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CAPILLARITY

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IN GÖTTINGEN

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Literature

Textbooks and monographs.

- Thomas Young, “Essay on the cohesion of fluids,” Trans. Roy. Phil. Soc. London, 1805.
- P. S. Laplace, “Théorie de l’action capillaire,” Supplément au livre dixième de la *Mécanique céleste*, Paris, 1806. The latter is also in Blainville, J. de Phys. **2** (1806), pp. 120. Both of them are in *Oeuvres* 4, Paris, 1845, and *Oeuvres* 4, Paris, 1880; German version in Ann. Phys. (Leipzig) **33** (1809).
- C. F. Gauss, “Principia generalia theoriae figurae fluidorum in statu aequilibrii,” Comment. soc. reg. scient. Gotting. recent **7** (1830), reprinted in *Werke* 5, Göttingen, 1867, pp. 29. Translated by R. H. Weber, in Ostwald’s *Klassiker d. exakten Wiss.*, no. 135, Leipzig, 1903.
- S. D. Poisson, *Nouvelle théorie de l’action capillaire*, Paris, 1831. Translated in a brief abstract by Link in Ann. Phys. Chem. **25** (1832), pp. 270; *ibid.* **27** (1833), pp. 193.
- E. Betti, “Teoria della capillarità,” Nouv. Cim. **25** (1867), pp. 81, 225.
- J. Plateau, *Statique expérimentale et théorique des liquides soumis aux seules forces moléculaires*, 2 vol., Ghent, 1873.
- J. C. Maxwell, “Capillary action,” Encyc. Brit., 9th ed., 1875, reprinted in *Scientific Papers* 2, Cambridge, 1890, pp. 541.
- J. W. Gibbs, “Equilibrium of heterogeneous substances,” Connecticut Acad. Trans. **3**, New Haven, 1876 and 1878, German version in *Thermodynamische Studien*, translated by W. Ostwald, Leipzig, 1892, pp. 66.
- É. Mathieu, *Théorie de la capillarité*, Paris, 1883.
- J. D. van der Waals, *Die Continuität des gasförmigen und flüssigen Zustandes*, 2nd ed., Leipzig, 1881, Part 1, Leipzig, 1899.
- B. Weinstein, “Untersuchungen über Capillarität,” Ann. Phys. Chem. **27** (1886), pp. 544.
- J. D. van der Waals, “Thermodynamische Theorie der Kapillarität unter Voraussetzung stetiger Dichtänderung,” Verh. f. Kon. Akad. v. Wet. Amsterdam, Deel 1, no. 8 (1893), transl. in Zeit. phys. Chem. **13** (1894), pp. 657; Arch. Néerl. **28** (1894).
- Fr. Neumann, *Vorlesungen über die Theorie der Capillarität*, publ. by A. Wangerin, Leipzig, 1894.
- H. Poincaré, *Capillarité (Leçons)*, Paris, 1895.
- Bibliography: Domke, Wiss. Abhandl. der kais. Normalaichungskommision, Berlin, 1902, pp. 81-99.
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1. Capillarity and cohesion. – A fluid exhibits a special form of energy at its boundary with the surrounding medium that influences, in particular, the form and position of free fluid surfaces, such as, e.g., the height that of the fluid will rise into a capillary tube, and that form of energy has generally taken on the name of *capillarity* from that particular phenomenon. That energy is obviously coupled with the change of state across a separation surface, which can be discontinuous or rapidly continuous. Theoretically, it will either be established directly by a term that is proportional to the surface area of the separation surface and whose proportionality factor will give a *surface tension*, or it will be explained by the potential energy of special forces that attract all mass particles to each other, but will make perceptible contributions only at extremely small distances. The main part of that energy will then be proportional to the volume of the fluid, where the proportionality factor, taken negatively, will give a *spatial pressure* that one calls the *cohesion* of the fluid.

The first conception of capillarity shall be presented here, which assigns that form of energy to the separation surface as its exclusive seat. That conception will then seem to be a mathematically simpler special case of the other deeper conception, which assumes that all masses are the arena for forces of cohesion.

I. – Capillarity as surface energy.

2. Surface energy and its variation. – A separation surface between a fluid *A* and a second medium *B* is coupled with a potential energy $T_{AB} F_{AB}$, where F_{AB} is the area of the surface, and T_{AB} is a constant that depends upon the media that lie on both sides. In that way, *A* and *B* are thought of as homogeneous, and changes in temperature and density shall not come under consideration initially. T_{AB} has the dimensions of erg / cm², and called the *surface tension* of *A* with respect to *B*. For a fluid, one understands the surface tension, *per se*, to mean the pressure against its saturated vapor, which often shows no difference from a separation surface with air (¹). For water against air, one has:

$$T = 74 \frac{\text{erg}}{\text{cm}^2} = 0.0075 \frac{\text{gr weight}}{\text{cm}},$$

for mercury against air, $T = 0.55$ gr weight / cm, and for mercury against water, $T = 0.42$ gr weight / cm.

The consequences of the existence of the term $T_{AB} F_{AB}$ in the energy can be exhibited most briefly on the basis of the remark that precisely the same expression for energy would find a place for an infinitely-thin elastic membrane that overlaps the separation surface if constant tension equal to T_{AB} were present everywhere in it; i.e., each of the two edges of a line that has been cut into it will experience a tension T_{AB} per unit length from the other one. However, introducing that comparison from the outset will imply the complication for the theory of capillarity that is based upon the fact that one cannot ignore the necessity of assuming the existence of pressure discontinuities that are transverse to a separation surface, but only deferring them to another chapter in

(¹) One can speak of surface tension against a gaseous phase, strictly speaking, only for fluids that coexist with the gaseous phase in chemical equilibrium.

mechanics. In order to achieve some clarity in the assumptions of the theory, it is therefore necessary to essentially follow the path of **Gauss** and pursue the possibility that the influence of the term TF in the energy is based in a general principle of mechanics, such as the principle that equilibrium can be characterized by a minimum of potential energy, or when one also considers thermodynamic factors, by a minimum of energy at constant entropy.

