx}\frac{dm}{dy}-\frac{dl}{dy}\frac{dm}{dx} = 0.$$

Consequently, we will have:

$$\frac{1}{R_1}+\frac{1}{R_2} = -\left(\frac{dl}{dx}+\frac{dm}{dy}\right),$$

and the expression for gU will become:

$$gU = \frac{\theta_1(0)}{2}\iint\left(\frac{dl}{dx}+\frac{dm}{dy}\right)dx\,dy,$$

or upon replacing the double integral in the right-hand side with a curvilinear integral that is taken over the cross-section of the tube:

$$gU = \frac{\theta_1(0)}{2} \int (l\,dy - m\,dx)\,.$$

The direction cosines of the tangent at a point on the cross-section of the tube are:

$$\frac{dx}{ds}, \qquad \frac{dy}{ds}, \qquad 0,$$

in which ds denotes an element of arc length of that cross-section, so those of the normal will be:

$$\frac{dy}{ds}, \quad -\frac{dx}{ds}\,, \qquad 0.$$

Consequently, the angle that is defined by the normal to the free surface of the liquid at a point of the separation curve and the normal to the surface of the tube, which is nothing but the contact angle φ, will have the cosines:

$$\cos\varphi = l\frac{dy}{ds} - m\frac{dx}{ds} + n\,(0)\,.$$

It will then result that the value of gU is:

$$gU = \frac{\theta_1(0)}{2} \int ds\ \cos\varphi, \tag{10}$$

which is a relation that Laplace wrote as:

$$gU = \frac{\theta_1(0)}{2} s\ \cos\varphi, \tag{11}$$

since he assumed that φ had the same value at any point of the contact curve.

13. Attraction of the matter that surrounds a cylindrical cavity to the liquid contained in the cavity. – Consider a volume T (Fig. 6) that is bounded by a cylindrical surface whose cross-section has an arbitrary form and an area of Ω, and at the same time, consider a material that occupies the volume $T' T''$ whose cylindrical surface is a boundary surface. We shall look for the component of the attraction that is exerted by the volume $T'T''$ on the volume T along the direction of the generators of that surface, which is a direction that we suppose to be vertical.

We first examine the case in which the upper part of the volume $T'T''$ is above that of the volume T, while the lower part of the latter volume is below that of the volume $T'T''$ (Fig. 6).

We decompose the volume T into elementary cylinders CD of section $d\omega$ and cut those cylinders with horizontal planes that are very close to each other. We will then get an infinitude of volume elements that have volume $d\omega\, dz$ and whose mass will be represented by the same product if we take the material considered to have unit density.

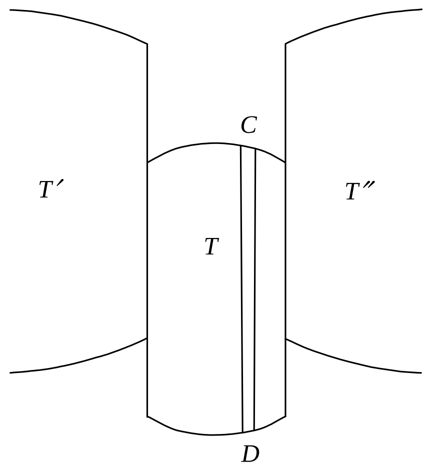

Figure 6.

Let V be the potential of the volume $T'T''$ at an exterior point. The force per unit mass that results will have the vertical component dV / dz, and as a result, the vertical component of the action of the volume $T'T''$ on the volume T will have the expression:

$$\iiint \frac{dV}{dz} d\omega dz = \iint d\omega \int \frac{dV}{dz} dz = \iint d\omega (V_1 - V_0),$$

in which V_1 is the potential at D and V_0 is the potential at C.

Now, the points like D that belong to the surface inside of the volume T are at a finite distance from the molecules of the volume $T'T''$. As a result, the potential of the latter volume at those points will be roughly zero, and we can write $V_1 = 0$. The points – such as C – that belong to the upper surface that bounds the volume T, are not all at a finite distance from the molecules of the volume $T'T''$; V_0 will not always be zero then. Consequently, the desired vertical component will have the expression:

$$-\iint V_0\, d\omega .$$

However, we have found that the potential at a point that is close to the surface that bounds an arbitrary volume is:

$$V = \theta(\varepsilon) - \frac{\theta_1(\varepsilon)}{2}\left(\frac{1}{R_1} + \frac{1}{R_2}\right).$$

The quantity $\theta_1(\varepsilon)$ is always very small, so we can neglect the term that contains that quantity as a factor and take $V_0 = \theta(\varepsilon)$. Under those conditions, we will have that the vertical component of the attraction is:

$$-\iint \theta(\varepsilon)\, d\omega\,. \tag{12}$$

When the volume T exceeds the volume $T'T''$ by its upper part, the potential V_0 will be zero, but V_1 will have the value $\theta(\varepsilon)$. Consequently, the vertical component of the attraction will be given by the preceding integral, when it is taken with the + sign.

In the case where the volume T exceeds the volume above and below, the various points such as C and D are at finite distances from the volume $T'T''$. V_1 and V_0 are zero, and the vertical component of the action of $T'T''$ on T is zero.

If the volume $T'T''$ goes beyond the upper and lower boundary surface of the volume T then the potential of T' at the various points of those surfaces will not be zero. However, the potentials V_0 and V_1 will be equal at the two points C and D, which belong to the same elementary cylinder. Consequently, the vertical component of the action of $T'T''$ on T will again be zero.

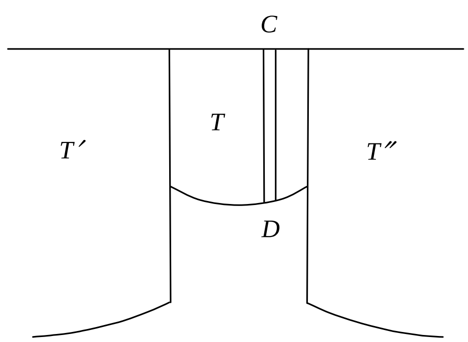

Figure 7.

We pass on to the case in which the two volumes T and $T'T''$ are bounded above by the same horizontal plane (Fig. 7), while the lower part of the volume $T'T''$ goes beyond that of the volume T.

Once more, we decompose the volume T into a cylinder CD of section $d\omega$, and we will get:

$$\iint (V_1 - V_0)\, d\omega$$

for the vertical component of the attraction of $T'T''$ to T.

The potential of the action of the volume $T'T''$ for the points of the lower bounding surface of T is:

$$V_1 = \theta(\varepsilon).$$

In order to find V_1, we a take a volume $T_1'T_1''$ that is symmetric to the volume $T'T''$ with respect to the horizontal plane. As a result of that symmetry, the potential at C of the volume $T_1'T_1''$ will be equal to the potential of the volume $T'T''$. If the latter is denoted by V_0 then the potential of the volume $T'T'' + T_1'T_1''$ will be $2V_0$. Now, the potential of $T'T'' + T_1'T_1''$ is approximately $\theta(\varepsilon)$. Consequently:

$$2V_0 = \theta(\varepsilon),$$

and the vertical component of the attraction of $T'T''$ to T will become:

$$\iint \frac{\theta(\varepsilon)}{2} d\omega. \tag{13}$$

Hence, in the various cases that can present themselves, that component will be zero or equal to the integral (12) or to the integral (13), which is one-half of the preceding one.

14. – We then calculate the integral (12).

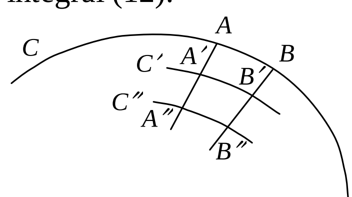

Figure 8.

Let C (Fig. 8) be the cross-section of the cylinder that separates the two volumes. Draw normals to that curve at two infinitely-close points A and B and trace out two curves C' and C'' that are parallel to C, the first of which is at a distance of ε, while the second one is at a distance of $\varepsilon + d\varepsilon$. We then form a surface element $A'B'A''B''$ whose edge $A'A''$ has a length of $d\varepsilon$ and its side $A'B'$ has a length that is roughly equal to the element of the curve $AB = ds$, since C and C' are two parallel curves that are very close to each other. Take that element to be the section $d\omega$ of the elementary cylinder CD that was considered before. We will then have:

$$\iint \theta(\varepsilon)\, d\omega = \iint \theta(\varepsilon)\, d\varepsilon\, ds = s\int \theta(\varepsilon)\, d\varepsilon$$

for the desired integral.

One of the limits of ε is 0; the other one is greater than the radius of molecular activity, since it is excessively small. Since $\theta(\varepsilon)$ is roughly zero for distances that are greater than that radius, we can take 0 and ∞ to be limits of the latter integral.

We will then have:

$$\int_0^\infty \theta(\varepsilon)\, d\varepsilon = [\varepsilon\,\theta(\varepsilon)]_0^\infty - \int_0^\infty \varepsilon\,\theta'(\varepsilon)\, d\varepsilon$$

for that integral. However, the functions $\theta(\varepsilon)$ and $\theta_1(\varepsilon)$ are defined by (3) to be:

$$\theta(\varepsilon) = \int_\varepsilon^\infty 2\pi\,\psi(z)\, dz, \qquad \theta_1(\varepsilon) = \int_\varepsilon^\infty 2\pi z\,\psi(z)\, dz.$$

Consequently:

$$\theta'(\varepsilon) = -\,2\pi\,\psi(\varepsilon),$$

and as a result:

$$\int_0^\infty \varepsilon\,\theta'(\varepsilon)\,d\varepsilon = \int_0^\infty 2\pi\varepsilon\,\psi(\varepsilon)\,d\varepsilon = -\,\theta_1(0).$$

The quantity $[\varepsilon\,\theta(\varepsilon)]_0^\infty$ is zero, since the first factor is zero for the limit 0 and the second factor will be annulled at the other limit. One will then have:

$$\int_0^\infty \theta(\varepsilon)\,d\varepsilon = \theta_1(0),$$

and

$$\iint \theta(\varepsilon)\,d\omega = s\;\theta_1(0). \tag{11}$$

15. New expression for the volume raised in a capillary tube. – We shall appeal to those quantities in order to find a new expression for the volume that is raised in a capillary tube.

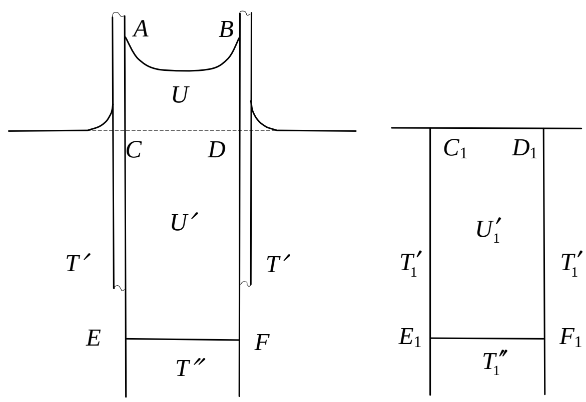

Figure 9.

Along with the volume U (Fig. 9), consider the volume U' that is bounded by the plane CD, the surface EF, and the prolongation of the cylindrical surface of the tube, and write down that the total volume $U + U'$ is in equilibrium under the action of the forces that act upon it.

Those forces are:

1. Its weight:

$$g\,(U + U'),$$

since the density of the liquid is taken to be unity.

2. The atmospheric pressure $p_0\;\Omega$ that is exerted upon the surface AB of the meniscus.

3. The hydrostatic pressure H on the surface EF.

4. The attraction of the liquid T' that surrounds the prolongation, which has a vertical component:

$$\iint \theta(\varepsilon)\, d\omega = s\ \theta_1\ (0).$$

5. The attraction of the glass tube. Since that tube exceeds the liquid volume $U + U'$ by the upper part, the vertical component of its attraction will be given by the preceding expression with the sign changed. However, in order to distinguish the action of a liquid to a liquid from the attraction of a solid to a liquid, we let $\eta\ (\varepsilon)$ denote the function of ε that corresponds to $\theta\,(\varepsilon)$, and we will get:

$$-\ s\ \eta\ (0)$$

for the vertical component of the attraction of the glass.

6. Finally, the attraction of the volume T'' that is situated below U' and whose vertical component will be denoted by H'.

Since the liquid is supposed to be in equilibrium, the algebraic sum of the vertical components of those forces must be zero; as a result:

$$g\ (U + U') + p_0\ \Omega - H + H' - s\ \eta_1\ (0) + s\ \theta_1\ (0) = 0.$$

In order to eliminate the quantities $p_0\ \Omega$, H, and H', we write down that the volume U_1' of the liquid, which is equal to U, but situated at a sufficient distance from the tube for C_1D_1 to be horizontal, must be in equilibrium under the action of the forces that act upon it.

Those forces are: weight gU', the atmospheric pressure $p_0\ \Omega$, the hydrostatic pressure H, the attraction H' of the volume T_1'', and finally, the attraction of the liquid T_1', whose vertical component will be:

$$\tfrac{1}{2} s\ \theta_1\ (0),$$

from (13) and (14).

One will then have:

$$gU' + p_0\ \Omega - H + H' + \frac{s}{2}\ \theta_1\ (0) = 0,$$

and the preceding relation will be written:

$$gU = s\left[\eta_1(0) - \frac{\theta_1(0)}{2}\right]. \tag{15}$$

16. Jurin's law. Laplace's law. – Suppose that the tube is formed inside of a cylinder of revolution of very small diameter d. The volume U that is raised in it is very roughly equal to that of a cylinder of the same diameter whose height is the distance z from the lowest point of the meniscus to the horizontal plane that forms the free surface of the liquid outside of the tube. As a result:

$$U = \pi \frac{d^2}{4} z \,.$$

Now, from the relation (13), gU will be equal to the perimeter $s = \pi d$ of the tube times a constant $k = \eta_1 - \theta_1 / 2$. Consequently:

$$g\pi \frac{d^2}{4} z = \pi\, dk,$$

so

$$z = \frac{4k}{g} \frac{1}{d} \,. \tag{16}$$

Laplace's theory then leads to that conclusion that the height that a liquid in a tube of very small diameter is raised will be inverse to the diameter of the tube. That law was stated for the first time by Borelli in 1670, then by Newton in 1704, and finally in 1708 by the English physicist Jurin who it was named for.

Suppose that the cross-section of the tube is a rectangle that has sides a and b, and one of the two – say, a – is very small. We will have:

$$s = 2\,(a + b),$$

and roughly:

$$U = abz.$$

The relation (15) will then give:

$$gabz = 2k\,(a + b),$$

so

$$z = \frac{2k}{g} \frac{a+b}{ab} \,.$$

If the side b becomes infinite, which will happen in practice when one considers the ascension of a liquid between two very close parallel layers, then one will have:

$$z = \frac{2k}{g} \frac{1}{a} \,.$$

Upon comparing that expression to the expression (16), one will see that the height that the liquid rises in a cylindrical tube of revolution will be twice the height that it will rise between two parallel layers whose spacing is equal to the diameter of the tube. That law is known by the name of *Laplace's law* today, and its experimental proof was due to Newton.

Laplace's theory then explains the two oldest known laws of capillary phenomena.

17. On the contact angle. – A comparison of the expressions (10) and (15) that were found for gU will yield the equality:

$$\frac{\theta_1(o)}{2}\int ds\cos\varphi = s\,[\eta_1\,(0) - \theta_1\,(0)].$$

If we set:

$$\int ds\cos\varphi = s\cos\varphi_0$$

then φ_0 will be the mean contact angle, and we will have:

$$\cos\varphi_0 = \frac{2\eta_1 - \theta_1}{\theta_1},$$

in which η_1 and θ_1 are constants for the same liquid and the same solid. We will see that the mean contact angle is a constant. That is all that we can deduce logically from Laplace's theory. It would not be permissible then to suppose, as Laplace did, that the contact angle itself is constant. It is true that in the special cases of a cylindrical tube of revolution and two very close parallel layers, that constancy will be obvious, by reason of symmetry.

Be that as it may, we assume, with Laplace, that the angle φ has the same value at every point of the contact curve. We will then have:

$$\cos\varphi = \frac{2\eta_1 - \theta_1}{\theta_1},$$

in which θ_1 and η_1 are positive quantities, so that angle will be:

acute	if	$2\eta_1 > \theta_1$,
obtuse	if	$2\eta_1 < \theta_1$,
right	if	$2\eta_1 = \theta_1$,
zero	if	$\eta_1 = \theta_1$.

If η_1 is greater than θ_1 then the preceding formula will lead to a value for the cosine that is greater than 1, but that is absurd. Laplace assumed that in that case, the liquid would wet the solid, and that it would be covered with a liquid sheath in such a way that everything would happen as if η_1 and θ_1 were equal.

Let us compare these results with the ones that Laplace obtained in his first paper. It results from the conclusions that were reached in (10) and (11) that the angle is:

acute	if	$2\rho > \rho'$,
obtuse	if	$2\rho < \rho'$,
right	if	$2\rho = \rho'$,
zero	if	$\rho = \rho'$.

Those results differ from the ones in his second paper only by the substitution of ρ for η_1 and ρ' for θ_1. They are identical if ρ and ρ' are proportional to η_1 and θ_1, respectively. Now, that is what happens if one assumes, like Laplace, that the laws of attraction of solid molecules to liquid molecules are the same as the laws of attraction of liquid molecules to each other, so the intensities of the attractive forces will differ by only a constant factor.

18. New way of obtaining the equation of the free surface. – We have seen how Laplace obtained the equation of the free surface of a liquid in the neighborhood of a solid wall:

$$gz = \frac{\theta(0)}{2}\left(\frac{1}{R_1} + \frac{1}{R_2}\right). \tag{8}$$

Let us now say a few words about another method that Laplace employed in order to arrive at that equation.

In the equilibrium state, the forces that are exerted upon a molecule of the surface of the liquid have a resultant that is normal to that surface. As a result, the virtual work that results from a displacement of a surface molecule in the tangent plane to the free surface must be zero. The virtual work done by gravity is $g\ \delta z$. If we let δJ denote the virtual work done by the capillary forces then we will have:

$$g\ \delta z + \delta J = 0,$$

and in order to get δJ, it will suffice to consider the tangential component of the capillary forces, since the work done by the normal component will be zero under the virtual displacement in question.

Take a system of coordinate axes that has its origin at a point O on the free surface, in which Oz is normal to the surface, Ox and Oy are the tangents to the indicatrices at the point O. The equation of the surface, when referred to those axes, will be:

$$z = ax^2 + by^2 + cx^3 + 3e\,x^2y + 3f\,xy^2 + hy^3 + \ldots,$$

and that of the osculating paraboloid will be:

$$z = ax^2 + by^2.$$

The attraction that is exerted by the liquid that is bounded by that paraboloid on a molecule that is situated at O is obviously (by reason of symmetry) directed normally to the surface. In order to get the tangential component of the capillary forces that are exerted at O, it will then suffice to consider the liquid that found between the free surface and the osculating paraboloid.

Take a surface element $ABCD$ (Fig. 10) in the xy-plane that is bounded on the one side by two arcs AB and CD of circles that have radii ρ and $\rho + d\rho$, and on the other by two lines that pass through the origin and make angles of θ and $\theta + d\theta$ with Ox.

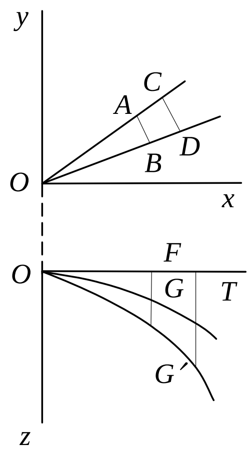

Figure 10.

Take the contour of that element to be parallels to the normal at *O*. We will get a cylinder that cuts out an element *G* on the free surface of the liquid and an element *G′* on the surface *S* of the osculating paraboloid. The portion of the cylinder that is found between *G* and *G′* is a volume element for which we have to find the tangential component of its attraction at *O*. Upon letting *z* and *z′* denote the distances from the elements *G* and *G′*, resp., to the *xy*-plane, we will have:

$$du = (z - z')\,\rho\, d\theta\, d\rho$$

for the volume of that element, in which $z - z'$ has the value:

$$z - z' = cx^2 + 3e\,x^2y + 3f\,xy^2 + hy^3 + \dots$$

In order for that value *du* to exert an appreciable effect on *O*, it is necessary that its distance from that point must be less than the radius of molecular activity. If that radius is considered to be a first-order infinitesimal then *x* and *y* must be likewise of order one, and *z* and *z′* must have order two. One can then consider all of the points of the small cylinder *FG* to be the same distance from the point *O*; i.e., assume that all of the points of the element *du* are at the same distance ρ from *O*. For the same reasons, one can regard all of the lines that join the point *O* to the various points of *du* as defining the same angle θ with the *x*-axis. As a result, the component along that axis of the attraction that *du* exerts on the point *O* will have the expression:

$$du\, f(\rho) \cos\,\theta,$$

and the component along that axis of the attraction of the volume that is found between the free surface and the paraboloid will be:

$$\int du\; f(\rho)\cos\theta = \int (z - z')\,\rho\; f(\rho)\cos\theta\, d\theta\, d\rho\,,$$

in which θ varies from 0 to 2π and ρ, from 0 to the value of the radius of molecular activity, or what amounts to the same thing, from 0 to ∞.

Now, $\frac{z-z'}{\rho^3}$ depends upon only θ, because:

$$\frac{x}{\rho} = \cos\,\theta, \qquad \frac{y}{\rho} = \sin\,\theta,$$

and as a result:

$$\frac{z-z'}{\rho^3} = c\,\cos^3\,\theta + 3e\,\sin\,\theta\cos^2\,\theta + 3f\,\sin^2\,\theta\cos\,\theta + h\,\sin^3\,\theta.$$

The preceding integral can then be written:

$$\int_0^{2\pi} \frac{z-z'}{\rho^3} \cos\theta\, d\theta \int_0^{\infty} \rho^4 f(\rho)\, d\rho\,.$$

If we let B denote the value of the integral that is defined with respect to ρ and perform the integration with respect to θ then we will get:

$$c\int_0^{2\pi} \cos^4\theta\, d\theta + 3e\int_0^{2\pi} \cos^3\theta \sin\theta\, d\theta + 3f\int_0^{2\pi} \cos^2\theta \sin^2\theta\, d\theta + h\int_0^{2\pi} \cos\theta \sin^3\theta\, d\theta$$

$$= \frac{3\pi}{4} c + \frac{3\pi}{4} f = \frac{3\pi}{4} (c+f),$$

and the double integration will give:

$$\frac{3B\pi}{4} (c+f).$$

In the same way, we will find that the component of the desired attraction along Oy is:

$$\frac{3B\pi}{4} (e+h),$$

and consequently, we will have:

$$\delta J = \frac{3B\pi}{4} [(c+f)\,\delta x + (e+h)\,\delta y]$$

for the virtual work done by capillary forces.

It still remains to introduce the radii of curvature. Now, one has:

$$\frac{1}{R_1} + \frac{1}{R_2} = -\left(\frac{dl}{dx} + \frac{dm}{dy}\right),$$

and

$$l = \frac{\frac{dz}{dx}}{\sqrt{\left(\frac{dz}{dx}\right)^2 + \left(\frac{dz}{dy}\right)^2 + 1}}, \qquad m = \frac{\frac{dz}{dy}}{\sqrt{\left(\frac{dz}{dx}\right)^2 + \left(\frac{dz}{dy}\right)^2 + 1}}.$$

However, x and y are first-order infinitesimals, so the derivatives:

$$\frac{dz}{dx} = 2a\,x + 3c\,x^2 + 6e\,xy + 3f\,y^2,$$

$$\frac{dz}{dy} = 2b\,x + 3e\,x^2 + 6f\,xy + 3h\,y^2$$

will also have order one. As a result, their squares will be negligible in comparison to unity, and one will have approximately:

$$l = \frac{dz}{dx}, \qquad m = \frac{dz}{dy}.$$

It will then result that:

$$\frac{dl}{dx} = 2a + 6cx + 6ey,$$

$$\delta\frac{dl}{dx} = 6\,(c\,\delta x + e\,\delta y),$$

$$\frac{dm}{dy} = 2b + 6f\,x + 6h\,y,$$

$$\delta\frac{dm}{dx} = 6\,(f\,\delta x + h\,\delta y),$$

$$\delta\left(\frac{dl}{dx} + \frac{dm}{dy}\right) = 6\,[(e+f)\,\delta x + (e+h)\,\delta y],$$

and consequently:

$$\delta J = -\frac{B\pi}{8}\left(\frac{1}{R_1} + \frac{1}{R_2}\right).$$

Finally, one will have:

$$gz = \frac{B\pi}{8}\left(\frac{1}{R_1} + \frac{1}{R_2}\right)$$

for the equation of the free surface, and its form does not differ from that of equation (8).

CHAPTER II

THEORIES OF GAUSS AND POISSON

19. Basis for Gauss's theory. – Like Laplace, Gauss considered bodies that were composed of molecules that attracted each other along the lines that connected them with an intensity that was proportional to their masses and depended upon the distance between them.

From the principle of virtual work, the sum of the virtual works will be zero when one gives a virtual displacement to the system in equilibrium that is compatible with the constraints. We shall look for those works for a ponderable liquid that is in contact with a solid wall.

If U is the volume of the liquid (whose density we continue to take to be unity) then the virtual work done by weight will be:

$$g\,U\,\delta z,$$

in which the z-axis is vertical and points downward.

Upon letting:

$$mm'\,f\,(r)$$

represent the attraction of two liquid molecules, the work that corresponds to an increment δr in the distance will be:

$$-\,mm'\,f\,(r)\;\delta r = mm'\;\delta\varphi\,(r),$$

in which the function φ is defined as it was in § **1**.

The work that is done by a displacement of a solid molecule with respect to a solid molecule is:

$$-\,m\mu\,f_1\,(r)\;\delta r = m\mu\;\delta\varphi_1\,(r)\,.$$

Consequently, an application of the principle of virtual velocities will yield the equation:

$$gU\,\delta z + \sum mm'\,\delta\varphi(r) + \sum m\mu\,\delta\varphi_1(r) = 0.$$

If one sets:

$$\sum mm'\,\varphi(r) = W,$$

$$\sum m\mu\,\varphi_1(r) = W_1\,,$$

and if one supposes that the fluid is incompressible, which will permit one to write:

$$gU\,\delta z = \delta(g\,Uz),$$

then that equation will become:

$$\delta(gUz + W + W_1) = 0. \qquad (1)$$

That is the relation from which Gauss deduced the equation of the free surface and the value of the contact angle.

We remark that the function:

$$-(gUz + W + W_1)$$

is nothing but the potential energy of the system. It will then be easy, in general, to recognize whether the equilibrium is stable, because one knows that there will be stable equilibrium when the potential energy passes through a minimum. That is one of the advantages of Gauss's method over that of Laplace.

20. Calculating the work done by molecular forces. – Consider a liquid volume; one will then have:

$$W = \sum mm'\varphi(r) = \iint \varphi(r)\, d\tau\, d\tau',$$

in which the sextuple integral is taken in such a way that the two elements $d\tau$ and $d\tau'$ are considered only once. If one does not restrict oneself with that condition and one calculates the integral by taking all permutations of two elements then one will get:

$$W = \tfrac{1}{2}\iint \varphi(r)\, d\tau\, d\tau'.$$

Regard $d\tau$ as fixed; the corresponding integral will be:

$$\int \varphi(r)\, d\tau'.$$

Now, that integral is the potential V of the entire volume at the center of gravity of the element $d\tau$; as a result:

$$W = \tfrac{1}{2}\int V\, d\tau.$$

However, we have found (6) for the potential at an exterior point that is very close to the surface that bounds the attracting volume:

$$V = \theta(\varepsilon) - \frac{\theta_1(\varepsilon)}{2}\left(\frac{1}{R_1} + \frac{1}{R_2}\right).$$

In the case that we are dealing with, in which the point considered is as interior point, we will have:

$$V = \theta(-\varepsilon) - \frac{\theta_1(-\varepsilon)}{2}\left(\frac{1}{R_1} + \frac{1}{R_2}\right),$$

and since θ_1 is very small with respect to θ, we can preserve the first term [which one cannot do in Laplace's theory, since the term $\theta(\varepsilon)$ will disappear from the equations]. As a result:

$$V = \theta(-\varepsilon).$$

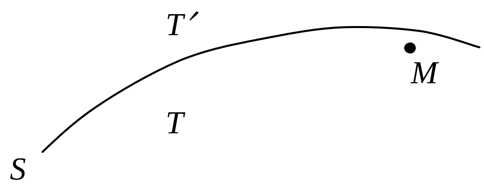

Figure 11.

Furthermore, it is easy to express $\theta(-\varepsilon)$ as a function of $\theta(\varepsilon)$. Indeed, let M be a point close to the separation surface S (Fig. 11) between two volumes T and T' of the same liquid. The potential at that point due to T is $\theta(-\varepsilon)$; the one that is due to T' is $\theta(\varepsilon)$. Consequently, the potential that is due to the volume $T + T'$ is $\theta(\varepsilon) + \theta(-\varepsilon)$. Now, that point M is at a finite distance from the surface that bounds $T + T'$. Hence, the resultant of the molecular forces that are exerted on it will be zero, and the potential of $T + T'$ at that point will be a constant A. One will then have:

$$\theta(-\varepsilon) = A - \theta(\varepsilon),$$

and:

$$W = \tfrac{1}{2}\int [A - \theta(\varepsilon)]\, d\tau = \frac{AU}{2} - \tfrac{1}{2}\int \theta(\varepsilon)\, d\tau\,. \tag{2}$$

The work done by forces that are exerted between solid molecules and liquid molecules can, in an analogous fashion, be expressed with the aid of the function $\eta(\varepsilon)$. We have:

$$W_1 = \iint \varphi_1(r)\, d\tau\, d\tau_1\,,$$

and since $d\tau$ and $d\tau_1$ refer to two different materials, we cannot introduce those two elements as we did in the expression W.

If we regard the element $d\tau$ as fixed then the portion of the corresponding integral will be:

$$\int \varphi_1(r)\, d\tau_1\,,$$

which is an integral that represents the potential V_1 of the solid at a point of $d\tau$. Since that element is exterior to the solid, V_1 will have a value $\eta(\varepsilon)$ that is approximately constant, and we will have:

$$W_1 = \int \eta(\varepsilon)\, d\tau\,. \tag{3}$$

We see that W and W_1 are given by integrals of the same form. Let us transform them.

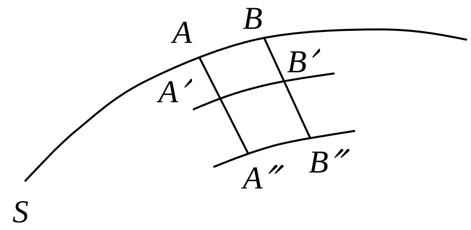

Figure 12.

Let AB (Fig. 12) be an element of the surfaces of a fluid. Draw normals to the surface at all points of its contour and cut the tube thus-obtained with two surfaces that are parallel to S, one of which is situated at a distance ε, while the other is at a distance $\varepsilon + d\varepsilon$. We have a volume element $A' B' A'' B''$ whose base $A'B'$ differs infinitely little from AB, since ε is very small. Upon letting $d\omega$ denote the area of the element AB, the volume of that element will be:

$$d\tau = d\varepsilon\, d\omega,$$

and that will give:

$$\int \theta(\varepsilon)\, d\tau = \iint \theta(\varepsilon)\, d\varepsilon\, d\omega,$$

in which the integration over ω is performed over the entire extent of the surface S that bounds the fluid, and the one over ε is performed from 0 up to the value of the radius of molecular activity, or what amounts to the same thing, from 0 to infinity. That integral can then be written:

$$\int_\varepsilon d\omega \int_0^\infty \theta(\varepsilon)\, d\varepsilon .$$

However, we have seen (14) that:

$$\int_0^\infty \theta(\varepsilon)\, d\varepsilon = \theta_1(0),$$

so as a result:

$$\int_\varepsilon d\omega \int_0^\infty \theta(\varepsilon)\, d\varepsilon = S\, \theta_1(0),$$

and from (2):

$$W = \frac{AU}{2} - \frac{S\,\theta_1(0)}{2} .$$

Upon transforming the expression (2) in the same way, it will become:

$$W_1 = S\, \eta_1(0).$$

In those equalities, S denotes the entire surface that bounds the fluid, and S_1 denotes the contact surface of the fluid and the solid.

We then have:

$$\delta W = -\frac{\theta_1}{2}\,\delta S, \qquad\qquad \delta W_1 = \eta_1\,\delta S_1$$

for the virtual work done by molecular forces.

21. Transformation of the equilibrium equation. – Substitute the preceding values for W and W_1 in the relation (1) and neglect the term AU / 2, moreover, which will disappear when one takes the variations; it will become:

$$\delta\left(gUz - \frac{\theta_1}{2}S + \eta_1 S_1\right) = 0.$$

If we let Σ denote the portion of the surface S that is not in contact with the solid then we will have:

$$S = S_1 + \Sigma,$$

and the preceding equation will become:

$$\delta\left[gUz - \frac{\theta_1}{2}\Sigma + \left(\eta_1 - \frac{\theta_1}{2}\right)S_1\right] = 0. \tag{4}$$

Let us calculate the variation of each of the terms of the quantity inside the brackets.

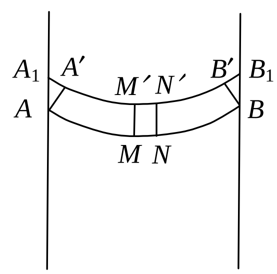

Figure 13.

Let AB be one of the surfaces that bound the fluid in its equilibrium position (Fig. 13) and let $A_1\,B_1$ be its position after displacement. Those two surfaces enclose a small volume between them that we decompose into volume elements by drawing normals MM', NN' to the surface AB through the contour of each element $d\sigma$ of that surface. Upon letting λ denote MM', the volume element will have the expression:

$$d\tau = \lambda\, d\sigma.$$

The term $gU\,z$ is the moment of the weight of the liquid with respect to the xy-plane. Its variation will then be the moment of the volume that is found between the equilibrium surface of the fluid and its surface after displacement; consequently:

$$\delta(gU\,z) = \int gz\lambda\, d\sigma\,.$$

In order to get the variation of the second term, compare the areas Σ and Σ_1 of the surfaces *AB* and A_1B_1 , resp., that are found between the lines of contact *L* and L_1, resp., of those surfaces and the solid walls; one will have:

$$\delta\Sigma = \Sigma_1 - \Sigma\,.$$

If we draw normals *AA′*, *BB′* to the surface *AB* through the points of *L* then those normals will cut the surface A_1B_1 along a line *A′B′* that bounds an area Σ' on that surface. Upon letting Σ'' denote the area that is found between *A′B′* and A_1B_1 , we can write the variation of Σ as:

$$\delta\Sigma = \Sigma' + \Sigma'' - \Sigma \;= \Sigma'' + \int d\sigma' - \int d\sigma\,.$$

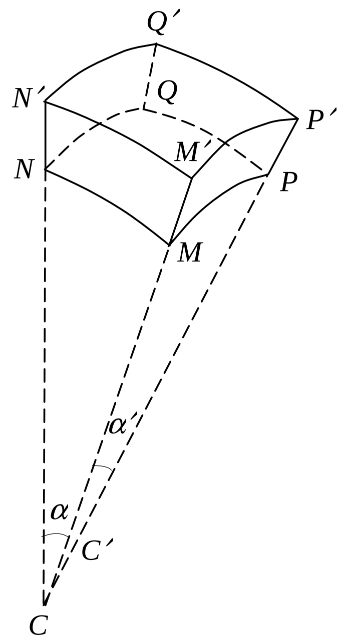

Figure 14.

Compare the surfaces $d\sigma$ and $d\sigma'$ of the elements *MN* and *M′N′*. In order to do that, suppose that the edges of the elements *MN* belong to two lines of curvature of the surface *AB* that passes through the point *M*. The lines of curvature will intersect at a right angle, so we will have:

$$d\sigma = MN \times MP,$$

in which *MN* and *MP* (Fig. 14) are the two sides of the element. The normals that are drawn through the points of *MN* and *MP* will cut the surface Σ_1 along two lines *M′N′* and *M′P′* that are roughly perpendicular; as a result:

$$d\sigma' = M'N' \times M'P'.$$

The points M and N belong to the same line of curvature, so the normals at those points will intersect at a point C. Upon letting R_1 denote the radius of curvature MC, one will have:

$$MN = \alpha R_1 , \quad MN = \alpha (R_1 + \lambda),$$

in which α is the angle between the normals M and N, because $M' N'$ is roughly perpendicular to the two normals.

One infers from this that:

$$\frac{M' N'}{MN} = 1 + \frac{\lambda}{R_1} .$$

Similarly, one has:

$$\frac{M' P'}{M' N'} = 1 + \frac{\lambda}{R_2} ,$$

and consequently:

$$\frac{d\sigma'}{d\sigma} = \left(1+\frac{\lambda}{R_1}\right)\left(1+\frac{\lambda}{R_2}\right),$$

or, upon developing this and neglecting the term in λ^2, which is a second-order infinitesimal, since λ has order one:

One deduces that:

$$d\sigma' - d\sigma = \lambda \, ds \left(\frac{1}{R_1}+\frac{1}{R_2}\right)$$

and

$$\int d\sigma' - \int d\sigma = \int \lambda \left(\frac{1}{R_1}+\frac{1}{R_2}\right) d\sigma .$$

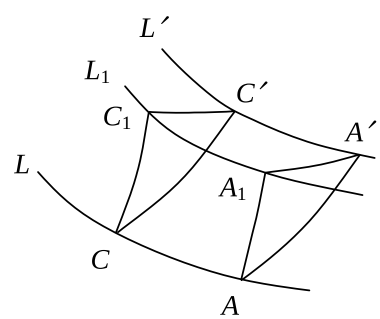

Figure 15.

Let us evaluate the annular area Σ''. Let A and C be two points that are infinitely-close to the contact curve L (Fig. 15). Draw normal planes to that curve through those points. They will cut out an element $A' \, C' \, A_1 \, C_1$ from the area Σ'' whose surface area is roughly:

$$d\omega = ds \times A_1 \, A',$$

in which ds denotes the element AC of the curve L. If φ is the contact angle in the equilibrium state then the contact element AA_1A' after the displacement can coincide with φ, and since the angle at A' is roughly a right angle, since AA' is normal to the surface Σ, one will have:

$$A_1A' = AA' \cot \varphi = \lambda \frac{\cos\varphi}{\sin\varphi}.$$

As a result:

$$d\omega = \lambda \frac{\cos\varphi}{\sin\varphi} ds$$

and

$$\Sigma'' = \int d\omega = \int_L \lambda \frac{\cos\varphi}{\sin\varphi} ds.$$

The variation of the second term is then:

$$-\frac{\theta_1}{2}\delta\Sigma = -\frac{\theta_1}{2}\left[\int \lambda\left(\frac{1}{R_1}+\frac{1}{R_2}\right)d\sigma + \int_L \lambda \frac{\cos\varphi}{\sin\varphi} ds\right].$$

The variation of the third term is easily obtained. Indeed, since S_1 is the contact surface of the liquid and the solid, δS_1 will be the area that is found between the contact lines L and L_1. An element of that area is AA_1C_1A (Fig. 15); consequently:

$$\delta S_1 = \int ds \times AA_1.$$

However, in the right triangle AA_1A', one has:

$$AA_1 = \frac{\lambda}{\sin\varphi};$$

hence:

$$\left(\eta_1 - \frac{\theta_1}{2}\right)\delta S_1 = \left(\eta_1 - \frac{\theta_1}{2}\right)\int_L \frac{\lambda}{\sin\varphi} ds.$$

The condition (4) will then become:

$$\int gz\,\lambda\,d\sigma - \frac{\theta_1}{2}\int \lambda\left(\frac{1}{R_1}+\frac{1}{R_2}\right)d\sigma - \frac{\theta_1}{2}\int_L \lambda\frac{\cos\varphi}{\sin\varphi}ds + \left(\eta_1 - \frac{\theta_1}{2}\right)\int_L \frac{\lambda}{\sin\varphi}ds = 0,$$

or

$$\int\left[gz - \frac{\theta_1}{2}\left(\frac{1}{R_1}+\frac{1}{R_2}\right)\right]\lambda\,d\sigma + \int_L\left(\eta_1 - \frac{\theta_1}{2} - \frac{\theta_1}{2}\cos\varphi\right)\frac{\lambda}{\sin\varphi}ds = 0. \tag{5}$$

22. Equation of the free surface. Contact angle. – That equation must be satisfied no matter what value is given to λ, provided that it is compatible with the constraints. Now, the liquid was assumed to be incompressible. Consequently, the algebraic sum of the variations of the volume that result from the virtual displacement of the bounding surfaces must be zero. We saw in the preceding number that the volume of an element that is included between the equilibrium surface and the deformed surface is $d\tau = \lambda\, d\sigma$. As a result, the incompressibility of the fluid will lead to the condition:

$$\int \lambda\, d\sigma = 0. \tag{6}$$

If we take that equality into account then the relation (5) will be satisfied for an arbitrary value of λ that is compatible with the constraints if:

$$gz - \frac{\theta_1}{2}\left(\frac{1}{R_1}+\frac{1}{R_2}\right) = K, \tag{7}$$

$$\eta_1 - \frac{\theta_1}{2} - \frac{\theta_1}{2}\cos\varphi = 0, \tag{8}$$

in which K is a constant.

Indeed, those conditions are sufficient, because if they are fulfilled then the second term in (5) will be zero, and the first one will reduce to the product of a constant with the integral of $\lambda\, ds$, which is zero, from (6).

Let us show that they are necessary; i.e., if they are not fulfilled then we can arrange things so that the relation (6) is satisfied, while the relation (5) is not.

First assume that:

$$gz - \frac{\theta_1}{2}\left(\frac{1}{R_1}+\frac{1}{R_2}\right)$$

is not a constant. It will then be a function of the coordinates that presents at least one maximum and one minimum, since it is applied to the bounding surface. If one then takes K to be a value that is found between that maximum and minimum then the function:

$$gz - \frac{\theta_1}{2}\left(\frac{1}{R_1}+\frac{1}{R_2}\right) - K \tag{9}$$

will be sometimes positive and sometimes negative. Give a value to λ that is zero along the contact curve and has values with the same sign as the preceding difference at any other point of the surface. Those values can always be chosen in such a way that the condition (6) is satisfied. If that is true then one will have:

$$\int K\lambda\, d\sigma = 0,$$

and as a result:

$$\int \left[gz - \frac{\theta_1}{2} \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \right] \lambda \, d\sigma = \int \left[gz - \frac{\theta_1}{2} \left(\frac{1}{R_1} + \frac{1}{R_2} \right) - K \right] \lambda \, d\sigma \, .$$

However, by hypothesis, λ always has the same sign as the difference (9). Consequently, the element of the latter integral will be positive, and that integral cannot be annulled. On the contrary, the second integral in (5) is zero, since the value of λ is zero along the integration contour. The relation (5) cannot be satisfied for all values of λ that are compatible with the constraints then under the conditions that we have imposed. The condition (7) is necessary then.

Suppose that it is fulfilled, but that (8) is not. One can always take λ to have values that satisfy (6) in such a way that the sign of those values along the contact line L is the same at each point at that of the quantity:

$$\eta_1 - \frac{\theta_1}{2} - \frac{\theta_1}{2} \cos \varphi \, .$$

The first integral in (5) will be zero then, while the second one will have a positive value since its element is positive; as a result, the relation (5) will not be satisfied.

The conditions (7) and (8), when combined with the condition (6), are necessary and sufficient then. The condition (7) is nothing but the equation of the free surface of the liquid; it is identical to the one that Laplace found.

One deduces from the condition (8) that:

$$\cos \varphi = \frac{2\eta_1 - \theta_1}{\theta_1} \, ,$$

which shows that the contact angle is constant, which is a result that could not have been obtained by Laplace's calculations.

23. Potential due to a liquid of variable density. – In 1831, the year that followed Gauss's publication, Poisson published his *Nouvelle Théorie de l'action capillaire,* in which he reproached Laplace for supposing that the density of the liquid was constant. The same criticism applies to Gauss's theory.

By some laborious calculations, Poisson succeeded in proving that it was impossible to imagine a system of liquid molecules in equilibrium under the action of their mutual attraction without any variation of their density, and that if one takes into account that variation of the density then one will nonetheless get back to Laplace's equation for the free surface, with the only difference being that the two constants that enter into it will have a more complex significance.

Fortunately, it is not necessary to repeat Poisson's analysis in order to arrive at that result. We shall arrive at it much more simply here.

We seek the potential of a liquid of variable density at a point M that is very close to its free surface S_1 (Fig. 16). Drop a normal MP_1 to the surface from that point. If one displaces along that normal towards the interior of the liquid then the density will vary in a continuous manner in the neighborhood of the free surface, and then take on a constant value.

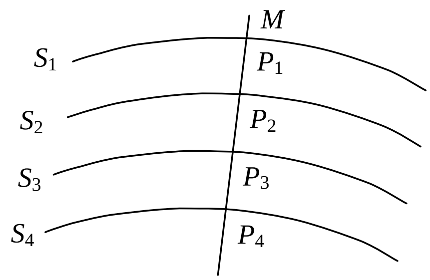

Figure 16.

Draw surfaces of equal intensity S_2, S_3, S_4 through the various points P_2, P_3, P_4, resp., along that normal. We suppose, for the moment, that the density varies in a discontinuous fashion when one crosses those surfaces and keeps a constant value in the space between the two of them.

Let ρ_1, ρ_2, ρ_3 be the values of the density between S_1 and S_2, between S_2 and S_3, and between S_1 and S_2, resp.; we assume that the density ρ_4 is constant outside of S_4. We can suppose that the shell of density ρ_1 is bounded by S_1, on the one hand, and extends to infinity, on the other, with the condition that one must add a shell of uniform density $\rho_2 - \rho_1$ that is bounded by S_2 and extends to infinity, a shell of uniform density $\rho_3 - \rho_2$ that goes from S_3 to infinity, and finally, a shell of uniform density $\rho_4 - \rho_3$ that goes from S_4 to infinity. The search for the potential at M will then be found to reduce to that of the potential due to various volumes of constant density.

Now, we know that the potential of a liquid of constant unit density is:

$$V = \theta(\varepsilon) - \theta_1(\varepsilon)\left(\frac{1}{R_1} + \frac{1}{R_2}\right).$$

Since θ_1 is very small with respect to θ, we can neglect the second term, and we will have:

$$V = \rho\,\theta(\varepsilon)$$

for the potential of a liquid of density ρ.

Set:

$$MP_1 = \varepsilon, \qquad P_1P_2 = \zeta_1, \qquad P_1P_3 = \zeta_2, \qquad P_1P_4 = \zeta_3;$$

we will then get:

$$V = \rho_1\,\theta(\varepsilon) + (\rho_2 - \rho_1)\,\theta(\varepsilon + \zeta_1) + (\rho_3 - \rho_2)\,\theta(\varepsilon + \zeta_2) + (\rho_4 - \rho_3)\,\theta(\varepsilon + \zeta_4)$$

for the potential at M, or upon setting:

$$\rho_0 = 0, \qquad \zeta_0 = 0,$$

we will get:

$$V = (\rho_1 - \rho_0)\ \theta(\varepsilon + \zeta_0) + (\rho_2 - \rho_1)\ \theta(\varepsilon + \zeta_1) + \ldots$$

or rather:

$$V = \sum (\rho_i - \rho_{i-1})\,\theta(\varepsilon + \zeta_{i-1})\,.$$

Consequently, if we now suppose that the density varies in a continuous manner then:

$$V = \int d\rho\,\theta(\varepsilon + \zeta)\,. \tag{10}$$

We remark that the position of the foot P_1 of the normal that is based at the point M can be determined on the surface S_1 with the aid of the two coordinates α and β. The position of a point such as P_2 will depend upon the value of the density, in addition. Consequently, the quantity ζ_1, which fixes the position of that point, will be a function of α, β, and the density ρ of the liquid.

24. Free surface and contact angle in the case of a variable density. – Hydrostatics teaches us that in a fluid in equilibrium the surfaces of equal density will coincide with the surfaces of equal pressure. Now, we have found (7) that the pressure at a point of a ponderable fluid is given by the equality:

$$p = V + gz + \text{const.},$$

without making any hypothesis on the density.

The surfaces of equal pressure, and as a result, the surfaces of equal density in a fluid in equilibrium will then have the equations:

$$V + gz = \text{const.} \tag{11}$$

However, one can neglect gz with respect to V. In order to see that, return to the case in which the density is constant; one will then have:

$$V = \theta(\varepsilon) - \theta_1(\varepsilon)\left(\frac{1}{R_1} + \frac{1}{R_2}\right),$$

and the equation of the free surface will be:

$$gz = \frac{\theta_1(0)}{2}\left(\frac{1}{R_1} + \frac{1}{R_2}\right).$$

Hence, for the free surface, gz has the same order as $\theta_1(0)$, while V has the same order as θ. The order of magnitude of V cannot change appreciably when one passes to the case of a variable density; similar statements will apply to the gz of the free surface. Since the density is variable only in the neighborhood of the free surface, moreover, the

gz of the surfaces of equal density will likewise have the same order of magnitude. Consequently, one can write equations (11):

$$V = \text{const.}$$

We show that it is possible to satisfy that condition by supposing that the surfaces of equal density S_1, S_2, S_3, S_4 are mutually parallel.

Indeed, when the surfaces are parallel, ζ_1, ζ_2, … will have the same value at any point of those surfaces, and consequently they will not depend upon the coordinates α and β, but only upon ρ. Therefore, if the point M belongs to one of those surfaces then ε will be constant, and $\theta(\alpha + \zeta)$ will depend upon only ρ. As a result, one will obtain a constant upon performing the integration of (10) between the value ρ_0 of the density at the point considered and its constant value of 1 at an appreciable distance from that point. The potential will then be constant along surfaces of equal density, and the equilibrium condition will be satisfied.

We do not know the form of the functions θ, so it would be impossible for us to show that there is no other solution to the problem. We shall assume that without proof.

However, if the potential V is a constant when ε is constant then that potential will generally be a function of only ε. It will become zero when ε is finite, because in that case $\varepsilon + \zeta$ will be likewise finite, and the integral element $\theta(\varepsilon + \zeta)\,d\rho$ will be zero. If the point is interior to the liquid and at an appreciable distance from the surface then ε will be negative and finite, and since ζ is always very small, $\varepsilon + \zeta$ will have a finite negative value. Now, we have shown that $\theta(-\varepsilon) = A - \theta(\varepsilon)$; consequently, $\theta(\varepsilon + \zeta)$ will reduce to a constant, and the same thing will be true for the integral V. In a word, the potential V will be a function of ε that enjoys the same properties as the function $\theta(\varepsilon)$ that represents the potential both Laplace's and Gauss's theories. Since we make use of only the properties of that function in the latter theory, it is obvious that we will arrive at the same conclusions as the ones that we have found by replacing the function $\theta(\varepsilon)$ with the function $V = \theta'(\varepsilon)$ everywhere. The free surface and contact angle will then be given by the same equations.

We shall return much later to some other theories of capillarity that are entirely independent of the hypothesis of central forces. We shall now apply the results that were found before.

For the moment, we observe only that the theory that is called the theory of *surface tension* will lead to the same identical result as Gauss's theory, and consequently, that of Laplace.

Indeed, under an arbitrary virtual displacement, the work that is done by that tension will be proportional to δS ; i.e., it will have precisely the same expression as the work done by molecular attraction under the hypotheses of Laplace and Gauss.

Therefore, experiments cannot decide between the theory of attraction and that of tension, which is currently in favor. All of the facts that are predicted by the one will be likewise predicted by the other.

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CHAPTER III

THIN FILMS

25. The equilibrium surface is minimal. – If we submerge a framework that is composed of flexible and rigid wires in a liquid then upon taking the framework back out of the liquid, we will get a system of thin films that are bounded by the wires. Let us look for the equilibrium surfaces of those films.

The general condition for stable equilibrium is that:

$$gUz - \frac{\theta_1}{2}\Sigma + \left(\eta_1 - \frac{\theta_1}{2}\right)S_1$$

must be maximum. The last term in that sum can be neglected in the case that we are concerned with, because the area of the contact surface S_1 of the liquid and the solids will be proportional to the thickness of the film, which is always excessively small. The volume U is likewise proportional to that thickness. As a result, it will be likewise very small, and the first term can be neglected with respect to the second one, provided that $\theta_1 / 2$, which represents what one can call the *surface tension* of the liquid, is nonetheless very small.

The condition of equilibrium then reduces to this one: $-(\theta_1 / 2)\ \Sigma$ must be a maximum, or rather, Σ must be a minimum. Now, in the case of just one film, the free surface Σ is composed of the two faces of the film, and those surfaces will be roughly equal if the thickness is very small. Consequently, in order for there to be stable equilibrium, it will suffice that the area $\Sigma / 2$ of one of those faces should be a minimum.

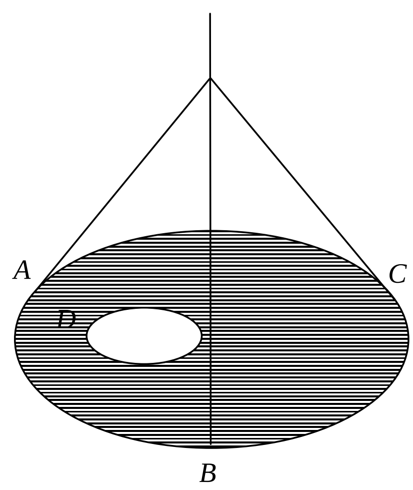

Figure 17.

That conclusion can be verified experimentally very easily by means of an experiment that is due to Van der Mensenbrugghe. One submerges a metallic hoop *ABC* (Fig. 17) that is suspended by three wires in a liquid – for example, the glycerin that

Plateau used. One withdraws the hoop and carefully places a ring of cotton thread that was previously moistened with the same liquid in the planar film that was obtained. That thread will take on an arbitrary form, but if one would like to burst the film in the middle of the ring that it is included in then the thread will tense briefly and become circular. Now, of all the curves with the same perimeter, the circumference will be the one that bounds the largest area. The area that is found between the circumference *D* and the contour of the metallic ring will then be minimal when the liquid is in equilibrium.

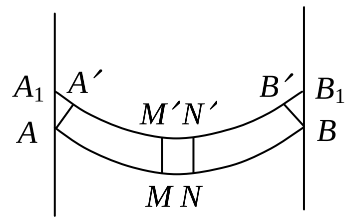

Figure 18.

26. The mean curvature of the surface must be zero in the equilibrium state. – Let *AMB* (Fig. 18) be one of faces of the liquid film. Draw a surface $A_1M'B_1$ that is very close and parallel to it. If *AMB* is a minimal surface then the areas *AMB* and $A_1M'B_1$ must be equal, up to second-order infinitesimals. Draw normals to that surface through the contour of *AB*. Those normals will cut out an area of Σ' from the surface $A_1M'B_1$, and if one lets Σ'' denote the annular area that is found between the line $A'B'$ and the line A_1B_1 then the preceding condition will be expressed by:

$$\Sigma' + \Sigma'' = \Sigma.$$

Now, we have previously found (§ **21**) that:

$$\Sigma' - \Sigma = \int \lambda \left(\frac{1}{R_1} + \frac{1}{R_2} \right) d\sigma \,,$$

$$\Sigma'' = \int \lambda \frac{\cos\varphi}{\sin\varphi} ds \,,$$

in which λ is the length of the normal, $d\sigma$ is the area of an element *MN* of the surface *AB*, *ds* is the length of an element of the contact curve of *AB*, and φ is the contact angle. Consequently, we must have:

$$\int \lambda \left(\frac{1}{R_1} + \frac{1}{R_2} \right) d\sigma + \int \lambda \cot\varphi \, ds = 0,$$

and since that condition must be satisfied for any λ, we must have:

$$\frac{1}{R_1}+\frac{1}{R_2}=0,$$
$$\cot\varphi=0.$$

The two radii of principle curvature of the surface must be equal and have opposite signs. The surfaces that enjoy that property have been given the general term of *minimal surfaces.*

The equality $\cot\varphi = 0$ expresses the idea that the contact angle must be a right angle. However, since the direction of the tangent plane to a wire is arbitrary, that condition will amount to saying that the surface must pass through the wire.