One must consider, above all, the virtual variability of TF . When **Gauss** first established the principle of variation of the double integral with variable boundaries by that on that occasion, he developed a fundamental transformation of the variation of TF . As **Gauss** also occasionally pointed out, one can generally easily make the result of that transformation plausible by infinitesimal considerations when one decomposes an arbitrary infinitely-small shift of the surface into a shift that makes each point advance normally to the surface and another that makes it advance tangentially. However, it seems appropriate to also give the actual analytical principle of the conversion that consists of a certain partial integration. Nonetheless, when one considers the fact that the calculus of variations, as it will ultimately be used here (namely, in the context of problems with auxiliary conditions), would not possess any generally-known representation to which one might otherwise simply refer, it might contribute to the transparency of things if we were to appeal to only the known tools of the integral calculus.

During a virtual motion under which the parameter w increases from $w = 0$, the separation surface F_{AB} , which we would like to think has a boundary, will run through a family of surfaces $F(w)$. We construct two mutually-orthogonal families of lines of curvature on each surface, and then two families of surfaces $u_2 = \text{const.}$, $u_1 = \text{const.}$, which cut out those lines of curvature from the $F(w)$. For the sake of simplicity, we imagine that all of the surfaces $F(w)$ lie on top of each other and in such a way that every point of a neighborhood that is filled with them will be assigned unique values of u_1 , u_2 , w . The directions from a point in which only u_1 , only u_2 , and only w increase shall be briefly suggested in the arguments of trigonometric functions, and n means the normal to $F(w)$ that points away from B . The directions of u_1 , u_2 , n shall always define a right-handed screw system, like the coordinate axes x , y , z (Fig. 1).

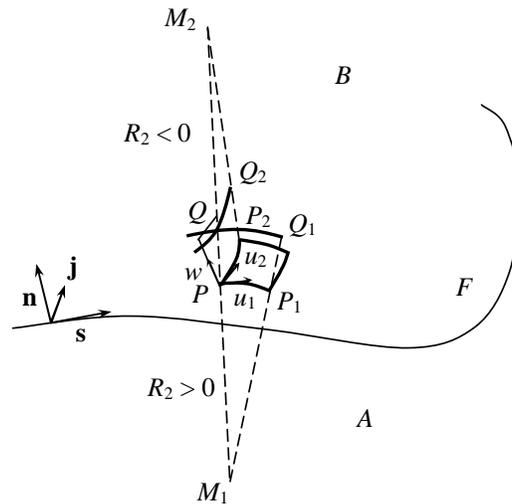


Figure 1.

The boundary of $F(w)$ will be represented by an equation $u_2 = \chi(u_1, w)$, and since we can introduce any function of u_1 and w as a new parameter in place of u_1 , we can assume that this equation does not include w : $u_2 = \chi(u_1)$. The square of the line element in the region that is filled with the $F(w)$ can be written as:

$$(1) \quad ds^2 = dx^2 + dy^2 + dz^2 = L_1^2 (du_1 - l_1 dw)^2 + L_2^2 (du_1 - l_1 dw)^2 + N^2 dw^2,$$

in which $L_1 > 0$, $L_2 > 0$, and $N / \cos(w n) = L > 0$, so N will be calculated with the sign of $\cos(w n)$. Now, one has:

$$(2) \quad F = \iint L_1 L_2 du_1 du_2,$$

$$\frac{dF}{dw} = \iint \left(L_1 \frac{dL_2}{dw} + L_2 \frac{dL_1}{dw} \right) du_1 du_2,$$

in which the double integral extends over the interior of $u_2 = \chi(u_1)$.

The expression here admits an important conversion by product integration⁽²⁾, on the grounds of the characteristic property of the lines of curvature that the normals along them define developable surfaces. A point $P(u_1, u_2, w)$ is associated with a point on the neighboring surface $F(w + dw)$ that has the smallest-possible distance $N dw = dn$, and thus, the point $Q(u_1 + l_1 dw, u_2 + l_2 dw, w + dw)$ along the normal to $F(w)$. Correspondingly, the point Q_1 lies normal to $P_1(u_1 + du_1, u_2, w)$ on $F(w + dw)$. Let M_1 be the center of curvature of the line of curvature PP_1 on $F(w)$, so it is the intersection point of the lines PQ and P_1Q_1 , and let R_1 be the radius of curvature of M_1P , which will be positive when M_1P points in the direction of n from B and negative otherwise. One has $PP_1 = L_1 du_1$. It follows from the similarity of the triangles M_1PP_1 and M_1QQ_1 , and when one recalls (1), that:

$$\frac{PQ}{M_1P} = \frac{QQ_1 - PP_1}{PP_1}, \quad \frac{dn}{R_1} = \frac{1}{L_1} \left(\frac{\partial L_1}{\partial n} dn + L_1 \frac{\partial l_1}{\partial u_1} dw \right);$$

i.e., when one drops the factor of dw :

$$\frac{N}{R_1} = \frac{1}{L_1} \left(\frac{\partial L_1}{\partial u_1} l_1 + \frac{\partial L_1}{\partial u_2} l_2 + \frac{\partial L_1}{\partial w} + L_1 \frac{\partial l_1}{\partial u_1} \right).$$

A corresponding relation is true for the second radius of principal curvature R_2 at P , and when one adds the two, one will get:

$$N \left(\frac{1}{R_1} + \frac{1}{R_2} \right) L_1 L_2 = L_1 \frac{\partial L_2}{\partial w} + L_2 \frac{\partial L_1}{\partial w} + \frac{\partial L_1 L_2 l_1}{\partial u_1} + \frac{\partial L_1 L_2 l_2}{\partial u_2}.$$

⁽²⁾ The infinitesimal considerations that follow serve only to rapidly convert that property of lines of curvature into a formula.

If one makes use of (2) in this and carries out partial integrations with respect to u_1 and u_2 then that will yield:

$$\frac{dF}{dw} = \int_{(f)} N \left(\frac{1}{R_1} + \frac{1}{R_2} \right) df - \int_{(s)} L_1 L_2 \left(l_1 \frac{du_2}{ds} - l_2 \frac{du_1}{ds} \right) ds,$$

in which df generally means the surface element of $F(w)$, and ds means the line element on its contour, when traversed positively around the normal. If one lets j denote the direction of the normal to ds that points to the interior of the surface $F(w)$ (cf., Fig. 1) then one will have:

$$\begin{aligned} L_1 \frac{du_1}{ds} &= \cos(u_2 j), & L_2 \frac{du_2}{ds} &= -\cos(u_1 j), \\ -L_1 l_1 &= L \cos(u_1 w), & -L_2 l_2 &= L \cos(u_2 w). \end{aligned}$$

If one further writes that $L \cos(w j) dw = dj$ then the last equation will imply the following representation for the first derivative of the capillary energy TF with respect to the variation parameter w :

$$(3) \quad T \frac{dF}{dw} = T \int_{(f)} \frac{dn}{dw} \left(\frac{1}{R_1} + \frac{1}{R_2} \right) df - T \int_{(s)} \frac{dj}{dw} ds,$$

which is to be applied to $w = 0$, in particular. The $dn = N dw$ in this then means the normals to the points of the separation surface, and the $dj = L \cos(w j) dw$ means the component of a shift dw of each for point of the boundary to the surface that corresponds to an increase and points normal to the contour. On the basis of that, one can immediately make the transformation (3) geometrically plausible, as was suggested above (^{2a}). When the signs of R_1 and R_2 are fixed as above, $\frac{1}{2} \left(\frac{1}{R_1} + \frac{1}{R_2} \right)$ shall be called

the *mean curvature* of the location df away from B .

Since the parameters of the lines of curvature have once more been eliminated in (3), that representation is not linked with the restriction in regard to the coordinates u_1, u_2, w that was made to begin with.

Let the volumes of A and B be V_A, V_B , resp., and let their densities be ρ_A, ρ_B , resp. We further remark that the volumes will vary by:

$$(4) \quad \frac{dV_A}{dw} = \int_{F_{AB}} \frac{dn}{dw} df, \quad \frac{dV_B}{dw} = - \int_{F_{AB}} \frac{dn}{dw} df$$

^(2a) We have avoided the otherwise-useful symbols $\delta F, \delta w$, etc. for the first variations, moreover, in order to make it obvious that we are ultimately dealing with only differential quotients in the ordinary sense.

under the virtual displacement in question, and furthermore, the potential energy of the two media together that is due to the force of gravity will experience a derivative with respect to w that is equal to:

$$(5) \quad g (\rho_A - \rho_B) \int z \frac{dn}{dw} df .$$

The z -axis in this is thought to point *vertically upwards*.

3. Differential equation for a free surface. – Let A and B move freely at their separation surface (B is a liquid or a gas like A), so only gravity comes under consideration, in addition to capillarity. Stable equilibrium of the system will be characterized by a minimum of the potential energy compared to all virtual displacements. However, an auxiliary condition is also present, in the form of the constancy of the total volume of A [or of B , cf., (4)]. In order to include that auxiliary condition in the calculation, we appeal to the rules of differential calculus for a so-called “relative extremum.”

We once more imagine that the separation surface F_{AB} is the element $w = 0$ in an arbitrary family of surfaces $z = \psi(x, y, w)$ that depend upon one parameter w , and which might all have the same contour. The auxiliary condition would generally not be satisfied any longer as w varies. However, if we imagine a second such arbitrary family of surfaces $z = \psi^*(x, y, w^*)$, which once more starts from the given surface when $w^* = 0$, and if we extend those two one-parameter families in any way to a two-parameter family of surfaces $z = \psi(x, y, w, w^*)$ that goes to the first one-parameter family when $w^* = 0$ and to the second family when $w = 0$ then the magnitudes of the volumes V_A for the surfaces of that more general family will become a function of two parameters, and inside of the two-parameter family, there will be a one-parameter family that is selected by the condition that $V_A(w, w^*) = V_A(0, 0)$ and is now an actual virtual motion of the separation surface. We must then formulate the condition that among all surfaces of the two-parameter family for which $V_A(w, w^*) = V_A(0, 0)$, the surface $w = 0, w^* = 0$ will yield the minimum of the potential energy:

$$E = T_{AB} F_{AB} + g \rho_A \int_A z dv + g \rho_B \int_B z dv .$$

(The notation here is understood to mean that dv runs through the volume element of A in the first integral, while it runs through B in the second one.) One now gets the following two equations for that extremum with the auxiliary condition:

$$\frac{\partial E}{\partial w} + \lambda_{AB} \frac{\partial V_A}{\partial w} = 0, \quad \frac{\partial E}{\partial w^*} + \lambda_{AB} \frac{\partial V_A}{\partial w^*} = 0 \quad (w = 0, w^* = 0)$$

from differential calculus in the known way, for a suitable constant λ_{AB} . The second equation now serves only to show that the value of λ_{AB} in no way depends upon the first family $z = \psi(x, y, w)$, which was assumed to be arbitrary, so it will have a well-defined meaning for the separation surface F_{AB} , *per se*, and when one expressly includes that