In summary, the problem that we have posed consists of determining the minimal surface that passes through a given contour.

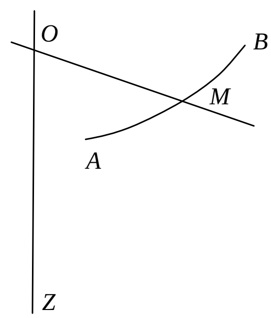

Figure 19.

27. The helicoid is an equilibrium surface. – Let *OM* (Fig. 19) be a line that is perpendicular to *OZ* and capable of moving while constantly being supported by *OZ* and a helix *AB* that is traced on a cylinder of revolution that has *OZ* for its axis. The surface that is generated by *OM* is a helicoid. In order to show that it is a minimal surface, it will suffice to show that there exist two mutually-perpendicular asymptotic lines at each point. Now, one of the asymptotic lines at *M* is obviously *OM* itself, so any rectilinear generator of a surface will always be an asymptotic line. The other one is the helix *AB*, because one can define the asymptotic lines by saying that their osculating plane agrees with the tangent plane to the surface. Now, the osculating plane to a helix is always normal to the cylinder on which that helix is traced. It will then pass through the line *OM*, and since it also passes through the tangent to the helix, it will coincide with the tangent plane to the helicoid. Since those two lines are perpendicular, because the cylinder is one of revolution, the surface will indeed be a minimal surface.

Schwarz realized that equilibrium surface experimentally. In order to do that, he stretched a wire along the axis *AB* (Fig. 20) of a glass cylinder by means of two metallic wires *CD* and *EF* that were supported by the bases of the cylinder. Those two wires were parallel, so he formed a planar film by supporting it with the three wires *AB*, *CD*, *EF*. Upon rotating *CD*, the film deformed and generated a surface *ECDF* that passed through *AB* and cut the surface of the cylinder normally. That surface was a helicoid.

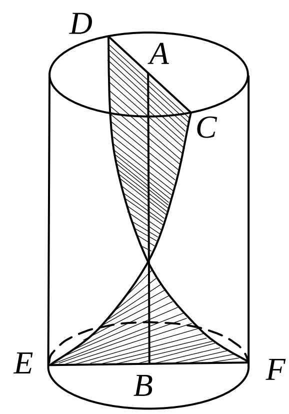

Figure 20.

With a little care, one can then obtain a surface with several turns. If one suppresses the vertical wire *AB* then the helicoid will nonetheless remain an equilibrium surface, but the equilibrium will no longer be stable, and it will be impossible to obtain a surface with several turns experimentally. Schwarz has himself said that if one constructs such a surface with the aid of the central wire and then cuts that wire then the helicoidal film will disappear and be transformed into two planar films that close the bases of the glass cylinder.

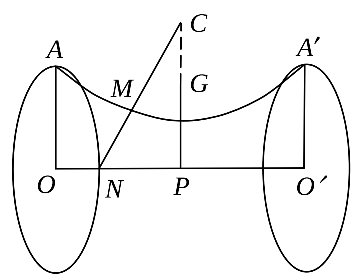

Figure 21.

28. The catenoid is an equilibrium surface. – Let us look for the form of the equilibrium surface for a liquid film that is supported by two circumferences A and A' (Fig. 21) whose planes are perpendicular to the line OO' that joins their centers.

That surface must be one of revolution around OO'. One of the radii of principal curvature at the point M will then be the radius MN of the circle of intersection of the surface with a plane that is perpendicular to the axis OO'. The other one will be the radius of curvature MC of the meridian curve AMA' of the surface. The form of that curve must then be such that one has $MN = MC$, and upon expressing that condition, one will have the equation of that curve.

Indeed, let l be the length of the curve, and let GP be the distance from its center of gravity G to the axis OO'. From Guldin's theorem, the surface that is generated by that curve will be $2\pi l \cdot GP$. One must compare the meridian AMA' of the equilibrium surface with the other curves that pass through the points A and A', and for which, the product $l \cdot GP$ must be greater than it is for the curve AMA'. However, we can confine ourselves to comparing it with those of the curves that have the same length l as the curve AMA'. The minimum of our product will take place at the same time as that of GP for the curves of the same length l. Consequently, the desired curve will be the one for which the center of gravity is the point that is closest to OO' – i.e., the lowest one possible if one supposes that the curve AMA' is in a vertical plane. Now, that is what will happen for a ponderous line under the action of gravity, and the form of that line will be a catenary. Upon rotating it around OO', that catenary will generate a surface that one calls a *catenoid*.

The catenoid is then an equilibrium surface for a thin film.

29. On the stability of equilibrium. – In order for equilibrium to be stable, it is necessary that the potential energy must pass through a relative minimum. Consequently, the condition for the stability of equilibrium is that the area of the surface Σ must be a relative minimum. Now, upon expressing the idea that the mean curvature of a surface is zero, we write only that the first-order variation must be zero. In order for it to have a relative minimum, it is necessary, in addition, that the second variation must likewise be zero. That subject requires a very delicate discussion, which was done in the most elegant fashion by Schwarz.

The consideration of geodesic lines will permit us to appeal to a simple example that will assist us in understanding the spirit of the method.

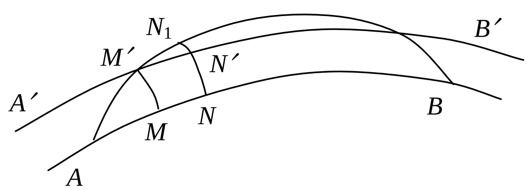

Figure 22.

Let AMB (Fig. 22) be a geodesic line on a surface. If it is possible to draw a geodesic line $A'M'B'$ that is very close to it and does not cut the latter then AMB will be a relative minimum.

Indeed, consider an arbitrary line $AM'B$ that is traced on the surface and ends at the points A and B. That line will meet the geodesic line $A'M'B'$ that is close to AB and a point M'. Draw an orthogonal trajectory through M' that cuts AB at the point M, and draw a second trajectory through a point N that is infinitely close to M. That trajectory will meet the geodesic line $A'M'B'$ at N', and the two segments MN and $M'N'$ will be equal. The corresponding segment $M'N_1$ of the curve $AM'B$ will be larger than $M'N'$, since the small triangle $M'N'N_1$ is rectangular at N'. Consequently, each element of the geodesic line AMB will correspond to an element of longer length on the line $AM'B$, and that element will be larger than the first one. The geodesic line will indeed be a relative minimum then.

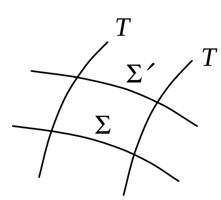

Figure 23.

Minimal surfaces exhibit an analogous property. Before establishing it, we shall show that if one traces out a tube that cuts a series of minimal surfaces orthogonally then the areas of the sections of those surfaces by the tube will be equal to each other.

Indeed, if Σ and Σ′ are two close minimal surfaces that cut the same tube *T* (Fig. 23) then the difference between the areas Σ and Σ′ of the sections will be:

$$\Sigma' - \Sigma = \int \lambda \left(\frac{1}{R_1} + \frac{1}{R_2} \right) d\sigma + \int \lambda \cot \varphi \, ds ,$$

from a general argument that was made already.

Now, the first integral is zero, since the surface Σ is a minimal surface, and as a result, its mean radius of curvature will be constant. The second one is likewise zero, because φ denotes the angle between the tangent to the surface Σ and the tangent to the surface of the tube. Since those two surfaces cut orthogonally, that angle will be a right angle, and cot φ will then be zero. As a result, the areas Σ and Σ′ will be equal.

We shall now show that if a minimal surface *AMB* (Fig. 22) is found in a region where the neighboring minimal surfaces do not intersect then the area of that surface will be smaller than that of any other surface *AM′B* that is bounded by the same contour as *AB*.

In order to do that, draw a tube that cuts the surface *AB* orthogonally through an element *MN* of that surface. It will cut out an element $M'N_1$ from the surface *AM′B* and an element *M′N′* from a minimal surface *A′M′B′* that is close to *AMB*, and that area of the latter element will be equal to that of *MN*, from the preceding. The volume $M'N'N_1$ can be considered to be a cylinder with parallel bases that has *M′N′* for a cross section. As a result, the area of $M'N_1$ will be larger than that of *M′N′* or the equal element *MN*. Since the minimal surfaces that are close to *AMB* do not intersect, by hypothesis, all of the elements of *AMB* will correspond to elements of *AM′B* whose areas are larger. Consequently, the area of the surface *AMB* will be smaller than that of any other surface that is bounded by the same contour.

We thus reach the conclusion that a surface with zero mean curvature will be a stable equilibrium surface when one can construct surfaces of zero mean curvature that are infinitely close to that surface and do not intersect it.

30. Unstable equilibrium. – On the contrary, when the surfaces of mean curvature that are close to the equilibrium surface do cut them, the area will not be a minimum and the equilibrium will not be stable.

In order to prove that property, we begin, as before, with a consideration of geodesic lines.

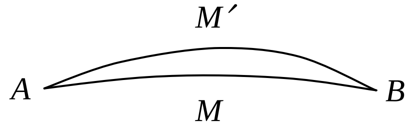

Figure 24.

Let *AMB* (Fig. 24) be a geodesic line that is cut by another geodesic line *AM′B* at *A* and *B*. Those two lines have different lengths, and the difference between those lengths will be a third-order infinitesimal, if one considers the distance between two points *M* and *M* of the two lines to be a first-order infinitesimal.

Indeed, we can characterize a geodesic line that passes through *A* by taking the parameter to be the angle that the line makes with an arbitrary line that is drawn through *A*. The length of the line will then be a certain function of the parameter. Upon letting α and $\alpha + d\alpha$ denote the values of the parameter that correspond to the two lines *AMB* and *AM′B*, resp., we will have:

$$f(\alpha) \quad \text{and} \quad f(\alpha + d\alpha)$$

for the lengths of those lines, respectively.

The difference between those lengths is then:

$$f(\alpha + d\alpha) - f(\alpha) = f'(\alpha)\, d\alpha + f''(\alpha)\frac{d\alpha^2}{1\cdot 2} + f'''(\alpha)\frac{d\alpha^3}{1\cdot 2\cdot 3} + \ldots$$

However, since the curves considered are geodesic lines, one will have:

$$f'(\alpha) = 0, \qquad f'(\alpha + d\alpha) = 0,$$

and one deduces from those two equalities that:

$$f''(\alpha) = 0.$$

Consequently, the difference between the lengths of the geodesic lines that end at *A* and *B* will reduce to:

$$f(\alpha + d\alpha) - f(\alpha) = f'''(\alpha)\frac{d\alpha^3}{1\cdot 2\cdot 3} + \ldots$$

It will then have order three.

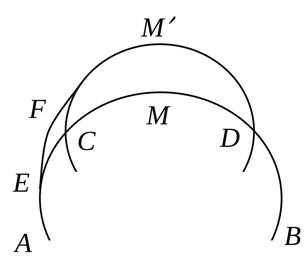

Figure 25.

We shall show that when a geodesic line *AMB* (Fig. 25) and the neighboring geodesic curves intersect, the line *AMB* will not be the shortest path that goes from *A* to *B*.

Indeed, if *CM′D* is a geodesic curve that intersects *AMB* then the lengths *CMD* and *CM′D* differ only by a third-order infinitesimal. Upon neglecting that quantity, one will have:

$$CMD = CM'D$$

and

$$ACMDB = ACM'DB.$$

Join an arbitrary point E of the first path with an arbitrary point F on the second one by means of a geodesic line. Its length will be shorter than the path ECF and will differ from it by a second-order infinitesimal quantity. Consequently:

$$ACM'DB > AEFM'DB,$$

or, from the preceding equality:

$$ACMDB > AEFM'DB,$$

which proves the stated proposition.

We now pass on to surfaces. One can show that if two infinitely-close minimal surfaces are bounded by the same contour then the areas of those surfaces will differ by only a third-order infinitesimal by an argument that is analogous to the one that is employed for geodesic lines.

Assume that is true and consider a minimal surface S that is bounded by a curve L and is cut by another neighboring minimal surface S' along L'. (L' is a closed contour that is interior to the contour L.) From the preceding, the areas that are bounded by L' and belong to S, in one case, and S', in the other, can be considered to be equal if one neglects third-order infinitesimals. As a result, the area S of the minimal surface S that is bounded by L will be equal to the area S'' that is found between L and L', plus the area S' that is bounded by L' and belongs to S'. Trace out a contour L_1 on the surface S that is interior to L, but exterior to L', and trace out a contour L_1' in the surface S' that is interior to L'. Pass a minimal surface Σ through the two curves L_1 and L_1' and also denote the area of that surface by Σ, which be annular and bounded by two contours L_1 and L_1'.

I will then let S_1 denote the area of the portion of S that is found between L and L_1, let S_2 denote the area of the portion of S that is found between L_1 and L', and let S_3 denote the area of the portion that is interior to L'.

I will let S_1' denote the area of the portion of S' that is found between L' and L_1', and let S_2' denote the area of the portion of S' that is interior to L_1'.

One will then have:

$$S_3 = S_1' + S_2',$$

up to third-order infinitesimals.

On the other hand:

$$\Sigma < S_2 + S_1'.$$

Hence:

$$S_1 + S_2 + S_3 > S_1 + \Sigma + S_2'.$$

Hence, $S_1 + S_2 + S_3$ (i.e., the total area of S) will be greater than the area $S_1 + \Sigma + S_2'$, which is also bounded the by the contour L. The area of that surface will not be minimal then, and the equilibrium will not be stable.

Consequently, an equilibrium surface corresponds to an unstable equilibrium when that minimal surface can be cut by a neighboring minimal surface.

31. The catenoid can correspond to either a stable or unstable equilibrium. – Let us see whether there exists a minimal surface that is infinitely close to the catenoid and cuts it. As a minimal surface, we can take a catenoid that has the same axis, and the problem will come down to looking for a catenary that can be cut by an infinitely-close catenary at two points.

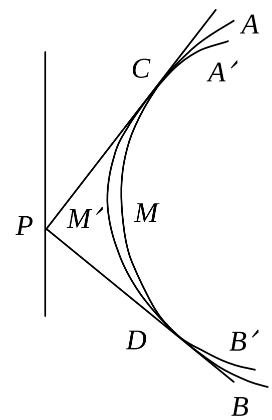

Figure 26.

If we can draw an arc of the catenary *A′M′B′* that is infinitely close to *AMB* and does not cut *AMB* then the revolution of those two arcs of the catenary will generate two catenoids – i.e., two minimal surfaces that are infinitely close and do not cut; the equilibrium will then be stable.

On the other hand, if we can draw an arc of the catenary *A′M′B′* that is infinitely close to *AMB* and *does* cut *AMB* at two points *C* and *D* (Fig. 26) then the two catenoids will cut along two circumferences that will be parallels to *C* and *D*. The set of those two parallels will form a closed contour *L′* that is interior to the contour *L* that bounds the catenoid *AMB* and is composed of parallels to *A* and *B*. The equilibrium will then be unstable.

Let *AMB* be an arc of the catenary. Take the infinitely-close catenary to be a homothetic catenary that has a point *P* on the axis for its pole and a homothety ratio of 1 – ε. If one can draw two tangents *PC* and *PD* to the catenary *AMB* through the point *P* then those lines will be likewise tangent to the homothetic catenary *A′M′B′*, and those curves, which are infinitely close, will intersect at the contact points *C* and *D*. Conversely, if the two catenaries intersect then the point of intersection will be very close to the two contact points of a tangent *PC* that is common to the two curves. The stability of equilibrium of a catenoid will then depend upon the possibility of finding a point on the axis where one can or cannot draw two tangents to the generating catenary.

If there exists a point *P* where one can draw two tangents to the arc *AMB* then the equilibrium will be unstable. If there exists a point *P* where one cannot draw any tangent to the arc *AMB* then that arc will not meet its homothetic transforms with respect to the point *P*, and the equilibrium will be stable.

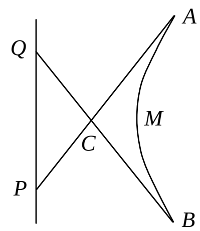

Figure 27.

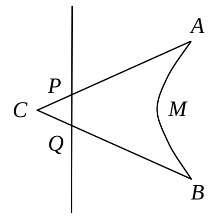

Figure 28.

Two cases can present themselves: If the tangents to the extremities A and B of the catenary cut at a point C (Fig. 27) that is located between the axis and the catenary then it will not be possible to draw the tangent to the curve at a point that is taken between P and Q. Consequently, there will exist infinitely-close catenaries that do not cut at AMB, and the equilibrium will be stable.

However, if the tangents at A and B cut beyond the axis (Fig. 28) then it will be possible to draw two tangents to AMB between P and Q, and the equilibrium will be unstable.

The passage from the stable equilibrium state to the unstable equilibrium state will take place when the tangents to the extremities of the catenary cut along the axis.

Schwarz, who worked with glycerin, could verify those conclusions experimentally. When the equilibrium ceases to be stable, the corresponding catenoid will disappear, and the liquid will form two circular planar films that pass through the contours of two rigid circumferences.

32. Riemann surfaces. – In an important paper, the geometer Riemann determined the minimal surfaces that pass through a given contour. The better part of his paper was dedicated to the case in which the surface was bounded by a skew polygon whose edges were rectilinear. Darboux presented Riemann's method in his *Leçons sur la théorie générale des surfaces*, along with the results that he obtained in the case that we just pointed out ([3]).

However, there is a case that Riemann studied and Darboux only pointed out ([4]). It is the one in which the contour is closed by two circles whose planes are parallel and not perpendicular to the line that joins their centers. The consequences of Riemann's study seem to be capable of being verified experimentally, so we shall present them.

Take the yz-plane to be a plane that is parallel to the planes of the two circles and take the xy-plane to be a plane that contains the line that joins their centers. The equation of the surface will have the form:

$$F\,(y+\alpha)^2 + z^2 + \beta = 0$$

which is obviously symmetric with respect to the xy-plane.

In order to express the idea that the surface is minimal, we seek the equation of the inverses of the radii of curvature.

([3]) Book III, Chapter X; *le Problème de Plateau.*

([4]) Note on page 426.

Draw a normal *MP* through a point *M* (x, y, z) on the surface. The direction cosines of that line are proportional to the derivatives:

$$X = \frac{dF}{dx}, \qquad Y = \frac{dF}{dy}, \qquad Z = \frac{dF}{dz}.$$

Consequently, if we set:

$$u = \frac{MP}{\sqrt{X^2 + Y^2 + Z^2}}$$

then the coordinates of the point *P* will be:

$$x + uX, \qquad y + uY, \qquad z + uZ.$$

Draw a normal $M'P'$ at a point *M* that is infinitely close to M'. The coordinates of the point P' will be:

$$x + uX + d\,(x + uX), \quad y + uY + d\,(y + uY), \quad z + uZ + d\,(z + uZ).$$

If one supposes that the points *M* and M' are found on the same line of curvature of the surface and that *P* and P' are the centers of curvature that correspond to *M* and M', resp., then the coordinates of *P* and P' will differ only by third-order quantities. Upon neglecting them, one will get:

$$d\,(x + uX) = d\,(y + uY) = d\,(z + uZ) = 0,$$

in which u then denotes the radius of curvature at *M*, up to a factor $\sqrt{X^2 + Y^2 + Z^2}$.

Upon developing the first of those equations, we will have:

$$dx + u\,dX + X\,du = 0$$

or

$$\frac{1}{u}dx + dX + X\,\frac{du}{u} = 0.$$

Set:

$$X_x = \frac{d^2F}{dx^2}, \qquad X_y = \frac{d^2F}{dx\,dy}, \qquad X_z = \frac{d^2F}{dx\,dz}, \qquad \ldots$$

We will have:

$$dX = X_x\,dx + X_y\,dy + X_z\,dz,$$

and consequently the preceding equation will become:

$$\left(\frac{1}{u} + X_x\right)dx + X_y\,dy + X_z\,dz + X\,\frac{du}{u} = 0.$$

In the same way, we will have:

$$Y_x\,dx + \left(\frac{1}{u} + Y_y\right)dy + Y_z\,dz + Y\,\frac{du}{u} = 0,$$

$$Z_x\,dx + Z_y\,dy + \left(\frac{1}{u} + Z_z\right)dz + Z\,\frac{du}{u} = 0$$

for the other two equations.

We add the following equation:

$$X\,dx + Y\,dy + Z\,dz = 0$$

to those three, which expresses the idea that the two points M and M' are on the surface $F = 0$.

In order for those equations to be satisfied for non-zero values of dx, dy, dz, du, it is necessary that their determinant must be zero; i.e., that one must have:

$$\begin{vmatrix} \frac{1}{u} + X_x & X_y & X_z & X \\ Y_x & \frac{1}{u} + Y_y & Y_z & Y \\ Z_x & Z_y & \frac{1}{u} + Z_z & Z \\ X & Y & Z & 0 \end{vmatrix} = 0.$$

That second-degree equation in $1 / u$ will determine the radii of curvature at M. In order for the surface to minimal, it will be necessary that the sum of the roots of that equation must be zero, which will then give the condition:

$$\begin{vmatrix} X_x & X_y & X \\ Y_x & Y_y & Y \\ X & Y & 0 \end{vmatrix} + \begin{vmatrix} X_x & X_z & X \\ Z_x & Z_z & Z \\ X & Z & 0 \end{vmatrix} + \begin{vmatrix} Y_y & Y_z & Y \\ Z_y & Z_z & Y \\ Y & Z & 0 \end{vmatrix} = 0.$$

In the case that we address, we have:

$$\begin{array}{lll} X = 2\alpha'(y + \alpha) + \beta, & Y = 2\,(y + \alpha), & Z = 2z, \\ X_x = 2\alpha''(y + \alpha) + 2a'^2 + \beta'', & X_y = 2\alpha', & X_z = 0, \end{array}$$

$$Y_x = 2\alpha', \quad Y_y = 2, \quad Y_z = 0, \quad Z_x = 0, \quad Z_y = 0, \quad Z_z = 2,$$

as a result of the form of the equation of the surface.

If we take those relations into account then the preceding equation will reduce to:

$$2XYX_y - X^2\,Y_y - Y^2\,X_x - Z^2\,X_x - X^2\,Z_z - Z^2\,Z_z - Z^2\,Y_y - Y^2\,Z_z = 0,$$

or

$$4X(\alpha' Y - X) - (Y^2 + Z^2)(X_x + 2) = 0,$$

or also to:

$$4X(\alpha' Y - X) - 4[(y + \alpha)^2 + z^2](X_x + 2) = 0.$$

X has degree one in y. The coefficient $\alpha' Y - X$ does not contain that variable. As a result, the first term in that equation will have degree one in y. $X_x + 2$ has degree one in y. The coefficient $(y + \alpha)^2 + z^2$ has degree zero, because that coefficient will be equal to $-\beta$, from the equation of the surface $F = 0$. Consequently, the preceding equation will have the form:

$$Ay + B = 0,$$

in which A and B are functions of only x.

In order for that to be satisfied for any point in question, it is necessary that one must have:

$$A = 0, \qquad B = 0,$$

separately, which are differential equations that permit one to find α and β.

There indeed exists a minimal surface that passes through the two circles then, and from its equation, any section by a plane that is parallel to those of the circles will be a circumference; that is a consequence that is easily accessible to experiment.

Riemann calculated the functions α and β; those calculations demanded the use of elliptic functions.

33. Remarks. – In order to show that the free surface of a thin film in equilibrium is a surface of zero mean curvature, we have expressed the idea that, from Gauss's theory:

$$gUz - \frac{\theta_1}{2}\Sigma + \left(\eta_1 - \frac{\theta_1}{2}\right)S_1$$

must be a maximum. We could have found that equilibrium condition just as simply by starting from the equation of the free surface that Laplace obtained:

$$gz - \frac{\theta_1}{2}\left(\frac{1}{R_1} + \frac{1}{R_2}\right) = \text{const.}$$

Indeed, consider two points M and M_1 (Fig. 29) that have the same z as the two faces of a thin film. From the preceding equation, $\frac{1}{R_1} + \frac{1}{R_2}$ must have the same value at those two points.

However, since M and M_1 are very close (since the film is thin), the radii of principal curvature at those points must have roughly the same absolute values. Since they have different signs (since one of the points is on the concave face and the other one is on the convex face), it will result that when one passes from M to M_1, the sum of the inverses of the radii of curvature must change sign without changing its absolute value appreciably.

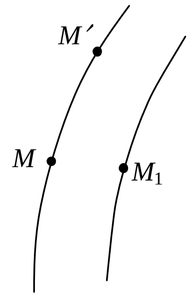

Figure 29.

That conclusion will be compatible with the preceding one only if the sum of the inverse of the radii of curvature is zero or very small.

Let us examine that analysis a bit closer. On the convex side, we have:

$$(1) \qquad gz - \frac{\theta_1}{2}\left(\frac{1}{R_1}+\frac{1}{R_2}\right) = C,$$

in which C is a constant, and on the concave side we have:

$$(2) \qquad gz' - \frac{\theta_1}{2}\left(\frac{1}{R_1'}+\frac{1}{R_2}\right) = C'.$$

If we compare the values of the various quantities at the points M and M_1 then we will see that $z = z'$, $R_1' = - R_1$, $R_2' = - R_2$, and that $C = C'$, moreover, since the pressure must be the same on both sides, in such a way that equation (2) will become:

$$(3) \qquad gz + \frac{\theta_1}{2}\left(\frac{1}{R_1'}+\frac{1}{R_2}\right) = C.$$

Upon subtracting (1) from (3), what will remain is:

$$(4) \qquad \frac{\theta_1}{2}\left(\frac{1}{R_1'}+\frac{1}{R_2}\right) = 0.$$

That is the condition that we reached previously. However, it is only a combination of (1) and (3). If we would like to satisfy both (1) and (3) then that would be impossible, in general. We could achieve that approximately if θ_1 were very large, because the terms gz and C would become negligible. That would show us that a strong surface tension is a good condition for the preservation of thin films.

34. – However, that is not the true explanation. For example, suppose that a framework is planar and vertical. The equilibrium form for a thin film will be bounded by two vertical and parallel planes. If one imposes a very small displacement to the film in such a fashion that the two bounding surfaces remain two parallel surfaces then the work that is done by gravity will be negligible, as well as the capillary forces. That is what we showed above, but we can imagine some other infinitely-small virtual displacements.

For example, imagine that after that displacement the liquid is bounded by two planes that make very small angles with the vertical, but in opposite senses, in such a fashion that the film becomes thinner above than it is below. *The virtual work that is done by weight will then be positive.*

It then seems that equilibrium cannot be maintained. However, in order for the film to be thinner on the upper part and thicker in the lower one, it is necessary that the various liquid layers should slide over each other. Experiments show that with certain liquids, that sliding can be produced only extremely slowly. The liquid would then seem to exhibit considerable resistance that is analogous to viscosity. Nonetheless, it is not ordinary viscosity. It is much larger and obeys other laws; one can call it the *surface viscosity.*

That surface viscosity, which was pointed out by Plateau, has been studied even less than the ordinary kind. We shall see some other effects in Chapter V.

That resistance will come into play whenever shears are produced in the surface part of a liquid. It opposes those shears, so it opposes the possibility that two surfaces that bound a thin film, which are supposed to be parallel to begin with, will cease to be that way, or more generally, it will oppose variations of the very small angle that those two tangent planes define at two corresponding points on those two surfaces.