fact, the first equation will already appear in the system of both of them. Hence [cf., (3), (4), (5)], with a suitable constant λ_{AB} that is ultimately determined from the value of V_A , the condition:

$$\int_{F_{AB}} N \left[T_{AB} \left(\frac{1}{R_1} + \frac{1}{R_2} \right) + g (\rho_A - \rho_B) z + \lambda_{AB} \right] df = 0$$

must then be true. Due to the arbitrariness in the choice of the family $F(w)$, the function $N = dn / dw$ is subject to the single restriction on the surface F_{AB} that it must be continuous everywhere and equal to zero on the boundary. The integral in question can prove to be continuously equal to zero for N in that neighborhood only when the factor of N vanishes at every location inside of F_{AB} ; i.e., the form of the free surface must satisfy the differential equation ⁽³⁾:

$$(6) \quad T_{AB} \left(\frac{1}{R_1} + \frac{1}{R_2} \right) + g (\rho_A - \rho_B) z + \lambda_{AB} = 0.$$

F_{AB} can also consist of several separate pieces, while λ_{AB} has the same value for the different pieces.

In any event, a minimum for E is possible here only when $T_{AB} \geq 0$, since otherwise E could be reduced arbitrarily by bending the separation surface back and forth about any position.

We might have $\rho_A \neq \rho_B$. If we set:

$$z_{AB} = - \frac{\lambda_{AB}}{g (\rho_A - \rho_B)}$$

then $z = z_{AB}$ will give us a well-defined horizontal plane that shall be called the *level plane*. If we assign $z = 0$ to the level plane then equation (6) will follow in the form:

$$(6a) \quad T_{AB} \left(\frac{1}{R_1} + \frac{1}{R_2} \right) = g (\rho_A - \rho_B) z.$$

In that way, the mean curvature away from B at each location on the separation surface can be concluded directly from the position of the level plane. *If $\rho_A > \rho_B$ then the locations of the separation surface where that mean curvature is positive (i.e., when the surface is convex-convex outward or convex-concave with a greater contribution from the first principal curvature at B) will lie below the level plane, and indeed the stronger that mean curvature gets, the deeper it will lie. Locations where that curvature is negative away from B will lie above the level plane, and locations where it is zero will necessarily lie at precisely the same height as that plane (Fig. 2). In particular, the separation surface can become asymptotically planar only at the same height as that plane, its relationship to the level plane is established with that.*

⁽³⁾ **Laplace**, *Supplément au livre X de la Mécanique céleste*, no. 4.

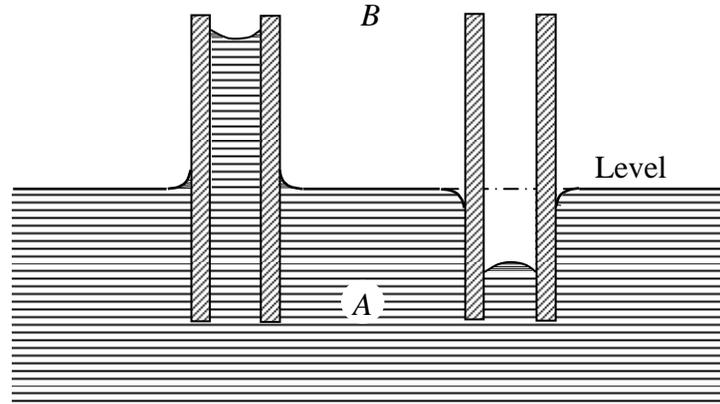


Figure 2.

4. Boundary angle. – In order to establish F_{AB} completely, one needs some further conditions for the boundary of the surface where A and B meet the third medium C , in addition to the differential equation (6).

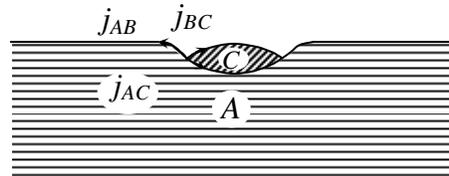


Figure 3.

If the three fluids A , B , C with three separation surfaces F_{AB} , F_{AC} , F_{BC} , in which the surface tensions T_{AB} , T_{AC} , T_{BC} prevail, are bounded a common curve (Fig. 3) then the opposite state of motion to every virtual state of motion of the boundary curve would also be virtual. After all (because the case of displacements that are not invertible in that sense would also come under consideration then), we would like to initially vary only the assumed equilibrium state (but not go through it), and we imagine a family of positions of that boundary that depends upon one parameter w (≥ 0) and has the same endpoints when the curve is not closed, and for certain positions of the three separation surfaces that are coupled with it. In that way, they will all constantly lie on the boundary curve, but otherwise keep their boundary segment fixed, and at the same time, their interior parts will experience deformations that leave the total volume of A , B , C unchanged. In order to express the idea that the total energy E is smallest in the equilibrium state for $w = 0$, we must then merely demand the inequality:

$$\frac{dE}{dw} \geq 0 \quad (w = 0)$$

of the initially one-sided variation. However, since, from (6), the separation surface already obeys equations that make the terms that appear as surface integrals in them equal to zero, from (3), that inequality will condense to:

$$- \int L [T_{AB} \cos (w j_{AB}) + T_{AC} \cos (w j_{AC}) + T_{BC} \cos (w j_{BC})] ds \geq 0,$$

in which the integral is extended over the given position of the boundary curve, and at each element ds , w is understood to mean the direction, $L dw$, the magnitude of the increase, dw , the corresponding displacement of the boundary point, and j_{AB} , j_{AC} , j_{BC} mean the inward-pointing normals to ds . Since the function L can be chosen arbitrarily here, except that it must be continuous and always ≥ 0 and vanish at the endpoints of the boundary curve, it will then follow that:

$$(7) \quad - T_{AB} \cos (w j_{AB}) - T_{AC} \cos (w j_{AC}) - T_{BC} \cos (w j_{BC}) \geq 0$$

along the entire boundary curve, and indeed even for arbitrary directions w . However, we can combine any direction w with its opposite, and the \geq sign can then be replaced with an $=$. In that way, the three vectors of lengths T_{AB} , T_{AC} , T_{BC} and directions that are parallel to j_{AB} , j_{AC} , j_{BC} , resp., must join together into a closed triangle (⁴). For example the angle $(j_{AB} j_{AC}) = \omega_A$ is then the exterior angle that is defined by the first two sides of that triangle and therefore has a constant value along the entire boundary curve that follows from the three tensions. That angle ω_A is called the *boundary angle* of A with respect to B and C .

A first requirement for the equilibrium that is now assumed is that one can define a triangle from the three lengths T_{AB} , T_{AC} , T_{BC} at all; i.e., that each of the three tensions is no greater than the sum of the other two. However, if one had, say, $T_{AB} > T_{AC} + T_{BC}$ then C would have to be found between A and B instead, and possibly from a thin layer with two separation surfaces that are closely-spaced compared to A and B , in such a way that some situations would arise that would have to be examined in more detail, based on the assumption that the capillary energy is spatially distributed.

The relation $T_{AB} > T_{AC} + T_{BC}$ serves as a sufficient explanation for the variegated capillary phenomena for the three media (⁵).

From **Marangoni's** observations (⁶), in all cases, the reciprocal surface pressure between two fluids is smaller than the difference between their surface pressures with air (¹), so that triangle of tensions can never be realized. The case of mercury and water, which **Marangoni** regarded as an exception, obeys that general rule (^{6a}). When water lies upon mercury as a drop, foreign components will adhere to the surface of the mercury that reduce its tension (⁷).

(⁴) That condition was posed by **F. Neumann**, and was first published in the dissertation of **Paul du Bois-Reymond** (Berlin, 1859).

(⁵) The article by **F. Pockels** in the *Handbuch der Phys.*, publ. by **A. Winckelmann**, v. 1 (Breslau, 1907) gives an overview of the methods and results of observations regarding capillarity that extends up to the present.

(⁶) **Marangoni**, "Sull' espansione delle gocce di liquido galleggiate sulla superficie di altro liquido," Pavia, 1865; Ann. Phys. Chem **143** (1871), pp. 348. The same facts were found by **van der Mensbrugghe**, Mém. cour. de l'Acad. de Belg. **34** (1869), and furthermore, **Lüdtge**, Ann. Phys. Chem. **137** (1869), pp. 362.

(^{6a}) **Quincke**, Ann. Phys. Chem. **139** (1870), pp. 66. Lord **Rayleigh**, *Scientific papers* **3**, pp. 562.

(⁷) The spreading of a drop of fluid over another fluid will take place in each case in characteristic forms that vary quite widely with the substances, namely, the **Tomlinson** cohesion figures; on this, cf., **O.**

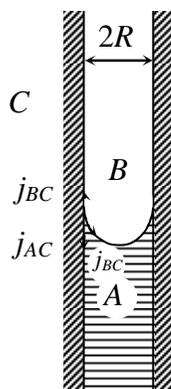


Figure 4.

If C represents a solid body then the separation lines between A , B , C can be freely displaced only on its surface, and we will get the relation (7) in the correspondingly-restricted context, namely, when C has no discontinuity on the tangent plane to the boundary curve (Fig. 4), in one case, such that w coincides with j_{AC} , and in the other case, such that w coincides with j_{BC} , and we conclude from this that:

$$(8) \quad \cos \omega_A = \frac{T_{BC} - T_{AC}}{T_{AB}},$$

in which ω_A again denotes the boundary angle ($j_{AB} j_{AC}$) of A with respect to B and C ⁽⁸⁾.

That relation would be impossible when the quotient on the right has a magnitude that is > 1 (or < -1). In the case of $T_{BC} > T_{AC} + T_{AB}$ (here T_{AC} , T_{BC} do not need to be ≥ 0), equilibrium would come about in such a way that the fluid A would *wet* the solid body C in a microscopically immeasurably thin layer along C , by which, both sides of the boundary line B in question would be bounded by A , and therefore from just that formula (8), in which one now takes A instead of C and $T_{AA} = 0$, the boundary angle of A would prove to be zero.

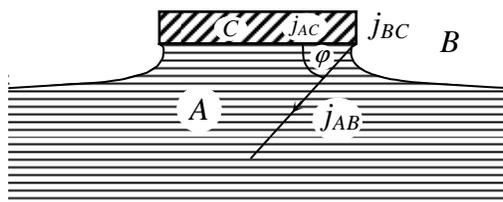


Figure 5.

If the wall of the solid body C has precisely one cut along the boundary curve [which is a case that can easily present itself with the adhesion of a fluid to a solid body (Fig. 5)]

Lehmann, *Molekularphysik* **1**, Leipzig, 1888, pp. 260; Paul du Bois-Reymond, *Ann. Phys. Chem.* **139** (1870), pp. 262.