The existence of that force will not change the preceding analysis, moreover. In order for equilibrium to persist *for a long time*, it will suffice that the virtual work should be zero *for all displacements that do not induce viscous resistance.* When that resistance is very large, it will then act like a *constraint*, and everything will happen as if the film were subject to remaining bounded by two parallel surfaces, and in order to get the conditions for stable equilibrium, it will suffice to express the idea that the potential energy is a minimum by taking that constraint into account. That is what we did in this chapter.

Certain liquids, such as soapy water and Plateau's glycerin, have a large surface viscosity. That explains the persistence of the films that are formed by those liquids.

35. – Before leaving the study of thin films, we shall explain why a film does not burst spontaneously and why it disappears completely when it does burst.

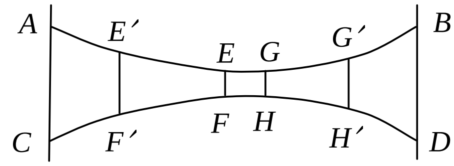

Figure 30.

In order for the film *ABCD* (Fig. 30) to burst spontaneously, a very small hole *EFGH* must begin to form, and the free surface *A* will become *AEFCBGHD*. Since that surface is larger than the original surface *ABCD*, and the potential energy is proportional to the area of the surface, that cannot happen without an expenditure of work; the hole cannot form in it.

However, once the hole is produced by an artificial cause, it will tend to enlarge, because the free surface:

$$AE'F'C + BG'H'D$$

that corresponds to a large hole ($E'F'G'H'$) will be smaller than the free surface *AEFC* + *BGHD* that corresponds to the small hole (*EFGH*).

CHAPTER IV

PLATEAU'S EXPERIMENTS

36. Equilibrium condition for an oil drop. – In his celebrated experiments, Plateau most frequently appealed to a mass of oil that was placed in diluted alcohol of the same density and held in place by two circular discs or two metallic rings of the same diameter.

In order to find the equilibrium condition for a mass of oil, from Gauss, it will suffice to write down that the potential energy of the system that is composed of the oil and alcohol is a minimum or a maximum.

Now, the forces that act upon that system are gravity and capillary action. The center of gravity will not displace, not matter how the oil is deformed, since the liquid that surrounds it has the same density that it has. As a result, the work done by gravity will be zero, and there will be no reason to take that force into account in the variation of the potential energy.

There are several types of capillary actions. One has the attractions:

1. Of the discs or rings to the oil.
2. Of the oil to itself.
3. Of the diluted alcohol to itself.
4. Of the alcohol to the oil.
5. Of the alcohol to the surroundings.

When one neglects the action of the matter that comprises the vessel on the liquid that it contains, that action will not enter into the variation of the potential energy that results from a deformation of the drop, provided that it is at an appreciable distance from the wall.

We introduce the notations:

Σ	the area of the contact surface between the oil and alcohol
S_1	the area of the contact surface between the oil and the solid supports
S	the total area of the solid supports
θ_1	the function that relates to the mutual attractions of the oil molecules
η_1	the function that relates to the attractions of the oil molecules to the solid molecules of the supports
θ_1' and η_1'	the corresponding functions for the alcohol
η_2	the one that relates to the action of the oil on the alcohol

We have that the potential energy that results from the capillary actions that were previously enumerated are:

1. $-\eta_1 S_1$,
2. $\frac{\theta_1}{2}(S_1 + \Sigma_1)$,

3. $\frac{\theta_1'}{2}(S - S_1 + \Sigma_1)$,
4. $-\eta_2\,\Sigma$,
5. $\eta_1'(S - S_1)$,

resp., while neglecting constants, moreover.

Consequently, the total potential energy will be:

$$\left(\frac{\theta_1'}{2} - \eta_1'\right)S + \left(\frac{\theta_1}{2} + \frac{\theta_1'}{2} - \eta_2\right)\Sigma - \left(\eta_1 - \eta_1' - \frac{\theta_1}{2} + \frac{\theta_1'}{2}\right)S_1,$$

up to a constant.

However, since the surroundings are solid, the area S will remain constant. In order to get the equilibrium condition, it will then suffice to write down that the variation of the last two terms is zero; i.e.:

$$\left(\frac{\theta_1}{2} + \frac{\theta_1'}{2} - \eta_2\right)\delta\Sigma - \left(\eta_1 - \eta_1' - \frac{\theta_1}{2} + \frac{\theta_1'}{2}\right)\delta S_1 = 0.$$

If we compare that condition to the condition (4) that we have obtained for the equilibrium of a liquid in contact with air and the solid walls (§ **21**) then we will see that they have the same form. They differ only by the value of the coefficients of $\delta\Sigma$ and δS_1, and by the disappearance of the term that relates to gravity. Now, upon transforming the equality (4), we will arrive at the following conditions:

$$gz = \frac{\theta_1}{2}\left(\frac{1}{R_1} + \frac{1}{R_2}\right) + \text{const.}$$
$$\varphi = \text{const.}$$

It will then be obvious that the condition that we just established can be replaced with:

$$\frac{1}{R_1} + \frac{1}{R_2} = \text{const.},$$
$$\varphi = \text{const.}$$

In other words, the separation surface of the oil and the alcohol must have constant mean curvature and must cut the solid support at a constant angle.

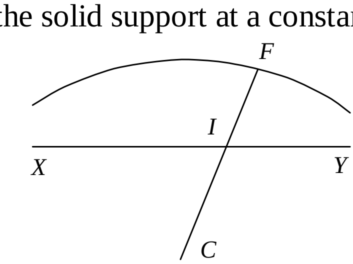

Figure 31.

37. The meridians of equilibrium surfaces of revolution are given by the rolling of a conic. – In Plateau's experiments, the planes of the two discs or rings that supported the oil were perpendicular to the line that joined their centers. As a result, that line would be a symmetry axis of the mass of oil, and the separation surface of the oil and alcohol would be a surface of revolution around that axis. In this case, if F is a point on the meridian and XY is the axis (Fig. 31) then one of the radii of principal curvature will be the length FI of the normal that is found between F and the axis, and the other radius will be the radius of curvature FC of meridian. Consequently, in order for there to be equilibrium, the meridian must be such that one has:

$$\frac{1}{FI}+\frac{1}{FC} = \text{const.}$$

We shall show that this condition is fulfilled by the curve that is generated by the focus of a conic when it rolls without slipping on a line.

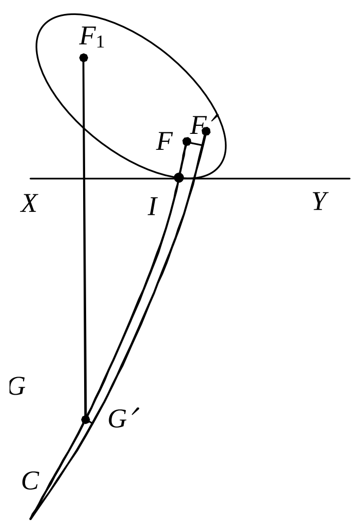

Figure 32.

Consider an ellipse whose foci are F and F_1 and roll it along a line XY (Fig. 32). The contact point I will be the instantaneous center of rotation, and one will have:

$$\frac{\text{velocity of } F}{\text{velocity of } F_1} = \frac{IF}{IF_1}.$$

Take the point G that is symmetric to the focus F_1 with respect to XY. That point will necessarily have the same velocity as F_1. On the other hand, from the properties of the ellipse, G will be found on the prolongation of the radius vector FI, and one will have:

$$IF_1 = IG.$$

Consequently, the preceding equality can be written:

$$\frac{\text{velocity of } F}{\text{velocity of } G} = \frac{IF}{IG}.$$

Draw a normal to that curve through a point F' that is infinitely close to F along the trajectory of that point. It will meet FIG at C, and that point will be the center of curvature of the trajectory, since, as a result of the properties of the instantaneous center of rotation, FIG will also be normal to the trajectory.

The length FG is equal to the sum of the radius vectors $FI + F_1I$. It will then be constant, and the trajectory of G will be parallel to that of F. As a result, the two infinitely-small triangles FCF', GCG' will be similar, and one will have:

$$\frac{FF'}{GG'} = \frac{CF}{CG}.$$

Now, the first ratio in that equality is equal to the ratio of the velocities of F and G; consequently:

$$\frac{\text{velocity of } F}{\text{velocity of } G} = \frac{CF}{CG}.$$

If we compare that value of the ratio of the velocities of F and G with the one that we obtained before then we will have:

$$\frac{IF}{IG} = \frac{CF}{CG}.$$

The four points F, I, G, and C are then harmonic conjugates. Now, one knows that one can express the idea that those points are harmonic conjugates by writing that:

$$\frac{1}{FI} + \frac{1}{FC} = \frac{2}{FG}.$$

The right-hand side of that equality is constant, so the condition that the meridian section of an equilibrium surface of revolution must fulfill is then found to be fulfilled by the trajectory of the focus F.

One can show in the same way that the trajectory of the focus of a hyperbola that rolls along a line will enjoy that same property.

In the case of the parabola, the trajectory of the focus is such that one will have:

$$\frac{1}{FI} + \frac{1}{FC} = 0,$$

since FG is infinite, so the parabola can be preserved like an ellipse with one of its foci pushed out to infinity. The surface of revolution that is generated by the trajectory will then be a surface of zero mean curvature in that case.

We already know of it: It is the catenoid.

38. Unduloid. – Plateau gave the name of *unduloid* to the surface of revolution that is generated by rotating the trajectory of a focus of an ellipse.

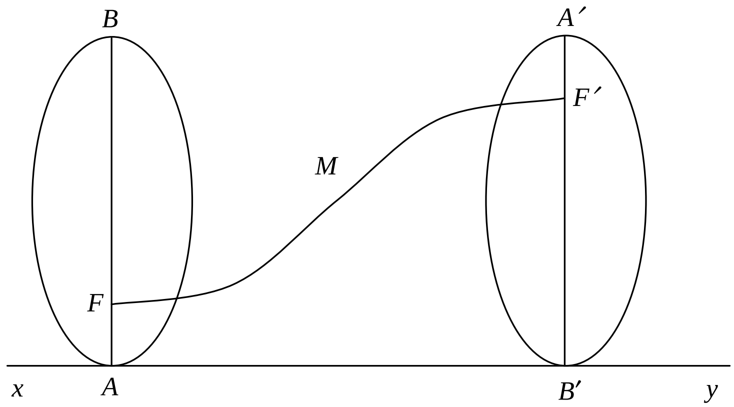

Figure 33.

In order to find its form, suppose that the generating ellipse is initially tangent to the line of rolling at the extremity *A* (Fig. 33) of its major axis. It is obvious that no matter what sense in which one rotates that ellipse, the curve that is described by *F* will have equal ordinates for equal abscissas. The curve will then be symmetric with respect to *AB*; we consider only the portion that is situated to the right of that axis.

If we draw a tangent to the ellipse and move its contact point from *A* to *B* then the distance from the focus *F* of that tangent will always increase. Consequently, when the conic rolls on *xy*, the ordinates of the trajectory of *F* will constantly increase until the extremity *B* of the major axis makes contact with the line of rolling motion at *B′*.

The abscissas will likewise increase, because they can cease to cross only when the tangent to the curve that is described by *F* will be perpendicular to *xy*, and as a result, the normal that is parallel to that line. Now, in that case, the instantaneous center of rotation would be found to have been pushed out to infinity, which is not true. The trajectory of the point *F* will then be a curve of the form *FMF′*.

If one continues to roll the ellipse then the curve that its focus describes will obviously be symmetric with respect to *A′B′* along the portion that was described above. It will then suffice to know the form of the curve *FF′* that is found between the symmetry axes *AB* and *A′B′* in order to be able to trace out the meridian of an unduloid completely.

In the particular case where the ellipse becomes a circumference, the two foci of the ellipse coincide with the center of the circumference. Under the rolling of that curve along *xy*, its center will describe a line that is parallel to *xy*. In that case, the unduloid will then reduce to a cylinder of revolution around *xy*.

If the ellipse is flattened indefinitely then the foci will gradually approach the summits, and the meridian of the unduloid will have points that are very close to the axis of rotation. In the limit, the ellipse will reduce to a line that has its two extremities for the foci, and the trajectory of one of the foci will be formed by a series of semi-circumferences that have their centers along the line *xy*. Consequently, the unduloid will then reduce to a series of mutually-tangent spheres.

39. Nodoid. – That is the name that Plateau gave to the surface that has the trajectory of a focus of a hyperbola for its meridian.

Consider the hyperbola in the position for which its summit is *A* (Fig. 34), which is in contact with the line *xy*. The axis *AB* of the conic in that position is a symmetry axis for the trajectory of the focus *F*.

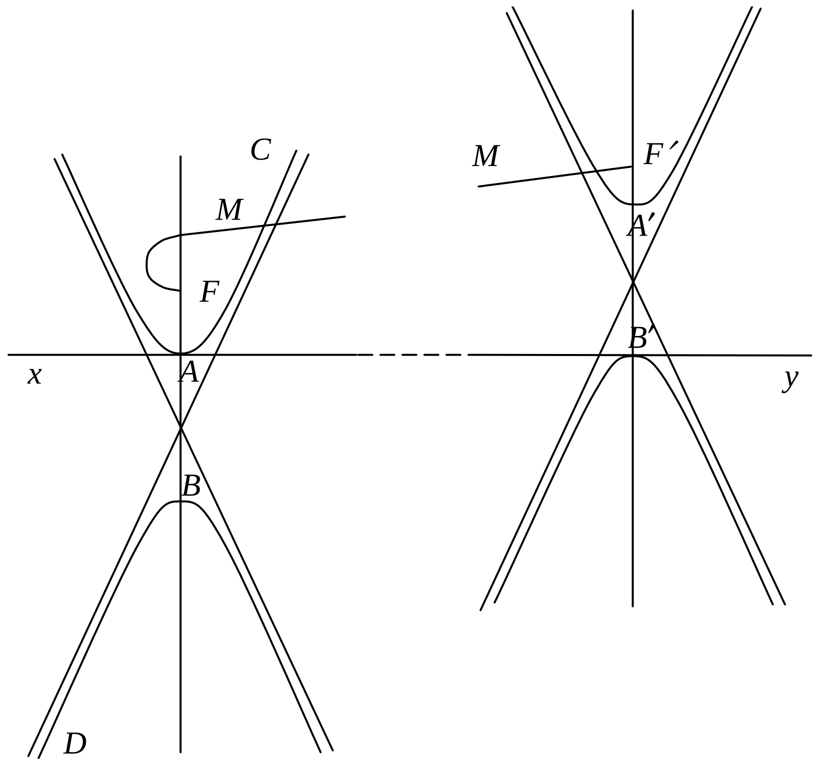

Figure 34.

Roll the hyperbola until the asymptote *CD* coincides with the line *xy*. The ordinate of the trajectory of *F* will always increase, because the distance from the focus of one hyperbola to a tangent whose contact point displaces from *A* to *C* will always be increasing.

When the asymptote *CD* coincides with *xy*, we must roll another branch of the hyperbola, and the contact will displace along the branch *DB* initially. The distance from the focus *F* to the tangent to that branch will constantly increase when the contact point of that tangent displaces from *D* to *B*, so the same thing will be true of the ordinate of the trajectory of *F* during the rolling.

Consequently, the ordinate will increase continuously from *F* to the point *F*′, which corresponds to the position of the hyperbola for which the contact with *xy* happens at *B*′, which is the second summit of the conic.

However, the abscissa will begin to decrease during the motion. When the asymptote *CD* coincides with *xy*, the instantaneous center of rotation will be found to have been pushed out to infinity. As a result, the normal to the trajectory of *F* at that instant will be parallel to *xy*, and the tangent will be perpendicular to that line. The abscissa will then cease to decrease, and it will then increase up to *F*′. Consequently, one will have a curve between *F* and *F*′ that has the indicated form *FMF*′.

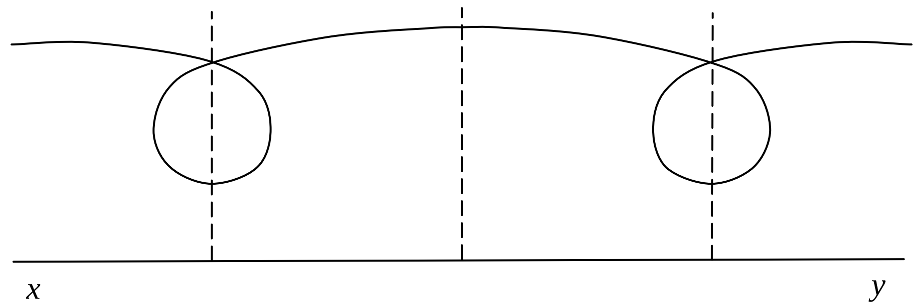

Figure 35.

The line $A'B'$ is obviously a symmetry axis like AB, so the meridian of the nodoid must have the form that is indicated in Fig. 35.

40. Experimental realization of those surfaces. – Plateau succeeded in realizing those different surfaces experimentally, as we have said.

When one employs two planar discs as rigid supports, one can succeed in obtaining a cylinder of revolution whose generators are supported by the boundaries of the discs by adding or subtracting from the oil with a pipette.

Upon gradually bringing these discs closer together, one will obtain a convex portion of the unduloid, and then a portion of the sphere, and then finally, a convex portion of the nodoid.

On the contrary, upon discarding the two discs, one will see a concave portion of the unduloid form that will gradually get thinner through the medium and finally separate into two pieces. The rupture must correspond to the moment at which (the ellipse being infinitely flattened) the unduloid gives rise to two spheres, if it does not have solid supports.

If one employs two rings of the same diameter as rigid supports then one will see the same surface reproduced in the same manner between the rings. However, at the same time, the surfaces that bound the mass of oil above the rings will deform, and conforming to the theory, the mean curvature of those surfaces will be equal to that of the surface that is found between the rings.

Hence, when the latter is a cylinder of revolution, the other two will be spherical caps whose radii are equal to twice that of the rings. Now, one of the radii of curvature for the cylinder of revolution will be infinite, while the other one will be equal to the common radius R of the rings; its mean curvature will then be $1 / R$. That of a spherical cap is $\frac{1}{2R}+\frac{1}{2R}$ or $\frac{1}{R}$; i.e., it is equal to the preceding value.

41. On the stability of equilibrium for a cylinder of revolution. – In his experimental studies, Plateau recognized that the cylinder of revolution is a stable equilibrium surface when the height of the cylinder is smaller that the circumference of the base, while the equilibrium will be unstable in the opposite case.

In order to look for the stability conditions for a cylinder of revolution theoretically, one must compare that surface with the equilibrium surfaces that are very close to it and find the cases in which the area of the surface of the cylinder is a relative minimum.

Plateau applied that method, but instead of comparing the surface of the cylinder to the surface of the unduloid (which is the equilibrium surface that results from a small deformation of the cylinder), he compared it to the surface of revolution that is generated by the rotation of a sinusoid.

That process is not entirely correct. Nevertheless, since the meridian of an unduloid differs only slightly from a sinusoid and that process will lead to the conclusion that is found in experiments, we shall present it anyway.

Take the axes of a rectangular coordinate system to have the line that joins the centers of two discs or rings for the x-axis; i.e., the axis of rotation of the equilibrium surface.

The equations of the planes of the cylinder bases are:

$$x = x_0, \qquad x = x_1,$$

and one of the generators of that cylinder that is situated in the xy-plane will have the equation:

$$y = a,$$

in which a is the radius of the discs or rings.

We can take the equation of the sinusoid that generates the surface to which are comparing the cylinder to be:

$$y = a - \mu + \beta \sin x. \tag{1}$$

Indeed, we can express the idea that this sinusoid is supported by the boundaries of the discs or rings by writing that:

$$\mu = \beta \sin x_0 , \quad \mu = \beta \sin x_1 .$$

In order for those two equations to be satisfied simultaneously, it would be sufficient for $x_1 - x_0$ to be equal to an integer multiple of 2π. We then set:

$$x_1 = x_0 + 2\pi,$$

which amounts to taking a unit of length such that height of the cylinder is represented by 2π, which is always possible.

Since μ and β are coupled by one of the preceding equalities, in order to succeed in determining the equation of the sinusoid, it will suffice to find a new relation between μ, β, and a. In order to do that, we express the idea that the mass of the oil must remain the same; i.e., that the volume that is generated by the rotation of the sinusoid must be equal to the volume of the cylinder.

The volume that is generated by the sinusoid is:

$$\int_{x_0}^{x_1} \pi y^2\, dx = \pi \int_{x_0}^{x_1} (a^2 - 2a\mu + \mu^2)\, dx + 2\pi \int_{x_0}^{x_1} (a-\mu)\beta \sin x + \pi \int_{x_0}^{x_1} \beta^2 \sin^2 x ,$$

or since the second integral on the right-hand side is zero:

$$\pi\,[2\pi\,(a^2 - 2a\mu + m^2) + \beta^2\pi].$$

Since the volume of the cylinder is:

$$\pi\, a^2 \times 2\pi,$$

it will then be necessary that one must have:

$$-\,4a\mu + 2\mu^2 + \beta^2 = 0.$$

Now, μ and β are infinitely-small quantities, since the sinusoid must differ only slightly from a straight line. Consequently, the preceding condition will be satisfied if:

$$4a\mu = \beta^2, \tag{2}$$

because μ is a second-order infinitesimal then, β has order one, and the term $2\mu^2$ is negligible.

Now, compare the surface that is generated by the sinusoid with the lateral surface of the cylinder.

An element *ds* of the sinusoid can be written:

$$ds = \sqrt{dx^2 + dy^2} = dx\sqrt{1 + y'^2} = dx\sqrt{1 + \beta^2\cos^2 x}\,.$$

That element will generate a surface when one rotates it:

$$2\pi y\, ds = 2\pi\,(a - \mu + \beta\sin x)\,\sqrt{1 + \beta^2\cos^2 x}\; dx,$$

and the surface that is generated by the sinusoid will be the integral of that expression, when it is taken between x_0 and x_1 . However, β^2 has order two, so we can write:

$$\sqrt{1 + \beta^2\cos^2 x} = 1 + \frac{\beta^2\cos^2 x}{2}$$

and

$$(a - \mu + \beta\sin x)\,\sqrt{1 + \beta^2\cos^2 x} = a - \mu + \beta\sin x + \frac{\alpha\beta^2}{2}\cos^2 x,$$

upon neglecting the infinitesimals of order higher than two. As a result, the desired surface area will be:

$$2\pi\int_{x_0}^{x_1}(a-\mu)\,dx + 2\pi\int_{x_0}^{x_1}\beta\sin x\,dx + 2\pi\int_{x_0}^{x_1}\frac{\alpha\beta^2}{2}\cos^2 x\,dx$$

or

$$2\pi\left[(a-\mu)\,2\pi+\frac{\alpha\beta^2\pi}{2}\right].$$

The surface area of the cylinder will be:

$$2\pi a + 2\pi,$$

so it will be smaller or larger than the area of the surface that is generated by the sinusoid according to whether:

$$-\,2\mu + \frac{\alpha\beta^2}{2}$$

is negative or positive. If one takes the equality (2) into account then that condition will amount to:

$$-\,\beta^2 + \alpha\beta^2 \neq 0$$

or

$$2\pi a + 2\pi \neq 0.$$

There will then be stable equilibrium if $2\pi a < 2\pi$, and unstable equilibrium in the contrary case. Since $2\pi a$ is the circumference of the base of the cylinder and 2π is its height (due to the unit of length adopted), one will indeed arrive at the conclusion that is deduced from experiment.

That will suffice to establish that equilibrium is unstable when the height is greater than the circumference of the base, but not to prove the converse, since one has compared the cylinder to only *one* of the possible surfaces that are infinitely-close.

42. – Mathieu revisited Plateau's analysis in his *Théorie de la capillarité*. Upon comparing ([5]) the surface area of a cylinder whose height is less than the circumference of its bases to the area of an infinitely-close surface that is generated by a sinusoid whose step is equal to the circumference of the bases, one will find that the area of the cylinder is less than that of the other surface, which is a result that is consistent with Plateau's.

However, since it was the experiments that first provided Plateau with the result that he then attempted to recover by theory, how does one explain the disaccord between that result and the result of Mathieu's calculations? One tries to do that in the following way:

> "The very small displacements that one ordinarily communicates to the liquid column – for example, by giving a vibratory motion to the vessel – are not absolutely arbitrary. One then agrees that the liquid column has a tendency to pass through figures of equilibrium. Indeed, that is what Plateau recognized. The meridian of the surface must then be a sinusoid whose step is equal to $2\pi a$, and the area of the form must be

([5]) See pp. 73, *et seq.* of the cited work.

greater than that of the cylinder if the height of the figure is less than $2\pi a$."

That explanation is obviously insufficient. The true cause of the disaccord between Plateau's results and those of Mathieu is that the latter supposed that the radius of the circumference of intersection of the surface of revolution and one of the plates could suffer an infinitely-small variation, while the former supposed that this radius was constant. That fact did not escape Mathieu completely, because he remarked that "the liquid can be maintained by the discs somewhat as a result of its adherence and friction," but he considered that be only a secondary consideration.

The resolution of the debate then amounts to knowing whether the base circumferences do or do not vary under deformation.

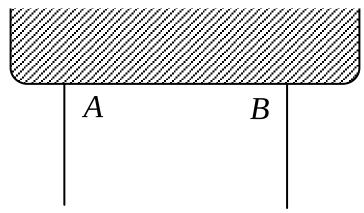

Figure 36.

In the experiments that were made with rings of fine wire, the answer was immediate: The surface of revolution must pass through those rings, so the radii of the base circumferences must keep the same value – viz., the common radius of the rings.

In the case where plates are employed, the constancy of the radii is not as obvious, because if the cylinder cuts the plates at points like A and B (Fig. 36) that are situated at a certain distance from the boundaries then the circumferences can vary under a small deformation. However, if we remark that the contact angle of the liquid surface and the surface of the plate must have a constant value along the intersection curve (which is not generally a right angle) then we will deduce that the contact can take place only along the boundary of the disc, where the contact angle can take a suitable value, since the edge is always more or less blunt. Under those conditions, the radius of the base circumferences will again preserve a constant value.

43. – Under that hypothesis, we shall prove, in full rigor, that the cylinder of revolution is a relative minimum under the conditions that were pointed out by Plateau.

We shall first show that it is suffices to compare that cylinder with a surface of revolution with the same axis.

Let Σ be an arbitrary solid that has the same volume as the cylinder, but a smaller area. I say that there exists a solid of revolution Σ' with the same volume and a smaller area than the solid Σ.

Cut Σ with a series of planes that are parallel to the bases. If Q is the area of one of those sections then $Q\,dx$ will be the very close volume that is included between two infinitely-close sections. We can imagine a solid of revolution Σ' whose circular sections have an area that is equal to the corresponding sections of Σ. The volume that is bounded by two infinitely-close sections of Σ' will be $Q\,dx$ then; i.e., the elementary volumes of the solids Σ' and Σ are pair-wise equal. Consequently, Σ' and Σ will have the same volume.

Consider the areas. Let C and C' (Fig. 37) be the sections of Σ by two parallel planes that are separated by dx. If we project the curve C onto the plane of C' then we will get a curve C'', and the annular area that is found between C' and C'' will be equal to dQ. Draw normal planes to the curve A at two neighboring points A and B on it. They will intersect C' at A' and B', and intersect C'' at A'' and B'', and we can consider the solid $AA'A''BB'B''$ to be a right triangular prism.