⁽⁸⁾ Quincke [*Ann. Phys. Chem.* **137** (1869), pp. 42] found that water or mercury would first yield a constant boundary angle along a thin, wedge-shaped, silver layer applied to glass where the thickness of the silver layer was at least 50×10^{-7} cm.

then two kinds of non-opposing displacements of the boundary curve of C can come under consideration. The result would be the same as when one imagines that the cut is the boundary of rounded forms. One would arrive at the inequality (7) in such a way that w would be represented by j_{AC} , but j_{BC} would be represented by the direction that is opposite to j_{AC} , in one case, and w would be represented by j_{BC} , but j_{AC} would be represented by the direction that is opposite to j_{BC} , in the other; one would then get:

$$-T_{AB} \cos(j_{AC} j_{AB}) - T_{AC} + T_{BC} \geq 0,$$

$$-T_{AB} \cos(j_{BC} j_{AB}) + T_{AC} - T_{BC} \geq 0;$$

i.e.:

$$(9) \quad (j_{AC} j_{AB}) \geq \omega_A, \quad (j_{AB} j_{BC}) \geq \pi - \omega_A,$$

in which ω_A means the angle ≥ 0 and $\leq \pi$ that is replaced by (8). It follows from the two relations that:

$$(j_{AC} j_{BC}) \geq \pi.$$

Hence, in the equilibrium state, the boundary line of the free surface can never lie along a finite piece of a concave cut in the solid body⁽⁹⁾.

The conditions for four fluids to come together at a point are obvious now with no further analysis. **Gibbs**⁽¹⁰⁾ discussed the possibility of the formation of a new separation surface along a line along which more than three fluids came together.

5. Capillary pressure. Surface tension. – If one would also like to employ the concept of fluid pressure in the phenomena of capillarity then it would be necessary to represent the fact that such a pressure would generally change discontinuously at the separation surface between two fluids. The discontinuities are made to agree with the center of mass theorem and law of areas in mechanics. If one would further like to establish the discontinuities without introducing any hypotheses about molecular forces then one would start from the Ansatz that a spatial density of energy exists at every location in a fluid that depends upon the mass density itself, as well as the differential quotients of the mass density with position. One would then have to pass to the limit in such a way that the differential quotients of the mass density would generally be set equal to zero, and they would become infinite only for certain surfaces in such a way that the mass density experienced a constant jump. The concept of pressure will then arise from the negative differential quotient of the energy of a mass with respect to its volume [eq. (42) in no. 18].

For the sake of brevity, we shall content ourselves here with the following more-axiomatic way of establishing it: The pressure varies continuously with the density inside of an individual fluid A , but is determined only up to an additive constant; with certain conventions in regard to that constant, we would like to speak of it as the *kinetic*

⁽⁹⁾ **Gauss**, “Principia generalia theoriae fluidorum,” art. 30.

⁽¹⁰⁾ **Gibbs**, “Equilibrium of heterogeneous substances,” pp. 453.

pressure. Now let A and B be two different fluids that are subject to gravity and are separated by a horizontal plane $z = 0$, and let each of them be arranged to have its density and temperature depend upon only the vertical height h everywhere. The kinetic pressure will then suffer a discontinuity at the transition from A to B that we would like to refer to as a *cohesion jump*. We can put the relevant increase in kinetic energy from A to B into the form $K_A - K_B$ such that K_A depends upon only A , and K_B depends upon only B .

The difference $P_A - K_A = p_A$ shall then be called the *hydrodynamical pressure* in A ; that pressure would then experience *no sort of discontinuity at the horizontal separation surface*. In a fluid A at rest in which the density can be regarded as nearly constant, the pressure p_A varies in such a way that it generally has the expression $p_0 - \rho_A g z$, where p_0 is a constant, which then depends upon the vertical height z .

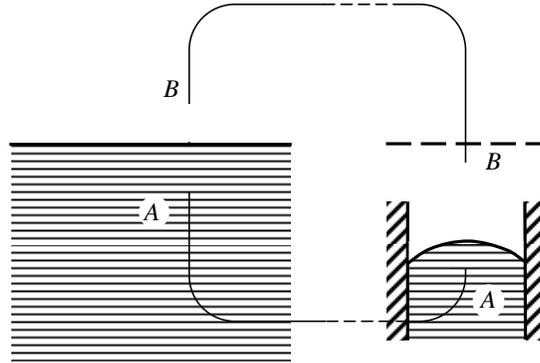


Figure 6.

Two fluids at rest A and B with differing densities might have an arbitrary separation surface F_{AB} that corresponds to the differential equation (6). We determine the level surface for it, choose it to be the plane $z = 0$, and on the other hand, imagine that A and B are likewise inside of a very wide vessel, and that both of them are separated by a horizontal plane, and indeed at precisely the height of that level surface, and finally couple both ends of A and both ends of B with communicating tubes (Fig. 6) then equilibrium will continue to exist according to equation (6a). Now, if p_0 is equal to the hydrostatic pressure in the horizontal separation surface between A and B then the pressure in A at a height of z will be equal to $p_A = p_0 - \rho_A g z$ and the pressure in B at a height of z will be equal to $p_B = p_0 - \rho_B g z$. From (6a), one will then find a pressure discontinuity of:

$$(10) \quad p_A - p_B = -g(\rho_A - \rho_B)z = T_{AB} \left(\frac{1}{R_1} + \frac{1}{R_2} \right)$$

at any location in the separation surface F_{AB} . That difference is called the *capillary pressure* at the location of A .

If B represents the saturated vapor of the fluid A then p_0 will be the saturation pressure over a planar fluid surface, and if, in contrast, p_B is the vapor pressure that is found to be in equilibrium with the fluid over a location in the fluid that exhibits a mean

curvature of $\frac{1}{2}\left(\frac{1}{R_1} + \frac{1}{R_2}\right)$ towards the vapor then the latter vapor pressure p_B will exceed the pressure p_0 by ⁽¹¹⁾:

$$\frac{\rho_B}{\rho_A - \rho_B} T_{AB} \left(\frac{1}{R_1} + \frac{1}{R_2} \right).$$

It follows from this that, e.g., there is an increased tendency the smallest water droplets to evaporate in air, because with the equilibrium pressure of the vapor over a planar water surface still does not reach the equilibrium pressure over the surface of the droplet.

If the pressure discontinuity of the capillary pressure is introduced in that way then the existence of the separation surface energy would be exhausted completely, from the derivation of the expression (3), with the further assumption that, in addition, a constant tension of T_{AB} per unit length of the boundary line would prevail at every boundary element of the separation surface that would be inward-pointing normal to the boundary.

When one now also applies formula (3) to an arbitrary section of the separation surface, as far as virtual work is concerned, the capillary pressure along the surface and that tension on its boundary will be equivalent to the assumption that *a constant pressure equal to T_{AB} prevails everywhere inside of the separation surface*. However, when we speak of a pressure inside of the entire surface in such generality, that basically means just: A potential energy of $T_{AB} F_{AB}$ exists for the separation surface, which is just what we said to begin with.

Thomas Young ⁽¹²⁾ based a complete theory of capillary phenomena on that analogy between a fluid surface and an elastic membrane that generally forfeited its clarity by his avoidance of mathematical symbols. **Segner** ⁽¹³⁾ introduced the concept of surface tension in a fluid.

6. Formation of free surfaces. Drops. – The differential equation of a free surface comes under consideration in experiments in two types of situations especially: Namely, one is mostly dealing with either surfaces of revolution around a vertical axis or cylindrical surfaces with horizontal generators, and the latter surfaces can also serve as approximations to the former for large cross-sections.

In the case of a *surface of revolution around the z-axis*, let r be the distance from the axis to the meridian curve, let φ be the angle of inclination of the tangent with respect to

⁽¹¹⁾ **W. Thomson**, Edinburgh Proc. Roy. Soc. **7** (1870), pp. 63. – In a capillary tube of radius 0.00012 cm in which water rises by 1300 cm, the equilibrium expression for the water vapor would be, say, 1 / 1000 smaller than the value for the level plane. The superheating (*Siedeverzug*) of fluids that are free of air is also connected with the situation that is given by the relation (10), as well as the difficulty in forming the first bubbles in electrolysis.

⁽¹²⁾ **Th. Young**, “Essay on the cohesion of fluids,” Trans. Roy. Phil. Soc. London, 1805. – For a critique of **Young**’s achievements, cf., Lord **Rayleigh**, Phil. Mag. **30** (1890), pp. 285, 456 (*Scientific Papers* 3, pp. 397).

⁽¹³⁾ **Segner**, Comment. soc. reg. Gotting. **1** (1751), pp. 310. – **Plateau**, *Statique des liquides*, Chap. V, gave a historical overview of the work done on the theory of surface tension that led up to 1869. **Van der Mensbrughe** especially has devoted various documents to that theory.

the horizontal r -axis (Fig. 7), so $\tan \varphi = dz / dr$, so the curvature of the curve will be $-\frac{1}{R_1}$
 $= \cos \varphi \frac{d\varphi}{dr}$, and the reciprocal length of the normal will be $-\frac{1}{R_2} = \frac{\sin \varphi}{r}$, so equation (6)
 will then go to:

$$(11) \quad T_{AB} \frac{d(r \sin \varphi)}{r dr} = \lambda_{AB} + g (\rho_A - \rho_B) z.$$

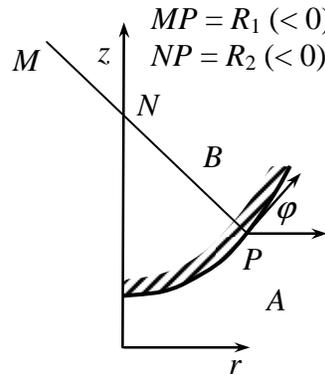


Figure 7.

For the most part, one deals with a particular solution of that equation that meets the axis and then necessarily pierces it perpendicularly in order for the surface to behave regularly at that location. The solution depends upon only one constant, since one demands that $dz / dr = 0$ for $r = 0$. If one lays the coordinate origin at that point of intersection with the curve then $2 T_{AB} / \lambda_{AB}$ will mean the radius of curvature itself, and when one chooses that quantity to be the unit of length, the form of the curve will depend upon only *one* parameter, which must mediate the relationship between the prescribed value of the boundary angle of A at the end of the meridian curve and the volume of A .

Laplace ⁽¹⁴⁾, and later Lord **Kelvin** ⁽¹⁵⁾ have constructed the meridian curve of the capillary surface of revolution approximately from small circular arcs with a continuous succession of tangents by calculating the curvature at the origin of that arc using equation (11). **C. V. Boys** ⁽¹⁶⁾ made that method especially manageable when he described the circular arcs by a fixed mark along a (transparent) ruler along which the center of rotation was successively varied, which ensured the continuity of the tangents at the successive circular arcs. In addition, the tick marks along the ruler denoted their reciprocal distances from the fixed mark at which one finds ∞ itself. **Bashforth** ⁽¹⁷⁾ produced extensive tables of that particular solution of (11). **C. Runge** ⁽¹⁸⁾ took the equation as an illustrative example of a numerical method for integrating second-order differential

⁽¹⁴⁾ **Laplace**, *Connaissance des Temps*, 1812.

⁽¹⁵⁾ **W. Thomson**, "Capillary attraction," *Proc. Roy. Inst.* **11** (1886), reprinted in *Popular lectures and addresses* 1, London, 1889. The essay contains various diagrams for illustrating the procedure. – **J. C. Schalkwijk**, *Leiden Communic.*, no. 67 (1901).

⁽¹⁶⁾ **C. V. Boys**, *Phil. Mag.* (5) **36** (1893), pp. 75.