Upon letting ds denote the element of arc length AB of the curve C, the areas of the faces of that prism will be:

$$d\omega = ds\,AA' \qquad \text{(for } AA'BB'\text{)},$$
$$d\omega_1 = ds\,AA' \qquad \text{(for } AA''BB''\text{)},$$
$$d\omega_2 = ds\,AA' \qquad \text{(for } A'A''B'B''\text{)},$$

and since the triangle $AA'A''$, which is perpendicular at A'', gives:

$$\overline{AA'}^2 = \overline{AA''}^2 + \overline{A'A''}^2,$$

one will have:

$$d\omega^2 = d\omega_1^2 + d\omega_2^2.$$

However, $d\omega$ is an element of the surface of the solid Σ; as a result, the area of that solid will be:

$$\int d\omega = \int \sqrt{d\omega_1^2 + d\omega_2^2}\,.$$

Now, one has:

$$\int \sqrt{d\omega_1^2 + d\omega_2^2} > \sqrt{\left(\int d\omega_1\right)^2 + \left(\int d\omega_2\right)^2}\,,$$

because if, for the moment, we regard $d\omega_1$ and $d\omega_2$ as the variations of the coordinates of a point on a planar curve then the left-hand side of the inequality will represent the length of a finite arc along that curve, while the right-hand side will be the square root of the sum of the squares of the differences between the ordinates of the extreme points of the curve and the squares of the differences between their abscissas; i.e., the length of the straight line that joins those points. Since the straight line is the shortest distance between two points, the inequality will indeed be exact.

One will then have:

$$\int d\omega > \sqrt{\left(\int d\omega_1\right)^2 + \left(\int d\omega_2\right)^2}\,.$$

The solid of revolution is an exception. Indeed, in that case, the elementary areas $d\omega$, $d\omega_1$, $d\omega_2$ will have constant ratios; it will then result that the inequality must be replaced with an equality, so:

$$\int d\omega = \sqrt{\left(\int d\omega_1\right)^2 + \left(\int d\omega_2\right)^2}\ .$$

However, $\int d\omega_2$ is the area that is included between the curves C' and C'', i.e., dQ.

On the other hand, since AA'' is the distance between the two sections that are parallel to the bases and infinitely-close to each other, one will have:

$$d\omega_1 = ds\ AA'' = ds\ dx$$

and

$$\int d\omega_1 = s\ dx,$$

in which s is the length of the curve C. Hence, the area S of portion of the solid Σ that is included between our two infinitely-close planes that are parallel to the yz-plane will be:

$$S = \int d\omega > \sqrt{s^2 dx^2 + dQ^2}\ .$$

If the curve C is a circle of area Q then its perimeter will be equal to $\sqrt{4\pi Q}$. Since the circle has the property that among all figures with the same area, it has the smallest perimeter, one must have:

$$s > \sqrt{4\pi Q}$$

for a solid section Σ that is not a solid of revolution, and consequently:

$$S > \sqrt{4\pi Q\, dx^2 + dQ^2}\ .$$

For the solid of revolution Σ′, the preceding inequalities must be replaced with equalities, and we will have:

$$s = \sqrt{4\pi Q}\ ,$$

and consequently:

$$S' = \sqrt{4\pi Q\, dx^2 + dQ^2}\ .$$

The area of the solid of revolution Σ′ is then smaller than that of the solid Σ. As a result, if we succeed in proving that the area of the right cylinder is smaller than the solid of revolution with the same volume and the same bases then, by that fact itself, we will have proved that it is also smaller than that of an arbitrary solid of the same volume and bases, and the area of the cylinder will indeed be a relative minimum. In order to arrive at that goal, we must prove two lemmas.

44. –

Lemma I. – *Suppose two arcs AMB, AM′B′ of the meridians of two unduloids with the same infinitely-close axes* (Fig. 38) *have a common extremity A, and that their extremities B and B″ lie along a normal BB′ to AM′B′. If those arcs intersect at a point C such that the volumes that are generated by AMCM′A and CB′B are equal then the areas of the surfaces that are generated by rotating those arcs will be equal.*

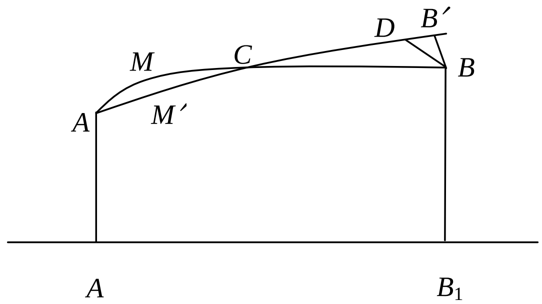

Figure 38.

Let S be area of the surface that is generated by AMB, while $S + \delta S$ is the area of the surface that is generated by $AM'B'$. Let V be the volume that is generated by A_1AMBB_1, so $V + \delta V$ will be the volume that is generated by $A_1AM'CB'BB_1$.

By hypothesis, those two volumes are equal, so δV will be zero; I propose to show that δS is zero.

Indeed, let $d\sigma$ be an element of the surface AMB. Draw a normal to that element and prolong it until it meets the surface $AM'B'$; let λ be the length of that normal.

Let dS be an element of the circumference that is generated by the point B, and let φ be the contact angle – i.e., the angle that the surface AMB makes with BB'.

A formula that we have applied many times will give us:

$$\delta V = \int \lambda \, d\sigma ,$$

$$\delta S = \int \lambda \left(\frac{1}{R_1} + \frac{1}{R_2} \right) d\sigma + \int \lambda \cot \varphi \, ds .$$

Since the angle φ is equal to $\pi / 2$, by hypothesis, the integral will be zero. However, the mean curvature of the unduloid is constant, so I can take $\frac{1}{R_1} + \frac{1}{R_2}$ out of the $\int$ sign, and the first integral will reduce to:

$$\left(\frac{1}{R_1} + \frac{1}{R_2} \right) \int \lambda \, d\sigma = \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \delta V = 0.$$

One will then have:

$$\delta S = 0.$$

The two areas AMB, $A'M' B'$ are equal then, if one neglects second-order infinitesimals.

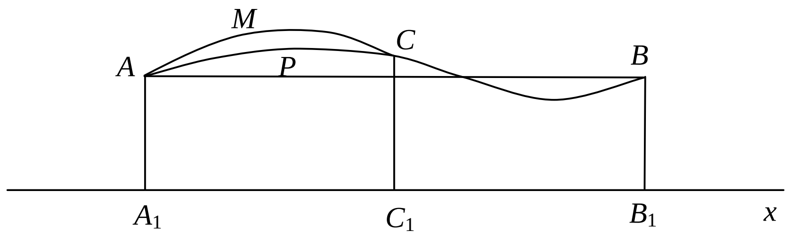

Figure 39.

45. –

Lemma II. – *If AMC* (Fig. 39) *is an arc of the meridian of a solid of revolution that results from the deformation of a cylinder of revolution whose height is smaller than the circumference of the bases then there will exist an arc of the unduloid APC that ends at the same extremities and generates a volume that is equal to that of the solid that is generated by AMC, and there will be only one of them.*

It is clear that one can always find at least one unduloid with the given volume that admits the two given circles as its bases.

Indeed, one can consider an oil drop whose volume is the given volume and which is supported by two solid discs that have the form of two given circles. That drop will have at least one equilibrium position. In other words, if one considers several solids of revolution that have the same volume and the same bases then the lateral surface area of those surfaces cannot decrease beyond all bounds. There will then be one of those solids for which that surface area is smaller than it is for all of the other ones and which must be an unduloid.

All of this is almost obvious. However, what I propose to show is that if the two bases (which are the circles of radii AA_1 and CC_1) have slightly different radii then among the unduloids that satisfy that question, there will be one and only one of them, in general, that differs only slightly from a cylinder.

Let:

$$y = f(x)$$

be the equation of the curve AMC. If x_0 and x_2 are the abscissas of the points A and C then if one lets a denote the radius AA_1, one will have:

$$f(x_1) = a, \qquad f(x_2) = a + \varepsilon,$$

in which ε must be very small, because $A'MCB$ is the meridian of the solid that is obtained by an infinitely-small deformation of the cylinder. The volume that is generated by the trapezoid A_1AMCC_1 is given by the integral:

$$\pi \int_{x_0}^{x_1} f^2(x)\, dx\,.$$

Since $f(x)$ differs only slightly from a, that integral will be equal to:

$$\pi\,[a^2\,(x_2 - x_0) + \varepsilon'],$$

in which ε' is a very small quantity.

Consider the unduloids with axis Ox. Their meridians depend upon the dimensions of the generating ellipse, as well as the position of the point of the line that is found in contact with a well-defined point on the conic (a summit, for example) during the rolling of that conic. Now, the ellipse is determined when one knows those two axes, and the position of the contact point of one of its summits with the line Ox with the abscissa of that point. The equations of the meridians of the unduloids with axis Ox will then contain three arbitrary parameters. One can eliminate one of those parameters by expressing the idea that those meridians pass through the point A, and the general equation of the meridians of the unduloid with axis Ox that passes through A will become:

$$y = \varphi(x, \alpha, \beta),$$

with the condition that:

$$a = \varphi_0\,(x_0, \alpha, \beta).$$

Suppose that the parameters are chosen in such a way that the unduloid reduces to the cylinder for $\alpha = \beta = 0$. For those values of the parameters, one will have:

$$a = \varphi(x_2, 0, 0).$$

The arc APC of the meridian of an unduloid will differ only slightly from the arc AMC, and since it differs only slightly from the straight line AB, the arc APC will differ only slightly from that straight line. As a result, the values of the parameters that correspond to that arc will be exceedingly small, and one can write:

$$\begin{aligned}\varphi(x, \alpha, \beta) &= \varphi(x_2, 0, 0) + \alpha\frac{d\varphi}{d\alpha} + \beta\frac{d\varphi}{d\beta} \\ &= a + \alpha\frac{d\varphi}{d\alpha} + \beta\frac{d\varphi}{d\beta}\end{aligned}$$

for that arc.

In order to express the idea that the arc of the unduloid passes through the extremity C of the arc AMC, it will suffice for us to write:

$$f(x_2) = \varphi(x_2, \alpha, \beta),$$

which will give us the condition:

$$\alpha\frac{d\varphi}{d\alpha} + \beta\frac{d\varphi}{d\beta} = \varepsilon. \tag{1}$$

Set:

$$\pi\int_{x_0}^{x_2} \varphi^2(x, \alpha, \beta)\,dx = \pi\,\psi(\alpha, \beta).$$

Since the arc of the unduloid reduces to the line *AB* for $\alpha = \beta = 0$, the preceding integral (which represents the volume of the unduloid) will then become:

$$\pi\,\psi(0, 0) = \pi a^2\,(x_2 - x_0),$$

and since α and β are very small for the arc *APC*, we can write:

$$\pi\,\psi(\alpha, \beta) = \pi\left[a^2(x_2 - x_0) + \alpha\frac{d\varphi}{d\alpha} + \beta\frac{d\varphi}{d\beta}\right].$$

Since we desire that this volume should be equal to that of the solid that is generated by the arc *AMC*, we must have:

$$\alpha\frac{d\psi}{d\alpha} + \beta\frac{d\psi}{d\beta} = \varepsilon'. \tag{2}$$

It is always possible to satisfy the conditions (1) and (2) with well-defined values of α and β *if the determinant:*

$$\frac{d\varphi}{d\alpha}\frac{d\psi}{d\alpha} - \frac{d\psi}{d\alpha}\frac{d\varphi}{d\beta} \tag{3}$$

is non-zero, and one can then show that there indeed exists an arc of the unduloid that satisfies the stated conditions. Let us see the significance of that condition.

If the preceding determinant is zero then one can satisfy the equations:

$$\alpha\frac{d\varphi}{d\alpha} + \beta\frac{d\varphi}{d\beta} = 0,$$
$$\alpha\frac{d\psi}{d\alpha} + \beta\frac{d\psi}{d\beta} = 0$$

with non-zero values of α and β, which amounts to saying that there will be an arc of the unduloid that has its extremities on the straight line *AB* and generates a volume that is equal to that of the cylinder that is generated by the segment of the line that is found between the extremities of the arc of the unduloid.

Now it will be impossible for that to be true for a length of that segment that is less than *AB* if that length it itself smaller than $2\pi a$, as the statement supposed.

Indeed, we have seen that the meridian of the unduloid is the trajectory of the focus of an ellipse that rolls along a line.

When the ellipse reduces to a circle of radius *a*, the unduloid will reduce to a cylinder of radius *a* that has a line *AB* for a meridian.

Consider the intersections of that line *AB* with a meridian of the unduloid that differs from it slightly; i.e., it is generated by an ellipse that differs slightly from a circle of radius *a*.

A line such as *AB* that is parallel to the line along which the generating ellipse of a meridian of the unduloid rolls will cut that meridian at a series of points *D*, *E*, *F* (Fig. 40).

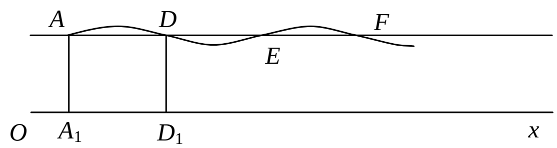

Figure 40.

The extremity C of the arc of the unduloid APC considered cannot coincide with the point of intersection D, because it is obvious that the volume of the unduloid that is bounded by planes that are perpendicular to Ox and pass through A and D is larger than the volume of the cylinder that is generated by the rectangle A_1ADP_1 . As a result, the point C must be one of the following points of intersection E, F, … Now, the points A and E of the meridian of the unduloid correspond to positions on the ellipse such that the same point of the ellipse is in contact with Ox in those two positions. Consequently, the difference between the abscissas of those points will be equal to the length of the ellipse. However, that length differs only slightly from $2\pi a$, because in order to obtain the line AB itself, the ellipse must reduce to a circle of radius a, and by hypothesis, the unduloid $ADEF$ will differ only slightly from the line.

It will then result from this that it will be possible to have an unduloid that is bounded by equal circles that have the same volume as the cylinder with the same bases only if the height of the unduloid is at least equal to the circumference of those bases. The determinant can be annulled only if that height is not smaller than that circumference. (I would even like to add, if it is a multiple of that circumference.)

Now, in the statement of the lemma, I have supposed that the distance between the two planes AA_1, BB_1, and *a fortiori*, that of the two planes AA_1, CC_1, was smaller than that circumference.

Our determinant cannot be annulled then, and the lemma is proved.

Here is how we can make use of that fact:

46. – Consider the solid $AMCBB_1A_1$ (Fig. 39) and a moving plane CC_1 that is parallel to the two bases; now construct the unduloid APC that was defined above.

When the plane CC_1 displaces continuously, that unduloid will deform in a continuous manner.

When C is very close to A, that unduloid will differ only slightly from the cylinder. Will it also differ only slightly when the point C goes to B?

In order to address that, here is how we shall argue:

Put the equation of the curve AMB into the form:

$$y = \xi f_1(x),$$

in which ξ is infinitely small and f_1 is finite.

The functions φ and ψ that were defined above also depend upon ξ and the abscissa x_2 of the point C, so the equations that define α and β can be put into the form:

$$\varphi(\alpha, \beta, \xi, x_2) = 0,$$

$$\psi(\alpha, \beta, \xi, x_2) = 0.$$

If we eliminate β from those two equations then we will have:

$$\Theta\ (\alpha, \xi, x_2) = 0.$$

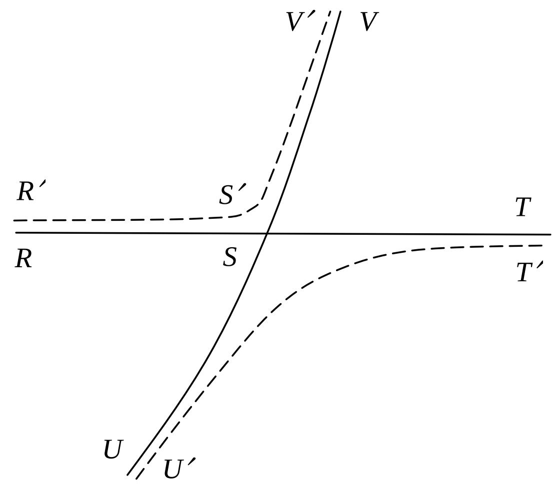

Figure 41.

If we regard α, ξ, and x_2 as the rectangular coordinates of a point in space, for the moment, then that equation will represent a surface. That surface passes through the line $\alpha = 0$, $\xi = 0$, which is the line *RST* in Fig. 41. The determinant:

$$\frac{d\varphi}{d\alpha}\frac{d\psi}{d\alpha} - \frac{d\psi}{d\alpha}\frac{d\varphi}{d\beta}$$

is annulled for $\alpha = \xi = 0$, $x_2 = 2\pi a$, which must say that the plane $\xi = 0$ is tangent to the surface at the point *S* that has the coordinates 0, 0, and $2\pi a$. That plane will then cut the surface along a curve that presents a double point at *S* and which will, consequently, decompose into the line *RST* and a curve *USV* that passes through *S*.

If we now cut the surface with a plane $\xi = \xi_0$ (ξ_0 being very small) then we will get two branches of the curve $R'S'V'$, $U'T'$ that are denoted with dashed lines in the figure.

When the point *C* displaces continuously, the point (α, ξ, x_2) will describe the branch $R'S'V'$ of a continuous motion. One sees that as long as x_2 is smaller than $2\pi a$, the point that describes $R'S'$ will stay very close to the line *RST*, and the unduloid will correspond very closely to the cylinder. When x_2 becomes larger than $2\pi a$, our point will describe $S'T'$, and it will move away from the line *RST*; i.e., the corresponding unduloid will not remain only slightly different from the cylinder.

Hence, if *AB* is smaller than $2\pi a$ then the continuous deformation of the unduloid will reduce it to the cylinder (which it will never be far from) when the point *C* goes to *B*.

However, the same thing will no longer be true if *AB* is larger than $2\pi a$.

47. –

Theorem. – *If the height of a right circular cylinder is smaller than the circumference of its bases then the lateral surface area of that cylinder will be smaller than that of any solid of revolution that has the same volume and the same bases.*

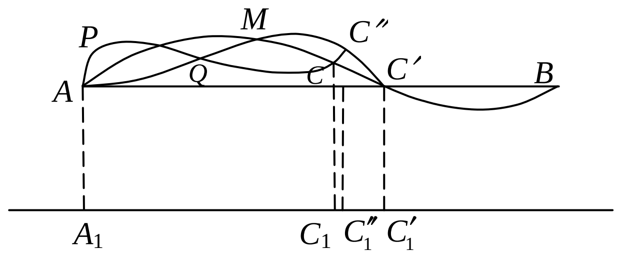

Figure 42.

Let AB (Fig. 42) be the generator of the cylinder, and let AMB be the meridian of the surface of revolution. Take an arbitrary point C on that meridian. From the preceding lemma, we can trace out an arc of the unduloid APC such that the volume that is generated by A_1PCC_1 will be equal to the volume that is generated by A_1AMCC_1. Suppose that we have shown that the surface area of that unduloid is smaller than that of the latter volume and that if we consider a point C' of $AMC'B$ that is infinitely close to C then the unduloid that is supported by the circles of radii AA_1 and $C'C_1'$ (and which has the same volume as the solid that is generated by $AM_1MC'C_1'$) will also have an area that is less than the latter solid.

Indeed, let AQC' be the arc of the second unduloid. If we draw the normal CC'' to that arc at C then we will have two arcs of the unduloids APC and AQC'' that have a common extremity A and are, on the other hand, bounded by a normal to one of them. Moreover, the volumes that are bounded by the surfaces that generate those arcs will be equal, since one has:

$$\text{volume } A_1AMC'C_1' = \text{volume } A_1AQC'C_1',$$

and since the area of the triangle $CC'C''$ is a second-order infinitesimal, upon neglecting the volumes that are infinitely-small of that order, one will have:

$$\text{volume } A_1AMCC_1 = \text{volume } A_1AQC''C_1'',$$

or rather:

$$\text{volume } A_1APCC_1 = \text{volume } A_1AQC''C_1'',$$

in which the volumes of the solids that are generated by A_1AMCC_1 and A_1APCC_1 are equal, by hypothesis.

The two arcs of the unduloids APC and AQC'' then fulfill the conditions of the statement of Lemma I. As a result, the areas of the surfaces that they generate will be equal up to second-order infinitesimals (CC' being of first order):

$$\text{area } APC = \text{area } AQC''.$$

If, as we have assumed, we have:

$$\text{area } APC < \text{area } AMC$$

then we will have:

$$\text{area } AQC'' < \text{area } AMC.$$

We add the following inequality:

$$\text{area } C''C' < \text{area } CC'$$

(which results from the fact that the line CC'' is normal to the arc AQC' at C'', so the element of the arc $C'C''$ will be smaller than the element CC') to the two sides of the last inequality and get:

$$\text{area } AQC' < \text{area } AMC'.$$

Hence, if it is true that the arc of the unduloid that joins A to an arbitrary point C on the curve $AMCB$ generates a surface whose area is smaller than that arc then that property will still be exact when one passes from C to a neighboring point C', since the volumes that are bounded by those respective surfaces are equal.

The theorem is obviously true for an unduloid of infinitely-small height. Upon displacing the point C little-by-little, one will arrive at B. Now, the unduloid that passes through A and B and has the same volume as the solid that is generated by the curve $AMCB$ will reduce to the cylinder of revolution. Consequently, the area of the surface of that cylinder will be smaller than that of an arbitrary volume of revolution that has the same bases and the volume.

I would like to say that when the point C goes to B, the unduloid will reduce to the cylinder.

By virtue of Lemma II, that will be true when AMB differs only slightly from the line AB and if the height AB of the cylinder is smaller than $2\pi a$ (viz., the circumference of the base).

Therefore, the cylinder of revolution whose height is smaller than that circumference will be a stable figure of equilibrium.

If the height of the cylinder grows larger then the conditions of the statement of the second Lemma will no longer be satisfied. Plateau's analysis will then teach us that the equilibrium of the cylinder is unstable.

48. Rotating oil drops. – When an oil drop is suspended in a liquid with the same density without being in contact with solid supports, the equilibrium condition of that drop will be obtained by setting $S = S_1 = 0$ in the equilibrium equation that was found in § **36**. One will then have:

$$\left(\frac{\theta_1}{2} + \frac{\theta_1'}{2} - \eta_2\right)\delta\Sigma = 0,$$

which expresses the idea that the contact surface of the oil and the alcohol must be as small as possible.

Among the solids with the same volume, the sphere satisfies that condition, and experience has shown that an oil drop that is equilibrium inside of a liquid of the same density will indeed affect a spherical form.

If one rotates the drop around an axis that passes through its center then the sphere will deform and transform into solids of revolution that are more or less flattened, and to which one gives the name of *spheroids*. We shall look for the form of the new equilibrium surfaces.

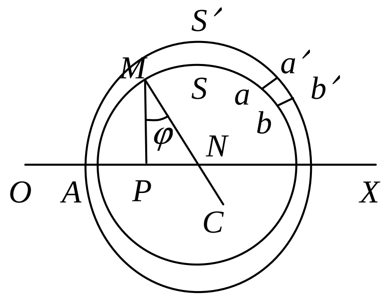

Figure 43.

Let S (Fig. 43) be one of those surfaces, and let S' be the one that results from an infinitely-small deformation of S. Upon passing from one of those surfaces to the other, the work done by forces that act upon the drop must be zero, since S is an equilibrium surface. Now, from what we saw in § **36**, the work done by capillary forces is equal to:

$$-\left(\frac{\theta_1}{2}+\frac{\theta_1'}{2}-\eta_2\right)\delta S.$$

On the other hand, the rotation of the drop will develop a centrifugal force whose work is:

$$\frac{\omega^2}{2}\,\delta I,$$

in which ω is the angular velocity of rotation, and I is the moment of inertia of the drop with respect to the axis of rotation.

Consequently, the equilibrium condition for the drop is:

$$\frac{\omega^2}{2}\,\delta I-\left(\frac{\theta_1}{2}+\frac{\theta_1'}{2}-\eta_2\right)\delta S=0$$

or

$$\delta S = \alpha\,\delta I,$$

in which α denotes a quantity that is proportional to the square of the angular velocity and becomes constant when that velocity does.

As a result of the deformation of S, an element $ab = d\sigma$ of that surface will correspond to an element $a'b' = d\sigma'$ of the surface S' that is obtained by drawing normals to S through the contour of ab. The variation of the surface S can then be written:

$$\delta S = \int d\sigma' - \int d\sigma .$$

However, we saw in § **21** that if we let λ denote the length of the normal aa' then we will have:

$$d\sigma' - d\sigma = \lambda\, ds\left(\frac{1}{R_1} + \frac{1}{R_2}\right).$$

Consequently:

$$\delta S = \int \lambda\, d\sigma \left(\frac{1}{R_1} + \frac{1}{R_2}\right).$$

The variation δI of the moment of inertia is equal to the sum of the moments of inertia of the volume elements, such as $ab\, a'b'$. Upon letting r denote the distance from the center of gravity of that element to the rotational axis Ox, one will get:

$$\delta I = \int r^2 \lambda\, d\sigma .$$

One will then have that the equilibrium condition is:

$$\int \lambda\, d\sigma \left(\frac{1}{R_1} + \frac{1}{R_2} - \alpha r^3\right) = 0,$$

to which one must add the condition:

$$\int \lambda\, d\sigma = 0,$$

which expresses the idea that the volume of the drop does not change.

In order for those two conditions to be satisfied simultaneously, it is necessary that:

$$\frac{1}{R_1} + \frac{1}{R_2} - \alpha r^2 = \beta,$$

in which β is a constant.

The surface that is defined by that equation is one of revolution, so one of the radii of curvature at M will be the radius of curvature MC of the meridian curvature; the other one MN will be bounded by the rotational axis. Upon letting φ denote the angle between the normal at M and the perpendicular MP to the rotational axis and letting ds denote an element of arc length, measured to be positive in the sense of increasing φ (i.e., in the sense MA), one will have:

$$R_2 = MC = \frac{ds}{d\varphi}, \qquad R_1 = MN = \frac{r}{\cos\varphi},$$

and the equation of the surface will become:

$$\frac{d\varphi}{ds} + \frac{\cos\varphi}{r} = \alpha r^2 + \beta,$$

which will give:

$$\frac{d\varphi}{ds} + \frac{\cos\varphi}{y} = \alpha y^2 + \beta$$

for the equation of its meridian that is located in the *xy*-plane.

Since one has:

$$dy = -\,ds\sin\varphi,$$

that equation can be written:

$$\frac{-\sin\varphi\, d\varphi}{dy} + \frac{\cos\varphi}{y} = \alpha y^2 + \beta,$$

or

$$\frac{d\cos\varphi}{dy} + \frac{\cos\varphi}{y} = \alpha y^2 + \beta\,.$$

In order to integrate, we remark that if the right-hand side is zero then the solution will be:

$$\cos\varphi = \frac{C}{y},$$

in which C is a constant. We now apply the method of variation of constants. We get:

$$\frac{1}{y}\frac{dC}{dy} = \alpha y^2 + \beta,$$

so

$$C = \frac{\alpha}{4}y^4 + \frac{\beta}{2}y^2 + \gamma\,, \tag{1}$$

and consequently:

$$\cos\varphi = \frac{C}{y} = \frac{\alpha}{4}y^3 + \frac{\beta}{2}y + \frac{\gamma}{y}\,.$$

However, one has:

$$dx = dy\cot\varphi.$$

Upon eliminating φ from those two relations, one will get the equation of the meridian curve in rectangular coordinates. One deduces from the first one that:

$$\sin\varphi = \sqrt{1 - \frac{C^2}{y^2}}\,,$$

and as a result:

$$\cot\varphi = \frac{C}{\sqrt{y^2 - C^2}}\,,$$

so one will have:

$$x = \int \frac{C\,dy}{\sqrt{y^2 - C^2}}, \tag{2}$$

in which C is the function of y that is defined by the equality.

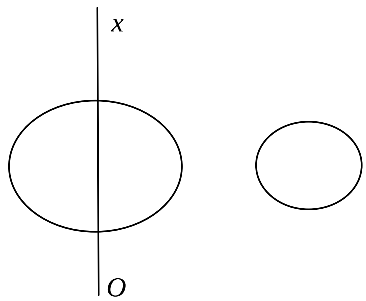

Figure 44.

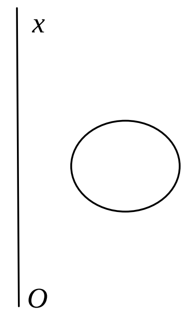

Figure 45.

The curve that this equation represents can be either a flattened closed curve in the neighborhood of the rotational axis or two closed curves that are symmetric with respect to the rotational axis according to the values of the constants that enter into that equation. The former case (Fig. 44) corresponds to a weak angular velocity, and the volume that is generated will be a spheroid, while the latter (Fig. 45) has a considerable angular velocity, and the mass of oil will form a ring.

The curve obviously admits the x-axis as a symmetry axis, but it likewise admits another symmetry axis that is perpendicular to the first one and which one can take to be the y-axis.

The points where the curve cuts the y-axis are the roots of the equation:

$$y^2 - C^2 = 0. \tag{3}$$

That remark will suffice to allow us to discuss the problem. Plateau observed that when one increases the angular velocity, the mass, which is initially unique, will decompose into a central mass and an annular one. The split will come about at the moment where equation (3) has two equal roots.

When the curve is unique and cuts the axis, the determination of the integration constants in the equality (2) will always be possible. The same thing will not be true when the rotational axis does not meet the curve.

49. – Plateau succeeded in establishing the spheroidal and annular forms experimentally. He stated that the latter is a stable equilibrium form. The theoretical proof of the stability of equilibrium of the ring presents some serious mathematical difficulties, since the integral in equation (2) is hyperelliptic.

We also point out that in the case of a body that is animated with a rotational motion, it is not necessary for the potential energy of the system to pass through a minimum in order for the equilibrium to be stable. Indeed, Dirichlet's theorem supposes that the axes to which the points of the body are referred are at rest.

When those axes are rotating ones, one must introduce the composite force that is defined by Coriolis's theorem, and Dirichlet's equilibrium condition, which is always sufficient, will no longer be necessary for stability.

We likewise observe that the equilibrium figures of an oil drop in rotation are not by any means comparable to those of the planets, although that opinion is very widespread. In order for that to be the case, it would be necessary that the Newtonian attraction should obey the same laws as the capillary force, which is not true. It even seems probable that the annular figures, which are stable for the capillary phenomena of Plateau's experiments, might become unstable in the case of Newtonian attraction.

50. Closed systems of thin films. – Upon submerging a metallic wire framework in a liquid, one can, in certain cases, obtain a system of thin films that bound all parts of a certain mass of air. As we shall show, the equilibrium surfaces of those films, which Plateau has studied experimentally, do not differ from the equilibrium surfaces of an oil drop that is placed in the diluted alcohol of the same density.

Indeed, consider a system that is composed of some films and the air mass that they enclose and give it an infinitely-small virtual deformation when one starts from an equilibrium position.

The work done by gravity $gU\ \delta z$ can be neglected, because, on the one hand, the liquid mass that defines the films is very small, since those films are very thin, and on the other hand, since the air mass that they enclose is also small, the air will have a very weak density. As a result, U will be very small.

Upon letting Σ denote the total area of the faces of the films that are in contact with the outside air, the area of the faces that are in contact with the interior air will be very roughly Σ, since the two faces of the same film are very close and can be regarded as parallel. The work done by capillary forces that result from a variation $d\Sigma$ of that area will then be:

$$2\left(-\frac{\theta_1}{2}d\Sigma\right),$$

in which θ_1 is the function that relates to the action of the liquid molecules on themselves.

If, at the same time, the contact surface of the liquid and the framework varies then we will have to take into account the work done by capillary forces that result from that variation. However, since that surface area is proportional to the thickness of the film, it will be small, and its variation can be neglected.

All that will remain then is the work $-\ \theta_1\ d\Sigma$. One must add the work done by pressure to that work. If one lets p_0 denote the outside air pressure and lets p denote the internal air pressure then the work done by internal pressure will be $p\ dV'$ and the work done by external pressure will be $-\ p_0\ dV$, in which dV' is the variation of the volume that is bounded by the internal faces of the films, and dV is the variation of the volume that is bounded by the external faces. Those faces are parallel and very close to each other, so dV and dV' will differ infinitely little, and one will have that the total work done by the pressures is:

$$(p - p_0)\,dV.$$

The equilibrium condition of the system is then:

$$-\theta_1\,d\Sigma + (p - p_0)\,dV = 0.$$

However, we have found (21) that:

$$d\Sigma = \int \lambda \left(\frac{1}{R_1} + \frac{1}{R_2}\right) d\sigma + \int \lambda \cot\varphi\, ds\,,$$

and on the other hand, that the variation of the volume that is bounded by the external faces is:

$$dV = \int d\sigma\,.$$

One will then have:

$$\int \lambda \left[p - p_0 - \theta_1 \left(\frac{1}{R_1} + \frac{1}{R_2}\right)\right] d\sigma - \theta_1 \int \lambda \cot\varphi\, ds = 0,$$

and since that relation must be satisfied for any deformation, it will be necessary that one must have:

$$p - p_0 = \theta_1 \left(\frac{1}{R_1} + \frac{1}{R_2}\right), \qquad \cot\varphi = 0, \qquad \text{so } \varphi = \frac{\pi}{2},$$

separately.

The internal and external pressures are uniform, since the weight of the air is negligible, so the first of those conditions expresses the idea that the mean curvature of the surfaces of films must be constant. That is one of the conditions that was found in § **36** for the equilibrium of an oil drop of the same density.

The condition $\varphi = \pi / 2$ seems more restrictive than the condition φ = const. that was found in the latter case. However, in reality, they will become identical if one remarks that, by definition, they reduce to the statement that the surfaces of the oil drop or the films must pass through the metallic wires of the frame or the boundaries of the discs.

The equilibrium surfaces of the films that form a system that is closed on all sides will then be those of an oil drop that is placed in a liquid of the density.

In particular, if one forms a soap bubble that passes through the contours of two parallel rings of metal wires with the same radius then one must get equilibrium figures in the form of the unduloid, the right cylinder, the nodoid, and the catenoid.

51. Soap bubbles. – Among the surfaces with constant mean curvature, the simplest one is the sphere. Experiments have shown that it is the form that a closed film will take when it does not touch any solid wall.

There are possibly other equilibrium surfaces that pertain to this case, because the equilibrium condition:

$$-\,\theta_1\, d\Sigma + (p - p_0)\, dV = 0$$

does not say that the area of the surface must be a minimum, as in the case of an oil drop that is suspended freely in a liquid of the same density. There have been attempts to prove that there is no other possibility, but the proofs that have been proposed leave much to be desired.

Be that as it may, in the case of a sphere of radius R, we must have:

$$p - p_0 = \frac{2\theta_1}{R}$$

for the difference between the internal and external air pressures.

That difference is positive, and it will become larger when the bubble becomes smaller. That has been verified quite sensitively by measuring that pressure difference with a manometer.

Consider two adjoining bubbles. They intersect along a circumference through which the liquid film that separates the two bubbles passes. Assume that this film is spherical and look for the relation that exists between the radii R, R', R'' of the three spherical surfaces when there is equilibrium.

Upon letting p and p_0 denote the air pressures that are internal to the first and second bubbles, resp., we will have:

$$p - p_0 = \frac{2\theta_1}{R},$$

$$p' - p_0 = \frac{2\theta_1}{R'},$$

$$p' - p = \frac{2\theta_1}{R''},$$

from which, we will deduce that:

$$\frac{1}{R'} - \frac{1}{R} = \frac{1}{R''}.$$

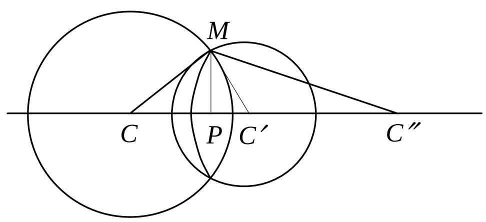

Figure 46.

One can believe that this equilibrium condition is not sufficient and that there is good reason to say, in addition, that the surface tensions that are exerted upon a point of the line of intersection of the three spheres must be in equilibrium. We shall show that this new condition amounts to the same thing as the preceding one.

Indeed, since the three spheres are composed of the same liquid, the surface tensions will be equal, and as a result, the spheres must intersect at angles of 120° in order for those tensions to produce equilibrium. Let C, C', C'' (Fig. 46) be the respective centers of those spheres, which are in a straight line since they all pass through the same circumference. Drop a perpendicular to that line of centers from a point M in the intersection, and let α, α', α'', resp., denote the angles between that perpendicular and the radii MC, MC', MC'', resp. Upon letting h denote the length of the perpendicular MP, we will have:

$$\frac{1}{R} = \frac{1}{h}\cos\alpha,$$

$$\frac{1}{R'} = \frac{1}{h}\cos\alpha',$$

$$\frac{1}{R''} = \frac{1}{h}\cos\alpha''.$$

One deduces from this that:

$$\frac{1}{R} - \frac{1}{R'} - \frac{1}{R''} = \frac{1}{h}(\cos\alpha - \cos\alpha' - \cos\alpha'').$$

Now, one has:

$$\alpha + \alpha' = 180^{\circ} - 120^{\circ} = 60^{\circ}, \qquad \alpha + \alpha'' = 120^{\circ},$$

and consequently:

$$\cos\alpha - \cos\alpha' - \cos\alpha'' = \cos\alpha - \cos(60^{\circ} - \alpha) - \cos(120^{\circ} - \alpha) = 0,$$

and that will give:

$$\frac{1}{R} - \frac{1}{R'} - \frac{1}{R''} = 0.$$

One will indeed recover the same condition that appeared in the consideration of pressures.

The case of a larger number of bubbles that are joined to each other reverts immediately to the preceding one. Indeed, Plateau asserted that there are never more than three liquid surfaces that intersect along the same line. Since the three surfaces are spherical, their radii must satisfy the preceding condition.

52. Films that intersect along the same edge. – The property of the bubbles that they always intersect in such a way that there are never any more than three surfaces that pass through the same edge is likewise observed when the films are planar.

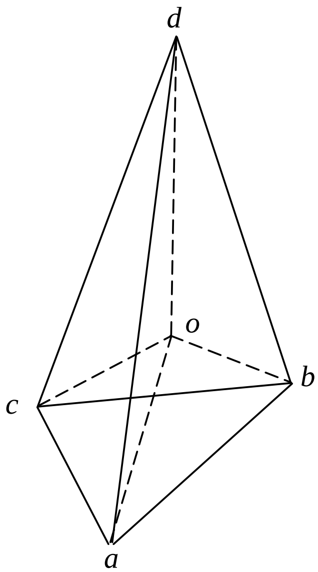

Figure 47.

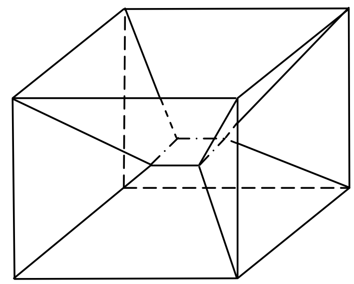

Figure 48.

Upon submerging a tetrahedral frame *abcd* (Fig. 47) in glycerin, Plateau obtained a system of thin films that was composed of ten planar films, four of which constituted the faces of the tetrahedron, while the other six were supported by the edges of that tetrahedron and intersected in such a way that each of the lines *oa*, *ob*, *oc*, *od* belonged to three films. The dihedral angles that are defined by the films that intersect along one of those edges will be necessarily equal to each other and to 120° in order for the surface tensions to equilibrate.

With a framework whose wires form the edges of a cube, one will get the liquid films that are represented in Fig. 48, and which intersect three-by-three along the liquid edges *abcd* and along the edges of the cube.

That system of thin films is much more complicated than the one that is formed by the four faces of the cube and its diagonal planes, and which seems to be formed as a result of the symmetry of the cube. However, it is easy to see that such a system can exist only in a stable equilibrium state.

Take some frames that are simpler than Plateau's, and are formed from two parallel wooden planks that are linked by metal wires that are normal to those planks. Upon submerging those frames in a liquid, one will get a system of planar films that are supported by the metal wires and are normal to the planks. If there are three wires *a*, *b*, *c* (Fig. 49) then we will have six films, three of which form the faces of a triangular prism, while the other three, which are represented by *oa*, *ob*, *oc*, will intersect along the same edges *o* and make dihedral angles of 120° between them.

If we take a plank that has four wires that form the edges of a right prism with a square base then we can never obtain the system of thin films that is represented in Fig. 50 and which includes the diagonal planes of the prism.

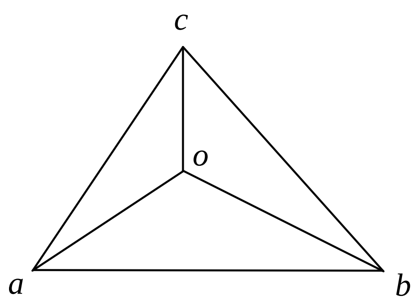

Figure 49.

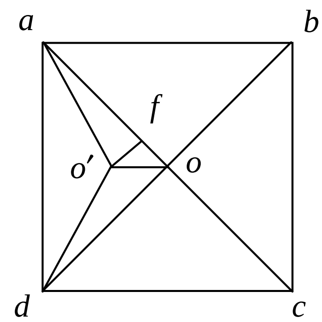

Figure 50.

That impossibility is due to the fact that such a system is not in stable equilibrium. Let us show that.

Since the films are planar, the radii of curvature will be infinite, and the difference between the pressures of the two sides of a film will be zero. Consequently, under an infinitely-small displacement, the works done will reduce to the works done by capillary forces, namely, $-\theta_1 \, d\Sigma$. In order to have equilibrium, it is necessary that this expression should be zero, and in order for that equilibrium to be stable, it is necessary that $\theta_1 \, \Sigma$ must pass through a maximum; i.e., that Σ must be a minimum.

Now, if one supposes that the preceding system is deformed in such a way that the two films *ao* and *do* become *ao′* and *do′*, resp., and such that a new film will form from *o* to *o′*, then the sum of the areas of those three films will be smaller than the sum of the areas of the original two films. Indeed, if one drops the perpendicular *o′f* from *o′* to *oa* then one will have:

$$fo = oo' \cos foo'$$

or

$$fo > \frac{oo'}{2},$$

since the angle *foo′* is close to 45°. On the other hand, the angle *fao′* is infinitely small, so one will have, roughly:

$$af = ao',$$

and as a result:

$$af + fo > ao' + \frac{oo'}{2}$$

or

$$ao > ao' + \frac{oo'}{2}.$$

One will likewise find that:

$$do > do' + \frac{oo'}{2},$$

and one will obtain:

$$ao + do > ao' + do' + oo'.$$

It will then result that the sum of the areas of the films will not be a minimum for the system of thin films that contains the diagonal planes of the prism. That system cannot correspond to a stable equilibrium state then.

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CHAPTER V

PROBLEMS IN WHICH GRAVITY INTERVENES

In the preceding two chapters, the work done by gravity disappeared from the equilibrium equations, either because it was negligible in comparison to the work done by capillary forces or because it was zero. We shall now move on to the study of some problems in which the action of gravity intervenes in the equilibrium equations. The most important ones are the problems that relate to equilibrium in superposed fluids, the equilibrium figure of a drop that is placed on a horizontal plane, and the attraction or repulsion of two vertical walls that are submerged in a liquid.

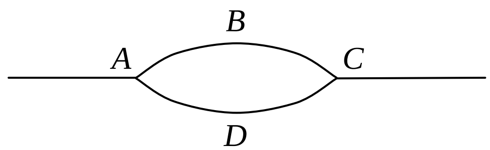

Figure 51.

53. Equilibrium of a liquid drop that rests upon a denser liquid. – Let *ABCD* be the drop (Fig. 51). Let *S* be its free surface *ABC*, and let S' be its contact surface *ADC* with the denser liquid upon which it rests, let S'' be the free surface of the latter liquid, and let $\frac{\theta_1}{2}, \frac{\theta_1'}{2}, \frac{\theta_1''}{2}$ be the surface tensions on the those surfaces. The work done by capillary forces that result from a virtual deformation of the drop has the expression:

$$-\frac{\theta_1}{2}\,\delta S - \frac{\theta_1'}{2}\,\delta S' - \frac{\theta_1''}{2}\,\delta S''.$$

Up to now, we have considered only one fluid, and we took the density of that fluid to be unity. In the case that we presently address, we call the density of the lower liquid ρ and that of the liquid that forms the drop ρ_1 . If we let U and U_1 be the respective volumes of those liquids, and let Z and Z_1 be the distances from their centers of gravity to the *xy*-plane then we will have:

$$g\rho\, U\, \delta Z + g\rho_1\, U_1\, \delta Z_1$$

for the work done by gravity, in which the *z*-axis is assumed to be directed downward.

Consequently, the equilibrium condition is:

$$g\rho\, U\, \delta Z + g\rho_1\, U_1\, \delta Z_1 - \frac{\theta_1}{2}\,\delta S - \frac{\theta_1'}{2}\,\delta S' - \frac{\theta_1''}{2}\,\delta S'' = 0, \tag{1}$$

to which one can add the two constraint equations:

$$\delta U = 0, \qquad \delta U_1 = 0, \tag{2}$$

which express the idea that the volumes of the liquids do not change.

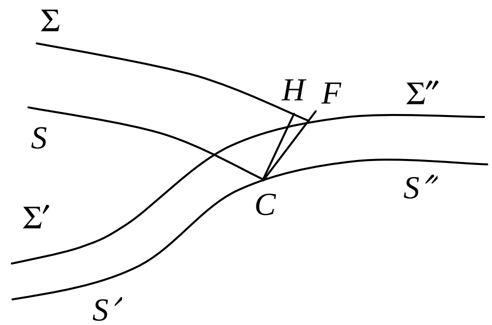

Figure 52.

In order to transform these equations, consider the new positions Σ, Σ′, Σ″ of the surfaces *S*, *S′*, *S″*, resp. (Fig. 52). If we draw normals to the former surfaces through each of the points of the original surfaces then the lengths λ of the normals between the original surfaces and the ones that result from their deformation will determine the latter surfaces. Upon letting $d\sigma$ denote the area of an element of *S*, we will have:

$$\delta S = \int \lambda \left(\frac{1}{R} + \frac{1}{R_1} \right) d\sigma + \int \lambda \, ds \cot \varphi$$

for the variation of that area (no. **21**), in which *ds* is an element of the contact curve, and φ is the angle between the line *CF* that joins two positions of a point on that curve and the tangent to the deformed surface at *F*. On the other hand, the triangle *CHF*, in which *CH* is the normal to *S*, is roughly a right triangle at *H*, and we will have the relation:

$$CH = CF \sin HFC$$

or

$$\lambda = \mu \sin \varphi,$$

in which μ denotes the length *CF*. Consequently, we can write:

$$\delta S = \int \lambda \left(\frac{1}{R} + \frac{1}{R_1} \right) d\sigma + \int \mu \, ds \cos \varphi .$$

We find similar expressions for the other variations:

$$\delta S' = \int \lambda \left(\frac{1}{R'} + \frac{1}{R'_1} \right) d\sigma' + \int \mu \, ds \cos \varphi' ,$$

$$\delta S'' = \int \lambda \left(\frac{1}{R''} + \frac{1}{R''_1} \right) d\sigma'' + \int \mu \, ds \cos \varphi'' .$$

In order to calculate δU_1, we remark that if only the surface S deforms then we will have:

$$\int \lambda \, d\sigma$$

for the variation of the volume.

However, since the surface S' deforms along with it, one will have:

$$\delta U_1 = \int \lambda \, d\sigma - \int \lambda \, d\sigma'.$$

Similarly, one will get:

$$\delta U = \int \lambda \, d\sigma' + \int \lambda \, d\sigma''.$$

Since the volumes are invariable, one can write:

$$U_1 \ \delta Z_1 = \delta U_1 \ Z_1 = \int \lambda z \, d\sigma - \int \lambda z \, d\sigma',$$

$$U \ \delta Z \ = \delta U \ Z \ = \int \lambda z \, d\sigma' + \int \lambda z \, d\sigma'',$$

in which the right-hand sides of those equalities express the idea that the variations of the moments of the weights of the liquid with respect to the xy-plane are equal to the sums of the moments of the weights of their elements with respect to that plane.

The equilibrium equation will then become:

$$\begin{aligned}\int \lambda \, d\sigma \left[g_1 \rho z - \frac{\theta_1}{2}\left(\frac{1}{R} + \frac{1}{R_1}\right)\right] + \int \lambda \, d\sigma' \left[g\rho z - g_1 \rho z - \frac{\theta_1'}{2}\left(\frac{1}{R'} + \frac{1}{R_1'}\right)\right] \\ + \int \lambda \, d\sigma'' \left[g\rho z - \frac{\theta_1''}{2}\left(\frac{1}{R''} + \frac{1}{R_1''}\right)\right] - \int \mu \, ds \left(\frac{\theta_1}{2}\cos\varphi + \frac{\theta_1'}{2}\cos\varphi' + \frac{\theta_1''}{2}\cos\varphi''\right) = 0,\end{aligned} \tag{3}$$

and the constraint conditions will become:

$$\left.\begin{aligned}\int \lambda \, d\sigma - \int \lambda \, d\sigma' = 0, \\ \int \lambda \, d\sigma' + \int \lambda \, d\sigma'' = 0.\end{aligned}\right\} \tag{4}$$

54. – Equation (3) must be true for any λ, provided that λ satisfies (4). In particular, it must be true when one has:

$$\int \lambda \, d\sigma = 0, \quad \int \lambda \, d\sigma' = 0, \quad \int \lambda \, d\sigma'' = 0, \tag{5}$$

which demands that one must have:

$$
\left.
\begin{aligned}
g\rho_1 z &= \frac{\theta_1}{2}\left(\frac{1}{R}+\frac{1}{R_1}\right)+\beta, \\
g(\rho-\rho_1)\, z &= \frac{\theta_1'}{2}\left(\frac{1}{R'}+\frac{1}{R_1'}\right)+\beta', \\
g\rho z &= \frac{\theta_1''}{2}\left(\frac{1}{R''}+\frac{1}{R_1''}\right)+\beta'', \\
\frac{\theta_1}{2}\cos\varphi &+ \frac{\theta_1'}{2}\cos\varphi'+\frac{\theta_1''}{2}\cos\varphi'' = 0,
\end{aligned}
\right\} \tag{6}
$$

in which β, β', β'' are constants.

However, in order for there to be equilibrium, equation (3) must be satisfied for any displacement, provided that it is compatible with the constraints. It must then be satisfied even when the conditions (5) are satisfied, provided that the equalities (4) are.

However, if we take the conditions (6) into account then equation (3) will reduce to:

$$\beta\int\lambda\,d\sigma+\beta'\int\lambda\,d\sigma'+\beta''\int\lambda\,d\sigma''=0,$$

or, upon taking the constraint equations (4) into account:

$$(\beta+\beta'-\beta'')\int\lambda\,d\sigma = 0.$$

In order for it to be satisfied for non-zero values of the integral, it is necessary and sufficient that one must have:

$$\beta+\beta'-\beta''=0.$$

That is the new condition that one must append to the conditions (6) in order to have equilibrium.

The first three of equations (6) are the equations of the surfaces S, S', S'', resp. The fourth one expresses the idea that the projection of the tensions at the point C onto the line CF is zero, since φ, φ', φ'' are the angles between that line and the tangents that are drawn through F in the normal plane to the intersection curve at that point. Since the direction of CF is arbitrary, that equation will express the idea that the three tensions at C must be in equilibrium.

That condition permits one to find the contact angles of the three surfaces when one knows the values of the tensions. In order to do that, it will suffice to construct a triangle whose edges are equal to the tensions. One of the angles of that triangle and the supplements of the other two will be the contact angles.

It can happen that the values of the tensions are such that the construction of the triangle will become impossible. In that case, there will be no equilibrium, since one of the equilibrium conditions is not satisfied, and the floating liquid will extend indefinitely on the surface of the denser liquid.

That is what happens for a drop of olive oil that is placed on the free surface of water. The surface tension of oil in contact with air is equal to 37 dynes, that of oil in contact with water is 21 dynes, and finally that of water in contact with air has the value 81, so one of the edges of the triangle will be greater than the sum of the other two, because:

$$81 > 37 + 21,$$

and equilibrium cannot be produced.

Meanwhile, if the oil drop has a small volume and the surface of the water is sufficiently large then one can confirm that the oil drop will cease to spread out before it reaches the walls of the vessel. There will then be an equilibrium state. However, that fact does not invalidate the theory, because it supposes that the distance between the surfaces S and S' that bound the oil is greater than the radius of molecular activity, which will cease to be true when the oil drop has spread out sufficiently.

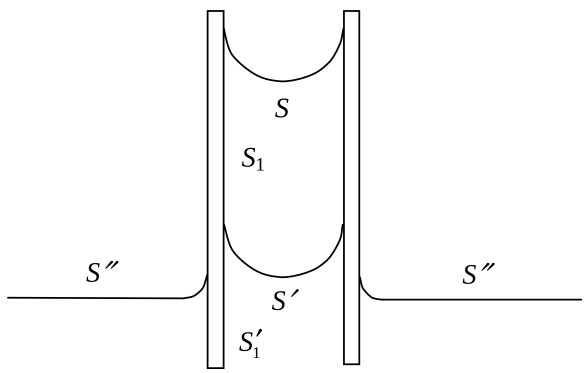

Figure 53.

55. Superposed liquids in a capillary tube. – As before, let S (Fig. 53) be the area of the free surface of the less dense liquid, S', the area of its contact surface with the lower liquid, and let S'' be the area of the free surface of the latter liquid. Let $\frac{\theta_1}{2}, \frac{\theta_1'}{2}, \frac{\theta_1''}{2}$ be the surface tensions on those surfaces. In addition, introduce the areas of the contact surfaces S_1 and S_1' of the tube with the upper liquid and the lower liquid, resp., as well as the coefficients that I called:

$$\eta_1 - \frac{\theta_1}{2}, \qquad \eta_1' - \frac{\theta_2'}{2}$$

in Chapters I and II, but which I will call η_1 and η_1' from now on, in order to abbreviate the writing, and thereby change the meanings of the notations that were employed up to now.

For a virtual displacement of the liquid inside the tube, the work done by capillary forces is:

$$-\frac{\theta_1}{2}\delta S - \frac{\theta_1'}{2}\delta S' + \eta_1\,\delta S_1 + \eta_1'\,\delta S_1'.$$

One will again have:

$$\delta S = \int \lambda\left(\frac{1}{R}+\frac{1}{R_1}\right)d\sigma + \int \lambda\, ds \cot\varphi,$$

$$\delta S' = \int \lambda\left(\frac{1}{R'}+\frac{1}{R_1'}\right)d\sigma' + \int \lambda\, ds \cot\varphi',$$

in which φ and φ' are the contact angles of the liquid with the tube.

If only the surface S deforms then, from a formula that was found before, the variation of S_1 will be:

$$\int \frac{\lambda\, ds}{\sin\varphi};$$

however, since S' deforms at the same time, one will have:

$$\delta S_1 = \int \frac{\lambda\, ds}{\sin\varphi} - \int \frac{\lambda\, ds}{\sin\varphi}$$

and

$$\delta S_1' = \int \frac{\lambda\, ds'}{\sin\varphi'}.$$

Substitute those values of δS, $\delta S'$, δS_1 , $\delta S_1'$ in the expression for the work done by capillary forces. It will become:

$$-\int \lambda \frac{\theta_1}{2}\left(\frac{1}{R}+\frac{1}{R_1}\right)d\sigma - \int \lambda \frac{\theta_1'}{2}\left(\frac{1}{R'}+\frac{1}{R_1'}\right)d\sigma + \int \lambda\left(\frac{\eta_1}{\sin\varphi} - \frac{\theta_1}{2}\cot\varphi\right)ds$$

$$+ \int \lambda\left(\frac{\eta_1'}{\sin\varphi'} - \frac{\eta_1}{\sin\varphi} - \frac{\theta_1'}{2}\cot\varphi'\right)ds'.$$

The work done by weight is:

$$g\rho\, U\, dZ + g\rho_1 U_1\, \delta Z_1 = g\rho \int \lambda z\, d\sigma' + g\rho_1 \int \lambda z\, d\sigma' - g\rho_1 \int \lambda z\, d\sigma',$$

which is easy to see, from what was said in no. **53**.

Upon writing out that the sum of those works must be zero, we will obtain the equilibrium condition:

$$\int\lambda\left[g\rho_1 z-\frac{\theta_1}{2}\left(\frac{1}{R}+\frac{1}{R_1}\right)\right]d\sigma-\int\lambda\left[g(\rho-\rho_1)\,z-\frac{\theta_1'}{2}\left(\frac{1}{R'}+\frac{1}{R_1'}\right)\right]d\sigma$$
$$+\int\lambda\left(\frac{\eta_1}{\sin\varphi}-\frac{\theta_1}{2}\cot\varphi\right)ds+\int\lambda\left(\frac{\eta_1'}{\sin\varphi'}-\frac{\eta_1}{\sin\varphi}-\frac{\theta_1'}{2}\cot\varphi'\right)ds'. \tag{7}$$

For the free *S*, one has:

$$U + U_1 = -\int_S z\,dx\,dy\,.$$

If we take into account equations (8), which give the values of z for the two surfaces *S* and *S′*, then we will get:

$$g\,(\rho-\rho_1)\,U=-\int_{S'}\left[\frac{\theta_1'}{2}\left(\frac{1}{R'}+\frac{1}{R_1'}\right)+\beta'\right]dx\,dy\,,$$

$$g\,\rho_1\,(U+U_1)=-\int_{S}\left[\frac{\theta_1}{2}\left(\frac{1}{R}+\frac{1}{R_1}\right)+\beta\right]dx\,dy\,.$$

Now one has:

$$g\,(\rho-\rho_1)\,U+g\rho_1\,(U+U_1)=g\rho\,U+g\rho_1 U_1\,.$$

The right-hand side of that equality is precisely the weight of the liquids that are contained in the capillary tube above the *xy*-plane. We will then have:

$$P=-\int_{S}\left[\frac{\theta_1}{2}\left(\frac{1}{R}+\frac{1}{R_1}\right)+\beta\right]dx\,dy-\int_{S'}\left[\frac{\theta_1'}{2}\left(\frac{1}{R'}+\frac{1}{R_1'}\right)+\beta'\right]dx\,dy$$

for that weight, but in no. **12** we showed that:

$$\frac{1}{R}+\frac{1}{R_1}=-\left(\frac{dl}{dx}+\frac{dm}{dy}\right),$$

in which l and m are the cosines of the normal to the free surface with the x and y-axes, and that one has:

$$\iint\left(\frac{dl}{dx}+\frac{dm}{dy}\right)dx\,dy=s\cos\varphi,$$

in which s is the length of the intersection curve of the interior surface of the tube with a planar cross-section. Consequently:

$$P=\frac{\theta_1}{2}\,s\cos\varphi+\beta\Omega+\frac{\theta_1'}{2}\,s\cos\varphi'+\beta'\Omega,$$

in which Ω is the cross-section of the tube. As a result of the relation (10) between β and β', that expression will reduce to:

$$P = \frac{\theta_1}{2} s \cos \varphi + \frac{\theta_1'}{2} s \cos \varphi',$$

which one can write:

$$P = \frac{\theta_1''}{2} s \cos \varphi'',$$

due to the relation (11).

Now, the latter expression is that of the weight of the liquid that was raised in a vertical capillary tube that is submerged in the denser liquid, since the liquid in the tube is in contact with air. We will then arrive at the conclusion that the weight of the liquid that is raised in a capillary tube that contains two superposed liquids will depend upon only the lower liquid.

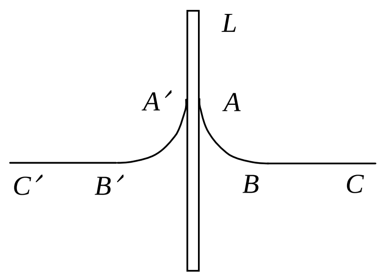

Figure 54.

57. Surface of a liquid in the neighborhood of a vertical planar film. – If that film L (Fig. 54) is sufficiently large then we can regard the surfaces ABC, $A'B'C'$ of the liquid on either side of the film as being cylindrical. The general equation of the surface ABC:

$$g\rho\, z = \frac{\theta_1}{2}\left(\frac{1}{R} + \frac{1}{R_1}\right) + \beta$$

will then reduce to:

$$g\rho\, z = \frac{\theta_1}{2}\frac{1}{R} + \beta,$$

since of the radius of curvature R_1 will become infinite.

Take the xy-plane to be the horizontal plane that passes through the free surface of the liquid at a considerable distance from the film. One must have $z = 0$ for $R = \infty$; as a result, β will be zero. If we set:

$$\frac{\theta_1}{2} = \mu\, g\rho, \tag{12}$$

to simplify, then the equation of the surface ABC will become:

$$z = \frac{\mu}{R}. \tag{13}$$

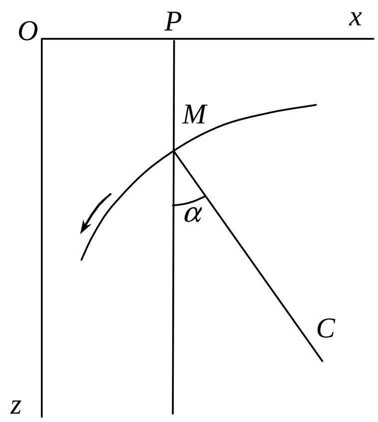

Figure 55.

Consider a point M on that surface (Fig. 55) and draw the parallel PM to the z-axis that passes through that point, as well as the normal MC. Since the angle between those two directions is α, we will have:

$$\frac{1}{R} = \frac{d\alpha}{ds}$$

for the value of the radius of curvature MC, in which the arc length s is measured positively in the sense of the arrow. In addition, we have:

$$dz = ds \sin \alpha.$$

Consequently, equation (13) can be written:

$$z = \mu \frac{\sin \alpha \, d\alpha}{dz},$$

or

$$d \cos \alpha = -\frac{z\,dz}{\mu}.$$

One will then deduce that:

$$\cos \alpha = -\frac{z^2}{2\mu} + \gamma.$$

If we suppose that the origin O of the coordinate axes is sufficiently far from the film then we will have:

$$\alpha = 0, \qquad \cos \alpha = 1, \qquad z = 0.$$

As a result, the integration constant γ must have the value 1, and we will have:

$$\frac{z^2}{2\mu} = 1 - \cos\alpha = 2\sin^2\frac{\alpha}{2};$$

hence:

$$z = 2\sqrt{\mu}\sin\frac{\alpha}{2}. \tag{14}$$

In order to get x, we remark that:

$$dx = -ds\cos\alpha = -dz\cot\alpha;$$

consequently, x is given by the elliptic integral:

$$x = -\int dz\cot\alpha.$$

However, one does not need to consider that integral in order to discuss the curve; equation (14) will suffice.

By way of example, we propose to calculate the ordinate of a point on the contact line. Upon letting φ denote the contact angle, we will have:

$$\varphi = 90^{\circ} + \alpha;$$

as a result, the desired ordinate will be:

$$z_1 = 2\sqrt{\mu}\sin\frac{\varphi - 90^{o}}{2} = 2\sqrt{\mu}\sqrt{\frac{1-\sin\varphi}{2}},$$

or, upon replacing μ with its value that one deduces from (12):

$$z_1 = \sqrt{\frac{\theta_1}{g\rho}(1-\sin\varphi)},$$

in which the radical is taken with the + sign when the contact angle is acute, as it is in the case of mercury and glass, and with the – sign when the contact angle is obtuse.

58. Drops of large dimensions that rest upon a denser liquid. – In no. **54**, we saw that the angles that are formed between the tangent planes to the surfaces S, S', S'' that are drawn through a point on the line of contact can be determined by the construction of a triangle that has its edges proportional to the three surface tensions. In addition, when the drop has large dimensions, it is easy to fix the position of those planes in space.

The equations of the surfaces S, S', S'' are the first three equations of the group (6). When the drop is very large, one can equate those surfaces to cylindrical surfaces, and as a result, regard one of the radii of curvature as excessively large. Those equations will then become:

$$g\,\rho_1\,z = \frac{\theta_1}{2}\frac{1}{R} + \beta,$$

$$g\,(\rho - \rho_1)\,z = \frac{\theta_1'}{2}\frac{1}{R'} + \beta',$$

$$g\,\rho\,z = \frac{\theta_1''}{2}\frac{1}{R''} + \beta''.$$

We remark that at a point of the surface S that is sufficiently far from the contact curve, the radius of curvature will be infinite, so the surface will coincide with a horizontal plane. Consequently, if z_0 is the distance from that plane to the xy-plane then β will be equal to $g\rho_1\,z_0$. If we set:

$$\frac{\theta_1}{2} = \mu\,g\rho_1$$

then the first of the preceding equations will become:

$$z - z_0 = \frac{\mu}{R},$$

and by a transformation that is analogous to the one that we applied to equation (13) in the preceding paragraph, we will get:

$$z - z_0 = 2\sqrt{\mu}\sin\frac{\alpha}{2}.$$

We have similar expressions for the other two surfaces:

$$z - z_0' = 2\sqrt{\mu'}\sin\frac{\alpha'}{2},$$

$$z - z_0'' = 2\sqrt{\mu''}\sin\frac{\alpha''}{2}.$$

However, we have seen that the constants β, β', β'' of the equations of the surface are coupled by the relation:

$$\beta + \beta' - \beta'' = 0.$$

Here, one will then have:

$$g\rho_1\,z_0 + g(\rho - \rho_1)\,z_0' - g\,\rho\,z_0'' = 0.$$

Now, if we multiply $z - z_0$, $z - z_0'$, $z - z_0''$ by $g\rho_1$, $g(\rho - \rho_1)$, $-g\rho$, respectively, then we will get:

$$g\rho_1 (z - z_0) + g(\rho - \rho_1)(z - z_0') - g\rho (z - z_0'')$$
$$= - g\rho_1 z_0 - g (\rho - \rho_1) z_0' + g\rho\, z_0'',$$

additionally.

That sum of products is zero then, from the preceding relation.

Consequently, we will have:

$$g\rho_1 \sqrt{\mu} \sin\frac{\alpha}{2} + g (\rho - \rho_1) \sqrt{\mu'} \sin\frac{\alpha'}{2} + g\rho \sqrt{\mu''} \sin\frac{\alpha''}{2} = 0.$$

One can add two other relations to the relation between α, α', and α'' that express the ideas that the tangent planes define angles φ, φ', φ'' between them that are determined from the triangle of tensions, as we have recalled. Now, one has three relations then that determine the angles α, α', α'' between the normals to those tangent planes and the z-axis. The positions of those planes are fixed in space then (at least approximately), since the argument supposed that the drop was infinitely large.

59. Drop resting upon a horizontal plane. – The free surface of the drop is always given by the equation:

$$g\rho\, z = \frac{\theta_1}{2}\left(\frac{1}{R} + \frac{1}{R_1}\right) + \beta.$$

Let us look for its volume U. The plane upon which the drop rests is taken to be the xy-plane, so that volume will be given by:

$$U = \iint z\, dx\, dy\,.$$

As a result:

$$g\rho\, U = \frac{\theta_1}{2}\iint\left(\frac{1}{R} + \frac{1}{R_1}\right) dx\, dy + \beta \iint dx\, dy\,.$$

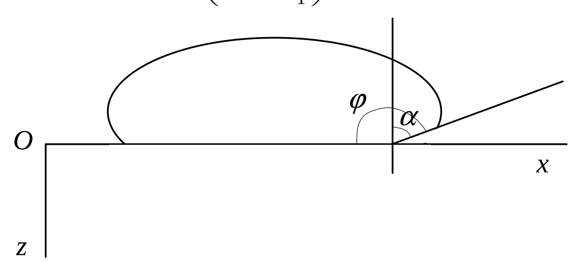

Figure 56.

If the drop is one of revolution and r is the radius of the circumference of contact AB (Fig. 56) then one will have:

$$\iint dx\, dy = \pi r^2.$$

On the other hand, we have seen (§ **12**) that one has:

$$\iint \left(\frac{1}{R} + \frac{1}{R_1} \right) = s \cos \alpha,$$

in which s is the perimeter of the contact curve, and α is the angle between the tangent plane to the surface at a point of that curve and the vertical. Upon calling the contact angle φ, one will have $\cos \alpha = \sin \varphi$. Consequently, one will have:

$$g\rho\, U = \frac{\theta_1}{2} 2\pi r \sin \varphi + \beta \pi r^2.$$

The constant β can be deduced from the height h of the drop, when that drop is large.

Indeed, since the drop is one of revolution, the two radii of curvature will be equal at the highest point, for which $z = h$. Consequently, one will have:

$$- g\rho\, h = \frac{\theta_1}{2} \frac{2}{R} + \beta,$$

which is a relation that determines β as a function of R and h. In the case where the drop is large, one will have roughly $R = \infty$, and the relation will become:

$$\beta = - g\rho\, h.$$

Observe that we have assumed that the drop is one of revolution. That hypothesis is legitimate, because if the drop were not one of revolution then we could always find a drop of revolution whose sections by the horizontal planes had areas that were equal to the sections of the drop considered by the same planes. The volumes of the two drops would be equal then, and we could regard one of them as the result of a deformation of the other one, while the contact surface with the plane would remain the same. Now, it is easy to show, as we did in the context of Plateau's experiments (§ **43**), that the surface of the drop of revolution is smaller than that of a drop that is not one of revolution. Consequently, when one passes from the former to the latter, the work done by capillary forces, which reduces to $-\theta_1 \delta S$, will be positive since the contact surface with the plane does not change. The work done by weight has the expression:

$$\delta \int g\rho\, \Omega\, dz\,,$$

in which Ω is the area of the section of the drop by a horizontal point. Since Ω has the same value for the two drops, that variation will be zero.

The sum of those works will then be positive, when one passes from the form that is not one of revolution to the one that is. Consequently, the energy of a drop that is not one of revolution will not be an absolute minimum. Such a drop cannot be in stable equilibrium then, and there is good reason to consider only the drops of revolution.

Meanwhile, experiments show that one can obtain drops on a planar surface that are not ones of revolution. In that case, equilibrium can be explained only by the viscosity of the liquid. Furthermore, one intends that word to mean a surface viscosity that is much larger than the ordinary viscosity, or resistance to internal motions.

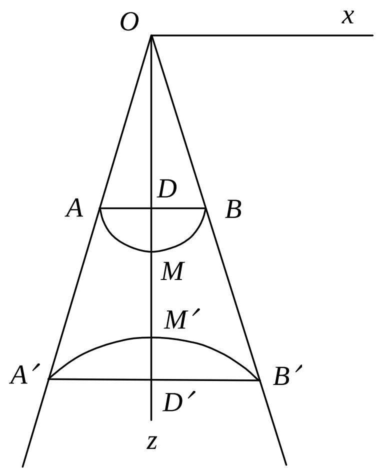

Figure 57.

60. Suspension of an index liquid in a capillary tube. – Consider a conical tube of revolution, and let *AB* and *A′ B′* (Fig. 57) be the free index surfaces in its equilibrium position. Take the *x*-axis to be a horizontal that passes through the summit *O* of the cone and the *z*-axis to be the axis of the tube, which we assume to be vertical.

If *Z* is the ordinate of the center of gravity of the index then the moment of the weight with respect to the *xy*-plane will be $g\rho UZ$. That moment will also be equal to the moment of the volume *O′ A′M′ B′*, minus the moment of the volume *OAMB*. If we neglect the moments of the volumes *AMBD*, *A′M′ B′D′* and let z and z' denote from the summit *O* to the planes *AB*, *A′B′*, resp., that pass through the contact curves then we will have:

$$\text{moment of } OAB = az^4,$$

in which a is a constant that is equal to the product of π with the square of the tangent of the angle that the generators form with the axis. The moment of *OA′B′* is given by an analogous expression, so we obtain:

$$g\rho\, UZ = az'^4 - az^4.$$

If we neglect the variations of the surfaces *AMB* and *A′M′ B′* then the term that is provided by the capillary actions will be $-\eta\, S_1$. Since S_1 is the area of the contact surface of the liquid and the tube, that surface will be the lateral surface of a frustum of the cone of height $z' - z$; it will then be equal to:

$$b' (z'^2 - z^2),$$

in which b' is a constant. We can then write down the potential energy of the two capillary actions:

$$-\eta\, S_1 = b' (z'^2 - z^2).$$

In order for there to be equilibrium, the total potential energy:

$$a\,(z^4 - z'^4) + b\,(z^2 - z'^2)$$

must be a minimum. As a result, one must have:

$$(2a\,z^3 + bz)\,dz - (2a\,z'^3 + bz')\,dz' = 0.$$

However, the volume of the drop remains constant, so one has:

$$z'^3 - z^3 = \text{const.},$$

and as a result:

$$2z^2\,dz - 2\,z'^2\,dz' = 0.$$

Upon eliminating dz and dz' from the two equations that contain those differentials, one will get:

(1) $$\frac{2az^2 + b}{z} = \frac{2az'^2 + b}{z'}.$$

It will then be necessary that the function $2at + b / t$ must take on two equal values for two different values of t that have the same sign. Now, that condition can be fulfilled, because the left-hand side of (1) admits a minimum for a certain value of z, and thus explains the possibility of equilibrium for an index in a conical tube.

We can argue in the same manner for a cylindrical tube, and it will be easy, moreover, to account for the situation in a tube in which one does not have equilibrium. Indeed, if one gives a downward displacement to the index then the work done by capillary forces will be zero, since the index does not deform, while the work done by gravity will diminish. The potential energy of the index in its original position is not a minimum then, and as a result, the index will not be in equilibrium.

Meanwhile, experiments show that there is equilibrium in a cylindrical tube. One often says that this fact comes from the fact that, in practice, a cylindrical tube is always a conical tube to a greater or lesser extent. However, that reason is not sufficient, and the equilibrium that is observed can be explained only by the existence of surface viscosity.

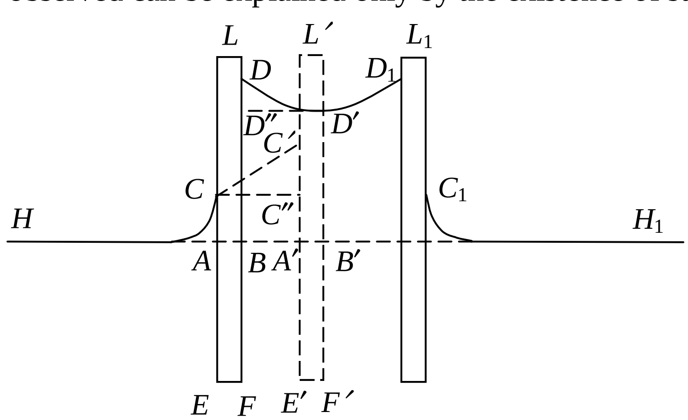

Figure 58.

61. Attraction or repulsion between two vertical films. – Let L and L_1 be two films (Fig. 58), and let X be the normal force that one must apply to the film L in order to maintain equilibrium. Give a virtual displacement to that film that takes it to L' in a parallel position, and write down that the sum of the works that are done by all forces in the system during the displacement is equal to zero. The equation thus-obtained will determine X.

In general, the form of the free surface of the liquid is modified by the displacement. However, since the sum of the work done by forces must be zero for an *arbitrary virtual* displacement, we can take the virtual displacement to be the one that corresponds to the free surfaces that are identical before and after that displacement.

Under that hypothesis, the work done by capillary forces is zero. Indeed, that work will have the expression:

$$T_c = -\frac{\theta_1}{2}\,\delta S + \eta_1\,\delta S_1\,,$$

in which S is the area of the free surface, and S_1 is that of the contact surface of the liquid and the film. Upon calling the length of the film that is perpendicular to the figures, one will have:

$$\delta S = l \times CC' - l\,DD',$$

and upon denoting the displacement AA' of the film by ε and the contact angle by φ:

$$CC' = \frac{\varepsilon}{\sin\varphi}, \qquad DD' = \frac{\varepsilon}{\sin\varphi},$$

so

$$\delta S = l\left(\frac{\varepsilon}{\sin\varphi} - \frac{\varepsilon}{\sin\varphi}\right) = 0.$$

On the other hand:

$$\delta S_1 = l\,(C'C'' - D'D''),$$

or

$$\delta S_1 = l\,(\varepsilon\cot\varphi - \varepsilon\cot\varphi) = 0.$$

The work done by capillary forces is indeed zero then.

Let us evaluate the work done by gravity: It is equal to the variation of the sum of the moments of the forces that are due to gravity with respect to a horizontal plane; for example, the plane HH_1 that passes through the free surface of the liquid far from the film. Since the film is displaced parallel to itself, the submerged portions $ABEF$, $A'B'E'F'$ will remain the same, and the center of gravity of everything that is situated below the plane HH_1 will remain in the same horizontal plane. The moment of the weight for that entire portion of the system will not vary then. For the portion that is situated above that plane, the sum of the moments of the forces due to weight will reduce to the difference between the moments of the volumes of the sections $ACA'C'$, $BDB'D'$, because by hypothesis, the displacement is such that the form of the free surfaces does not change. Now, those sections can coincide with the rectangles, $ACA'C''$, $BDB'D''$, since the triangles $CC'C''$, $DD'D''$ have areas that are second-order infinitesimals. Hence, one has:

$$T_p = \text{moment of the vol. } ACA'C'' - \text{moment of the vol. } ADA'D''$$

for the work done by weight, or:

$$T_p = -g\rho\, l\, \varepsilon\, CA \cdot \frac{CA}{2} + g\rho\, l\, \varepsilon\; DB \cdot \frac{DB}{2}$$

$$= -g\rho\, l\, \varepsilon \left(\frac{\overline{CA}^2 - \overline{DB}^2}{2} \right).$$

The work done by the force X has the value $-\varepsilon' X$, where the force is measured to be positive from right to left, so the equation of equilibrium will be:

$$-\varepsilon X - g\rho\, l\, \varepsilon \frac{\overline{CA}^2 - \overline{DB}^2}{2} = 0,$$

and one can write:

$$X = -g\rho\, l\, \varepsilon \frac{\overline{CA}^2 - \overline{DB}^2}{2}.$$

In order for X to be positive, or what amounts to the same thing, in order for the film considered to be attracted to the other one, it is necessary that one must have:

$$\overline{DB}^2 > \overline{CA}^2.$$

That condition can also be satisfied in the case where the liquid is raised in the neighborhood of the film (e.g., glass in water), as well as in the case where the liquid is lowered (e.g., glass in mercury). In the former case, it is necessary that the liquid must be raised more along the face BD than it is along the face AC. In the latter case, it is necessary that the liquid must be lowered more along BD than it is along AC.

62. – That condition can be expressed differently.

We previously saw (§ **57**) that in the neighborhood of a planar film, the surface of a liquid will satisfy the equation:

$$\cos\alpha = -\frac{z^2}{2\mu} + \gamma,$$

in which γ is a constant, α is the angle between the interior normal to the surface and the positive direction of the z-axis, and μ is defined by the relation:

$$\frac{\theta_1}{2} = \mu g \rho.$$

If we consider the portion of the surface HC that is situated outside of the film then we must have:

$$\alpha = 0 \qquad \text{and} \qquad z = 0$$

for a point that is sufficiently far from the film; as a result, $\gamma = 1$ for that portion of the surface.

For the surface that is found between the two films, γ can have an arbitrary value that depends upon the spacing of the films; let C be that value.

At the point C, we will have:

$$z = CA, \qquad \cos \alpha = \sin \varphi ;$$

hence:

$$\sin \varphi = -\frac{\overline{CA}^2}{2\mu} + 1.$$

For the point D:

$$z = DB, \qquad \cos \alpha = \sin \varphi,$$

and as a result:

$$\sin \varphi = -\frac{\overline{DB}^2}{2\mu} + C.$$

One will then have:

$$\overline{DB}^2 - \overline{CA}^2 = 2\mu (C - 1),$$

and consequently:

$$X = g\rho\, l\, \mu (C - 1) = \frac{\theta_1}{2} l\, (C - 1).$$

The sign of X depends upon the value of C. One sees that there will be attraction when C is greater than 1 and repulsion in the opposite case. Furthermore, it is almost obvious that if one seeks the force X that must be applied to the second film in order to keep it in equilibrium then one will find that same expression. One can then say that X represents the mutual attraction or repulsion of the two films.

63. – Let us look for the sign of X in the various cases that can present themselves. We shall not suppose that the two films are composed of the same substance.

First, suppose that the contact angles between the surfaces of the films and the surfaces of the liquid are all acute. The angle α will be negative at the point D and positive at the point D_1. There will then exist a point on the surface DD_1 for which α is zero. One will have:

$$1 = C - \frac{z^2}{2\mu}$$

for that point, and since $z^2 / 2\mu$ is an essentially-positive quantity, it will be necessary that one must have:

$$C > 1.$$

The films will then attract each other.

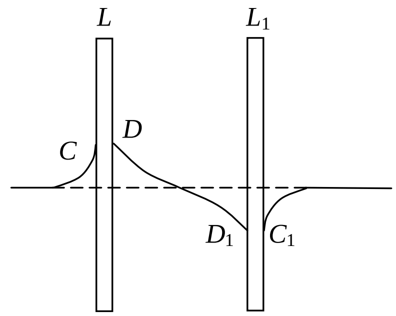

Figure 59.

If we suppose that the contact angles are obtuse then α will be positive at the point D and negative at the point D_1 . Consequently, there will exist a point for which α is zero, and one will once more reach the preceding conclusion.

When the contact angles with one of the films are acute and the contact angles with the other one are obtuse, the surface DD_1 will generally intersect the *xy*-plane (Fig. 59). As a result, z will change sign when one passes from D to D_1 , and since one has:

$$z = \frac{\mu}{R},$$

the radius of curvature would likewise change sign. That change of sign can be produced only if R becomes infinite. The curve DD_1 will then possess an inflection point. Now, if one constructs the curves that are represented by the equation:

$$\cos \alpha = C - \frac{z^2}{2\mu},$$

while giving values to C that are, in turn, less than unity, equal to unity, and greater than unity, then one will find that the curves that correspond to values that are smaller than 1 will be the only ones that can have inflection points at a finite distance. It will then be necessary that one must have $C < 1$ in the case considered, and there will be repulsion then.

However, the contact angles can be acute for one of the films and obtuse for the other without the liquid surface that is included between the films having to intersect the *xy*-plane. The intersection curve of that surface with the plane in the figure will not present an inflection point then, and C will have to be greater than or equal to unity. In the latter case, the films will necessarily attract each other; when $C = 1$, there will be equilibrium. Let us see what kind of forms for the liquid surfaces will correspond to that equilibrium.

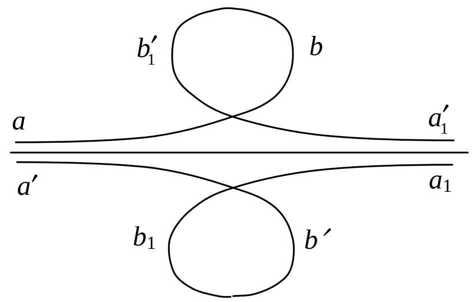

Figure 60.

Since C = 1, the section of the free surface of the liquid belongs to the curve:

$$\cos \alpha = 1 - \frac{z^2}{2\mu}.$$

If one constructs that curve by giving all of the values between – α and + α to α then one will get Fig. 60. However, when one is dealing with vertical films, one cannot obtain all of the portions of that curve, because α can vary only between – π / 2 and + π / 2 since φ is always found between 0 and π and one has $\alpha = 90^\circ - \varphi$. The portions of the curve that correspond to those values of α extend from infinity to the points where the tangent to the curve is vertical. They are the arcs ab, $a'b'$, a_1b_1, $a_1'b_1'$ then. Moreover, since the free surface of the liquid will become planar at a sufficiently large distance from the films, the section of the liquid surface that is situated to the left of film L will necessarily be a portion of ab or $a'b'$. For the same reason, the section of the liquid surface that is situated to the right of the film L_1 must be a portion of b_1a_1 or $b_1'a_1'$.

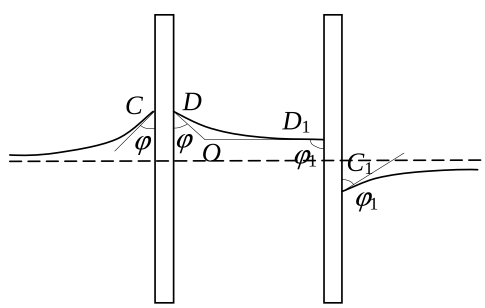

Figure 61.

Suppose that the contact angle with L is acute and the contact angle with L_1 is obtuse. The only portions of the curve that can then coincide outside of the films will be ab for the one on the left and a_1b_1 for the one on the right. Between the two films, one can have a curve that is symmetric to either the portion of ab that was used or the portion of a_1b_1 that was used, because it is obvious that the contact angles of the free surface that is interior to the films with the films will be equal to the respective exterior contact angles in those two cases. Figures 61 and 62 represent the sections of the three free surfaces in the two cases. One easily sees that in the first figure, the sum $\varphi + \varphi_1$ of the contact angles is less than two right angles, while, on the contrary, that sum will be greater than two right angles in the second case.

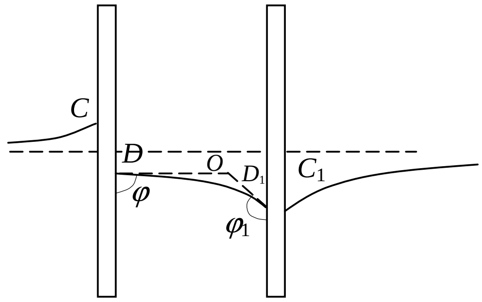

Figure 62.

It remains for us to see whether the equilibrium state that corresponds to those forms for the free surfaces is stable or unstable. If we move the films together then the lengths of the arcs DD_1 will diminish, but the angle DOD_1 that is defined by the tangent at D and D_1 will remain constant, since the contact angles do not vary. Consequently, the absolute value of the radii of curvature at a point of those arcs will diminish, and since $z = \mu / R$, the absolute value of z will increase. It will then result that the equation:

$$\cos \alpha = C - \frac{z^2}{2\mu},$$

which was satisfied by $C = 1$ originally, can be maintained further only for values of C that are greater than unity. The films will then attract each other as long as one displaces them towards their equilibrium position.

By an analogous argument, one will see that if one moves the films apart then a repulsive force will be produced. Equilibrium will then be unstable.

In summary, when the contact angles with the films are both acute or both obtuse, there will always be attraction. When the contact angle with one of the films is acute and the contact angle for the other film is obtuse then there will generally be repulsion, but in that case, one can have attraction, or even find the films in an unstable equilibrium state.

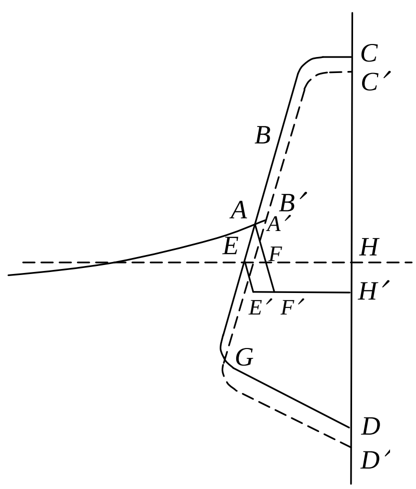

Figure 63.

64. Buoyancy experienced by a partially-submerged body of revolution. – Let *CAD* (Fig. 63) be body of revolution around an axis *CD* that we suppose to be vertical. Calculate the buoyancy *X* that the body experiences when it is in equilibrium after being partially submerged in a liquid of density ρ.

In order to do that, we give a vertical displacement ε to the body such that the form of the free surface *MA* is unchanged, but merely extended up to the contact point with the body in the new position $C'B'D'$, and write down that the sum of the works done by all forces in the system during that displacement is zero.

The work done by capillary forces has the value:

$$T_c = \eta_1\,\delta S_1 - \frac{\theta_1}{2}\,\delta S,$$

in which δS_1 is the variation of the area of the contact surface of the solid and the liquid, and δS is that of the free surface. Upon denoting the radius of the parallel that passes through the contact curve *A* by *r*, one will have:

$$\delta S_1 = 2\pi r\,AB,$$
$$\delta S = 2\pi r\,AB',$$

and since the constants η_1 and $\theta_1 / 2$ are coupled by the relation:

$$\eta_1 = \frac{\theta_1}{2}\cos\varphi,$$

in which φ is the contact angle *MAE*, one will have:

$$T_c = \frac{\theta_1}{2}\,2\pi r\,(AB\cos\varphi - AB').$$

However, the angle BAB' is opposite to the summit of the angle φ, so it will be equal to the latter, and the quantity in parentheses will represent the projection of the contour $B'AB$ onto the direction AB'. That quantity will then be equal to the projection of the vertical BB' that closes the contour. Now, BB' is equal to CC', and as a result, to ε. As for the angle between BB' and AB', it is the angle that is defined by the tangent plane to the free surface at the point *A* and the vertical. Upon calling that angle α, one will have:

$$T_c = \frac{\theta_1}{2}\,2\pi r\,\varepsilon\cos\alpha.$$

Let us now evaluate the work done by weight.

Since the body is in equilibrium, its weight is equal and directly opposite to the buoyancy that it receives on the part of the liquid. Since that was denoted by *X*, the work done by weight that is exerted on the body will be:

$$X\varepsilon$$

for the displacement considered.

The work done by forces that are due to weight and exerted upon the liquid is equal to the variation of the moment of those forces with respect to a horizontal plane – for example, the plane that passes through the free surface of the liquid far from the body. Since we have supposed that the free surface extends only up to its contact with the body under the given virtual displacement of the system, that variation will reduce to:

$$T_p = -\text{ mom. of } GDD' + \text{mom. of } ELG + \text{mom. of } AB'EL,$$

or

$$T_p = -\text{ mom. of } LHGD' + \text{mom. of } EHGD + \text{mom. of } AB'EL.$$

Now, one can write:

$$\text{mom. of } LHGD' = \text{mom. of } E'H'G'D' + \text{mom. of } LE'HH',$$

in which EE' is a vertical that is drawn through the contact point E of the xy-plane with the meridian of the body. The volume $LE'HH'$ differs slightly from that of a right cylinder of height $HH' = \varepsilon$. It will then be a first-order infinitesimal, and its moment with respect to the xy-plane will have order two. As a result, one can neglect that moment, and get:

$$T_p = -(\text{mom. of } E'H'G'D' - \text{mom. of } EHGD) + \text{mom. of } AB'EL.$$

However, $E'H'\,G'D'$ is nothing but the displaced volume $EHGD$; as a result, the difference between their moments will be equal to the product of the vertical displacement ε by the weights of one of those volumes; one will then have:

$$T_p = -\varepsilon g\rho \text{ vol. } EHGD + \text{mom. of } AB'EL.$$

It remains for us to evaluate the moment of the liquid volume $AB'EL$. The surface of the triangle $AA'B'$ is a second-order infinitesimal, so the volume generated by the rotation of that triangle can be neglected with respect to the volume that is generated by $AA'EL$, in such a way that one will have, approximately:

$$\text{mom. of } AB'EL = \text{mom. of } AA'EL,$$

or rather:

$$\text{mom. of } AB'EL = \text{mom. of } AEF - \text{mom. of } A'LF,$$

in which F is the contact point of the vertical AA' with the xy-plane. If we prolong that vertical by a length FF' that is equal to ε then we will obtain a triangle $A'E'F'$ that generates a volume whose moment differs from the moment of the volume $A'LF$ only by a second-order infinitesimal. As a result:

$$\text{mom. of } AB'EL = \text{mom. of } AEF - \text{mom. of } A'E'F',$$

The volumes that are generated by AEF and $A'E'F'$ are equal, so the difference between their moments with respect to the same horizontal plane will be equal to the product of the weight of that volume with the quantity ε upon which one bases the center of gravity. One will finally have:

$$\text{mom. of } AB'EL = \varepsilon g\rho \text{ vol. } AEF,$$

and as a result:

$$T_p = -\varepsilon g\rho \text{ vol. } EHGD + \varepsilon g\rho \text{ annular vol. } AEF.$$

If we now write out that the sum of those various works will be zero then we will get:

$$T_c + X\varepsilon + T_p = 2\pi r\,\varepsilon \cos\alpha + X\varepsilon - \varepsilon g\rho\,(\text{vol. } EHGD - \text{vol. } AEF) = 0\ ;$$

hence:

$$X = = -\frac{\theta_1}{2} 2\pi r\,\varepsilon \cos\alpha + g\rho\,(\text{vol. } EHGD - \text{vol. } AEF).$$

That is the expression for the buoyancy that the floating body experiences.

If the free surface of the liquid is planar then the buoyancy will have the value:

$$g\rho \times \text{vol. } EHGD.$$

One will then see that if α is acute, as in the case of Fig. 63, then the capillary phenomena will have the effect of diminishing the buoyancy. However, if the contact angle is obtuse then the angle α will generally be likewise obtuse. Moreover, it will be easy to assure oneself that the term $g\rho$ vol. AEF must be taken with the + sign when the point A is below the xy-plane. Consequently, the capillary phenomena can sometimes have the effect of the increasing the buoyancy, and as a result, of permitting a body that is placed upon the surface of a less-dense liquid to be in equilibrium.

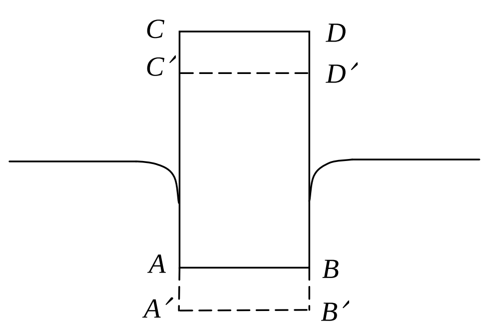

Figure 64.

65. – Let us exhibit that situation for a cylinder with vertical generators $ABCD$ (Fig. 64). Give that cylinder a vertical virtual displacement that does not change the free surface of the liquid. The work done by capillary forces will reduce to:

$$\eta_1\,\varepsilon\, l,$$

in which ε is the displacement and l is the perimeter of the cross-section of the cylinder. The work done by the weight P of the cylinder is $P\varepsilon$. The work done by the weight on the liquid will result from suppressing the cylinder $ABA'B'$. It will then be:

$$g\rho\,\Omega\,\varepsilon z,$$

in which Ω denotes the area of the cross-section of the cylinder, and z denotes the ordinate of a point on the base AB. The equilibrium condition will then be:

$$P\varepsilon - g\rho\,\Omega\,\varepsilon z + \eta_1\,\varepsilon\, l = 0,$$

so

$$P = g\rho\,\Omega\, z - \eta_1\, l.$$

However, η_1 is a negative quantity here, since one has $\eta_1 = (\theta_1 / 2) \cos \varphi$, $\theta_1 / 2$ is the surface tension of the liquid, which is an essentially positive quantity, and φ is the contact angle, which is obtuse, by hypothesis. Upon letting a denote the absolute value of η_1, one will get:

$$P = g\rho\,\Omega\, z + a\, l$$

or

$$g\rho_1\,\Omega\, h = g\rho\,\Omega\, z + a\, l,$$

in which ρ_1 is the density of the cylinder and h is its height, so one can deduce that:

$$h = \frac{\rho}{\rho_1} z + \frac{a}{g\rho_1}\frac{l}{\Omega}.$$

In order for the cylinder to float, it is necessary that h must be larger than z. That condition will not be incompatible with the preceding one, even if $\rho_1 > \rho$, provided that the second term $\frac{a}{g\rho_1}\frac{l}{\Omega}$ is sufficiently large. A body can float on the surface of a less-dense liquid if the contact angle is obtuse then.

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CHAPTER VI

APPLICATIONS OF THERMODYNAMICS TO CAPILLARY PHENOMENA

66. The thermodynamic potential. – In all of the preceding, we obtained the equilibrium conditions for fluids by writing out that the sum of all of the virtual works that are done by a deformation that starts from the equilibrium state is zero. In other words, we have assumed, with Gauss, that the principle of virtual velocities is applicable to capillary phenomena.

The legitimacy of that application was contested by various authors, and most recently by Duhem ([6]). The principle of virtual velocities will break down for phenomena in which changes in the state of the body considered are produced; for example, in the phenomena of fusion and evaporation. Now, when one deforms a liquid in equilibrium in contact with other liquids or solid walls, certain parts of the liquid that were originally in the immediate neighborhood of the wall or other liquids will then be found at an appreciable distance from the contact surfaces. Their densities will vary then; some parts of the liquids will have experienced a change of state. There is therefore no reason *a priori* to suppose that the principle of virtual velocities, which generally does not apply to systems that are capable of changing state, can be legitimately applied in the particular case of the study of the theory of capillary phenomena.

The application of the principles of thermodynamics to capillary phenomena, from which Lord Kelvin (viz., Sir W. Thomson), Moutier, Van der Mensenbrugghe have already deduced some interesting consequences, can be put into an elegant form by the introduction of the function that Duhem called the "thermodynamic potential," and whose definition I would like to recall.

Let U be the internal energy of a system, S, its entropy, V, its volume, T, its temperature, P, its pressure (which is assumed to be uniform), W, the external force function, and E, the mechanical equivalent of the heat. The function:

$$\Phi = E\,(U - TS) + PV + W \tag{1}$$

is what Duhem called the *thermodynamic potential* of the system of bodies.

Under an infinitely-small transformation at constant temperature, the variation of that function will be:

$$d\Phi = E\,dU - ET\,dS + P\,dV + dW.$$

However, the equivalence principle provides us with the relation:

$$E\,dQ = E\,dU + P\,dV + dW,$$

in which dQ is the heat that is supplied to the body during the transformation; as a result:

([6]) "Applications de la thermodynamique aux phénomènes capillaires," Ann. sci. Ec. norm. sup. (3) **2** (1885), pp. 207.

$$d\Phi = E\,(dQ - T\,dS).$$

On the other hand, Clausius's theorem teaches us that under an irreversible transformation, one will have:

$$dQ < T\,dS$$

and that under a reversible transformation:

$$dQ = T\,dS\,.$$

It will then result from this that any transformation at constant temperature will be accompanied by a negative variation in the thermodynamic potential, so that variation will become zero in the special case where the transformation is reversible. Thus, if the thermodynamic potential is a minimum in a certain state of the system then no transformation at constant temperature can be produced that begins from that state, since the variation of Φ would be positive then. As a result, the state considered will be an equilibrium state, and we will obtain the equilibrium conditions by writing out that the thermodynamic potential is a minimum.

67. – Let us look for the expression for that potential for a system of solids and liquids in contact.

First suppose that the bodies are homogeneous. Let M_1, M_2, … be their masses, let σ_1, σ_2, …, respectively, be their specific volumes, let u_1, u_2, …, resp., be their internal energies per unit volume, and let s_1, s_2, …, resp., be their entropies per unit volume. We will then have that the volume V of the system will be:

$$V = \sum M\sigma\,,$$

the internal energy will be:

$$U = \sum Mu\,,$$

and the entropy will be:

$$S = \sum Ms\,.$$

Consequently, the thermodynamic potential of the system will have the expression:

$$\Phi = E\left(\sum Mu - T\sum Ms\right) + P\sum M\sigma + V.$$

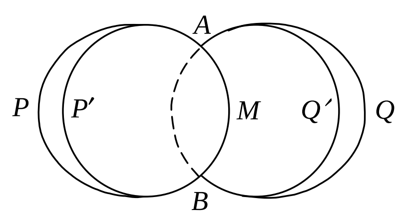

Figure 65.

However, as a result of the variation of the densities of the liquids in the immediate vicinity of the contact surface, the systems that one considers in capillarity are not composed of homogeneous bodies, and the preceding expression will be only approximate. Let us show that in order to account for the variation of the density, it will suffice to add terms that depend upon only the contact surfaces.

Let *AMB* (Fig. 65) be the contact surface of two bodies *APB* and *AQB*. If we transport one of the bodies to infinity then the capillary forces will do work. As a result, the internal energy *V* in the system that is composed of the two bodies will vary with the displacement. However, no matter what hypotheses one imposes upon their basic nature, the capillary forces will be exerted at only exceedingly small distances. Consequently, the variation of the internal energy that results from the transport to infinity of one of the two bodies *AP′B*, *AQ′B*, which have the same contact surfaces as the preceding ones, will be equal to the internal energy of the system of bodies *APB*, *AQB*. In other words, that variation will not depend upon the volumes of the bodies considered, provided that the contact surfaces are the same and that the other surfaces that bound the bodies are at finite distances from them.

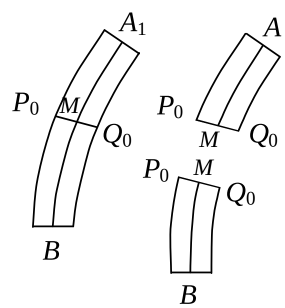

Figure 66.

Therefore, suppose that the two surfaces *APB* and *AQB* become surfaces $AP_0\,B$, AQ_0B (Fig. 66) that are parallel to *AMB* and distant from it by a length that is equal to the radius of molecular activity. Under those conditions the area of the section of the system by a surface $P_0\,MQ_0$ that is normal to the surface *AMB* will be infinitely small, and the work that results from the separation of the system into two parts $AP_0\,MQ_0$, $BP_0\,MQ_0$ will be infinitely small. Upon transporting the portion AQ_0M of one of the bodies to infinity, the capillary forces will do a certain amount of work T_0 ; upon transporting the portion BQ_0M of the same body to infinity, the corresponding work done will be T_0'. If we put *APM* and *BPM*, on the one hand, and *AQM* and *BQM*, on the other, back into contact with each other after that operation then the work done by capillary forces will be infinitely small. However, by definition, that series of operations will amount to the transport of the bodies $AP_0\,B$, $AQ_0\,B$ to infinity. Consequently, if one calls the corresponding work done *T* then one will have:

$$T = T_0 + T_0',$$

up to infinitesimals.

The work that relates to a contact surface *AMB* will then be equal to the sum of the works that relate to the partial surfaces into which one can decompose it; as a result, it will be proportional to the area of the surface.

It results immediately from this that the internal energy of a system that is composed of two bodies in contact with each other will contain a term that is proportional to that contact surface. An analogous argument will show that the entropy likewise contains a term of the same type. Consequently, the thermodynamic potential of a system of bodies in contact will have the general expression:

$$\Phi = E\left(\sum Mu - T\sum Ms\right) + \sum A\theta + P\sum M\sigma + W, \tag{2}$$

in which θ denotes the area of any of the contact surfaces, and A denotes a coefficient that depends upon T, σ, and even other variables, such as the ones that define the electric state of the system.

68. The equilibrium conditions. – As we have seen, in order to find the equilibrium conditions, it will suffice to express the idea that Φ is a minimum.

One must then have:

$$d\,\Phi = 0$$

for any virtual deformation. Suppose that deformation is such that σ remains constant. However, T and σ do not vary, so the functions u and s, which depend upon only those quantities, will themselves remain invariable. On the other hand, the masses M of each of the bodies do not change. As a result, the equilibrium equation reduces to:

$$d\,\Phi = \sum A\,d\theta + dW = 0.$$

We have thus recovered the equation to which the Laplace and Gauss hypotheses led us. The coefficient A, which is represented by $\theta_1 / 2$ in mechanical theories, is once more the surface tension in the contact surface.

Having recovered the fundamental equation of capillary phenomena, it is obvious that all of the consequences that we have deduced from the molecular theories of Laplace and Gauss will persist in Duhem's thermodynamic theory. By way of exercise, we shall look for the pressure difference between the sides of the contact surface of two fluids in equilibrium.

Let π_p and π_q be those pressures, and affect the quantities that were introduced before with the indices p and q when they pertain to the two respective fluids. Deform the contact surface in such a fashion that the volume of one of the bodies increases by dv and the volume of the other one diminishes by the same quantity; we then have:

$$dv = M_p\,d\sigma_p = -M_q\,d\sigma_q\,. \tag{3}$$

The specific volumes vary, so the same thing will be true for the internal energy and entropy of each of the bodies. If we set:

$$\pi_p = E\,(u_p - T\,s_p) + P\,d\sigma_p$$

then we will have:

$$d\varphi_p = E\,(du_p - T\,ds_p).$$

However, from the equivalence principle, upon letting dq denote the quantity of heat per unit mass that is provided to the body p, one will have:

$$E\,dq = E\,du_p - \pi_p\,d\sigma_p\,,$$

when one neglects the work done by weight. As a result:

$$d\varphi_p = E\,(dq - T\,ds_p) + P\,d\sigma_p - \pi_p\,d\sigma_p\,.$$

Now, we can suppose that the virtual deformation of the system is reversible. In that case:

$$dq = T\,ds_p\,,$$

and we will get:

$$d\varphi_p = P\,d\sigma_p - \pi_p\,d\sigma_p\,,$$

or, upon replacing $d\sigma_p$ with the value that we infers from the first of the equalities (3):

$$d\varphi_p = \frac{P - \pi_p}{M_p}\,dv\,.$$

We will likewise find that:

$$d\varphi_q = -\frac{P - \pi_q}{M_q}\,dv\,,$$

and as a result:

$$M_p\,d\varphi_p + M_q\,d\varphi_q = (\pi_q - \pi_p)\,dv.$$

However, from the general expression (2) for the thermodynamic potential and from the expressions that define φ_p and φ_q, one will have:

$$\Phi = M_p\,d\varphi_p + M_q\,d\varphi_q + \sum A\theta$$

for the thermodynamic potential of the system that is composed of the bodies p and q, upon neglecting the weight. Consequently, the equilibrium condition $d\,\Phi = 0$ will give:

$$(\pi_q - \pi_p)\,dv + \sum A\,d\theta = 0,$$

if one nonetheless assumes that A is constant, which is not entirely rigorous, because that coefficient depends upon σ, and the latter quantity can vary, by hypothesis. Upon supposing, in addition, that only the contact surface θ_{pq} of the two bodies p and q varies, one will have:

$$(\pi_q - \pi_p)\,dv + A\,d\theta_{pq} = 0.$$

Now, we have seen that the variation of the area of the contact surface of the two bodies has the value:

$$d\theta = \left(\frac{1}{R}+\frac{1}{R'}\right)\int \lambda\, d\omega = \left(\frac{1}{R_1}+\frac{1}{R_2}\right) dv\,;$$

as a result:

$$\pi_q - \pi_p = -\, A\left(\frac{1}{R_1}+\frac{1}{R_2}\right).$$

That is indeed the expression to which we arrived in the molecular theories.

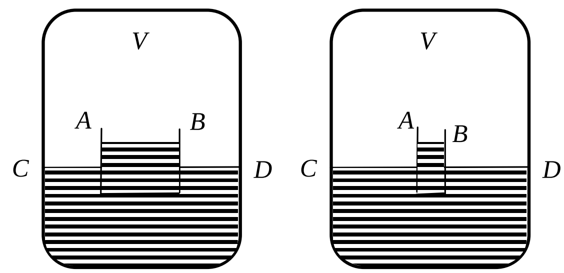

Figure 67. Figure 68.

69. Influence of the curvature of a liquid surface on the value of its maximum vapor pressure. – Consider a closed vessel *V* (Fig. 67) that contains a liquid and another larger vessel that contains the same liquid. Empty out *V* and suppose that the temperature of the system is uniform. The maximum tension in the two liquid masses will be equal then. If the two levels *AB* and *CD* are not on the same horizontal plane then the pressure that is exerted upon those surfaces will not have the same value; if it is equal to the maximum tension for the temperature of the system on the surface *CD* then it will be much less than that tension on the surface *AB*. Consequently, the latter surface will emit vapors that will condense upon the exterior surface of the liquid. The level *CD* will then go up at the same time that the level *AB* goes down, and there will be equilibrium in the system, just as when those two levels are found on the same horizontal plane.

The conclusion would not be the same if we had supposed that the level *AB* is originally lower than the level *CD*.

In the case where the interior vessel is a capillary tube (Fig. 68), there will necessarily be an equilibrium state again, but in that state the two free surfaces will no longer have the same height. Lord Kelvin assumed that it was obvious that those two surfaces would be the same, as if the capillary vessel communicated with the other one. Indeed, if that were not true then when one established that communication, the equilibrium that had been attained would be destroyed, and it could never be reestablished. It would produce a continual circulation of the liquid that evaporates from one of the surfaces, condenses on the other one, and returns to the first one by crossing the orifice of communication. That motion would be perpetual. Consequently, in the case where the contact angle of the liquid and the wall of the tube is acute, the surface *AB* would have to be found to be higher than the surface *CD* in the equilibrium state. However, when there is equilibrium, the surface *AB* will no longer emit vapor. The pressure that is exerted upon it will then be equal to the maximum tension in the liquid, and similarly for the surface *CD*. Now, the pressure on the latter surface is larger than it is on *AB*. Consequently, the maximum tension on the surface *AB* will be smaller than the maximum tension on the surface *CD* for the same temperature. The difference between those two values will be proportional to the mean curvature $\frac{1}{R_1}+\frac{1}{R_2}$ of the meniscus, since the difference between the pressures *AB* and *CD* will be proportional to the vertical distance that separates those surfaces.

If we had supposed that the contact angle was obtuse then the meniscus *AB* would be lower than the surface *CD* in the equilibrium state. We would have then found that the surface of the concave meniscus of the maximum tension of the vapor was larger than the maximum tension for a planar surface and that the difference between those tensions was proportional to the curvature.

70. Delay in boiling. – If one carefully heats a liquid that has no gas in it then one can bring it to a higher temperature than that of normal boiling. Lord Kelvin deduced a very simple explanation for that superheating from the preceding considerations.

Consider a bubble of vapor at the moment of its formation. It will then be very small, and its curvature will be very large. As a result, the maximum vapor tension at the surface of the bubble will differ noticeably from the tension in a planar surface; i.e., on the maximum normal tension. Since the bubble is convex on the liquid side, the former of those tensions will be smaller than the latter. Consequently, at the normal boiling temperature, the vapor tension in the bubble will be smaller than the pressure that the surrounding liquid exerts, and the bubble cannot develop. There will be no boiling then.

However, if one introduces a gaseous bubble inside of the liquid then the curvature of that bubble will be finite; as a result, the maximum vapor tension at the surface of that bubble will differ only slightly from the normal tension. When that becomes equal to the pressure in the gaseous atmosphere that is in contact with the free surface of the liquid, the vapor tension in the bubble will once more be a little less than the pressure that is exerted by the ambient liquid. However, for a very slight increase in temperature, the difference between those quantities will change sign, so the vapor bubble will develop and rise in the liquid. In that case, there will be only an inappreciable slowing in the boiling phenomena.

Lord Kelvin's conclusions can be recovered in an analytical form by considering the thermodynamic potential. Indeed, when a vapor bubble develops within a liquid, the area of the contact surface with the liquid will increase. For the same variation dv in the volume, the variation $d\theta$ in the surface area will become larger as the volume v gets smaller. Consequently, when the bubble is also excessively small, an increase in its volume will produce a variation of the term $\sum A\ \theta$ that will be very large in comparison to the variations that the other terms in the expression for the thermodynamic potential will experience, and it is that variation that will give the sign of $d\Phi$. Since θ increases, $d\Phi$ will be positive. Now, one must have $d\Phi < 0$ under any possible transformation. As a result, an increase in the volume of the bubble cannot be produced, and there must be a delay in boiling.

That application of the thermodynamic potential to the study of the vaporization was the subject of lengthy developments in the paper by Duhem that we cited. We refer the reader to that paper for those developments, as well as for their applications to the phenomenon of supercooling.