⁽¹⁷⁾ **Bashforth** and **Adams**, "An attempt to test the theories of capillary action," Cambridge, 1883.

⁽¹⁸⁾ **C. Runge**, *Math. Ann.* **46** (1895), pp. 167.

equations. **K. Lasswitz** ⁽¹⁹⁾ and **Th. Lohnstein** ⁽²⁰⁾ treated a development of z in powers of r for the solution of (11) that was convergent in the region $0 \leq \varphi < \pi/2$. One will find all kinds of approximation formulas for the radius of curvature for $r = 0$, the maximum value of r , etc., in **Poisson** ⁽²¹⁾, **Fr. Neumann** ⁽²²⁾, **A. König** ⁽²³⁾, **H. Siedentopf** ⁽²⁴⁾.

The forms of a drop of mercury on a horizontal base, a bubble that collides with a horizontal plane, and a drop of water that hangs from a horizontal plane are surfaces of revolution that are determined from the differential equation (11) by the demand that they must meet the axis, the boundary angle at the endpoint of the meridian curve, and the given volume.

If the solution of equation (6) does not depend upon y , so it is a *cylindrical surface with horizontal generators that are parallel to the y -axis*, then the equation of its vertical cross-section by the xz -plane will be:

$$(12) \quad T_{AB} \frac{d \sin \varphi}{dx} = T_{AB} \frac{d\varphi}{ds} = \lambda_{AB} + g (\rho_A - \rho_B) z,$$

when φ means the angle of the tangent with respect to the x -axis, and ds means the element of arc length. That is the equation for the equilibrium form that a uniformly infinitely-thin, rectilinear, elastic rod will assume in the absence of external forces when two equal and opposite forces that point in the directions of the positive and negative x -axis are applied to its ends, along with the force-couples that they define ⁽²⁵⁾. Differentiating (12) with respect to s will yield:

$$T_{AB} \frac{d^2 \varphi}{ds^2} = g (\rho_A - \rho_B) \sin \varphi,$$

and with that, assuming that $\rho_A > \rho_B$, the dependency of the angle $\pi - \varphi$ on s will be the same as the dependency of the deflection of an ordinary mathematical pendulum of length $T_{AB} / (\rho_A - \rho_B)$ on time. If $z = 0$ were laid through the level plane, so if one were to assume that $\lambda_{AB} = 0$, then one would correspondingly get the integral of the *vis viva* in the pendulum motion from (12) upon multiplying by $\tan \varphi dx = dz$ and integrating:

$$(13) \quad T_{AB} (c - \cos \varphi) = g (\rho_A - \rho_B) \frac{z^2}{2}.$$

⁽¹⁹⁾ **K. Wasswitz**, Inaug.-Diss. Breslau, 1873.

⁽²⁰⁾ **Th. Lohnstein**, Inaug.-Diss., Berlin, 1891.

⁽²¹⁾ **Poisson**, Nouv. théor. de l'act. capill., Paris, 1831.

⁽²²⁾ **Fr. Neumann**, Vorl. über Capill., 1894.

⁽²³⁾ **A. König**, Ann. Phys. Chem. **16** (1882), pp. 10.

⁽²⁴⁾ **H. Siedentopf**, Ann. Phys. Chem. **61** (1897), pp. 235.

⁽²⁵⁾ Cf., e.g., **A. E. H. Love**, *A treatise on the mathematical theory of elasticity* 2, Cambridge, 1893, arts. 227-229.

The integration constant in this will be $c = 1$ when the surface approaches the level plane asymptotically, and $c > 1$ when it otherwise has a horizontal tangent; on the other hand, when the surface possesses an inflection ($d\varphi/ds = 0$), one will necessarily have $c < 1$.

Fr. Neumann ⁽²⁶⁾ has treated the form of a cylindrical drop that hangs from a horizontal plane, which might arise when a fluid drips from a long tube. In order to evaluate the stability of its form, we must appeal to the **Jacobi** criterion for an extremum in a variational problem. If A wets the plane, and $2T_{AB} : g (\rho_A - \rho_B)$ is introduced as the unit of area, for the sake of simplicity, then that will define the variational problem of determining a continuous function $z(x)$ that vanishes at the ends of an interval $-x_0 \leq x \leq x_0$, whose length $2x_0$ one also seeks, such that:

$$\int_{-x_0}^{x_0} \left(\sqrt{1 + \left(\frac{dz}{dx} \right)^2} - 1 - z^2 \right) dx$$

will be a *minimum* when one is given that $\int_{-x_0}^{x_0} z dx = J$. At a certain depth $\frac{1}{2} z_0$ under the

horizontal plane, the dish-like profile of the drop will be exhibited by an inflection point of the level plane, and then, from (13), it will keep going down to the deepest point, which is a mirror image of the inflection point, such that z_0 will be the total depth of the drop. If 2θ is the inclination of the inflection tangent with respect to the horizontal, and $\kappa = \sin \theta$ then one will find that:

$$z_0 = 2\sqrt{2} \kappa, \quad x_0 = \sqrt{2} (2E - K), \quad J = x_0 z_0,$$

on the basis of (13), in which K and E are complete elliptic integrals of the first and second kind of modulus κ ; resp. The expression $J = x_0 z_0$ has a maximum at roughly $\theta = 35^\circ 32'$ with $J = 2.606$. Now, when the volume J of the drop per unit length of the tube lies below that quantity, there will be drop forms that correspond to the equations of the problem, and indeed a form that is broader, but not as deep, so one will have $\theta < 35^\circ 32'$, and a form that is narrower, but hangs lower, for which the greatest inclination with respect to the horizontal will be $> 35^\circ 32'$. Only the first form is stable.

The fact that the behavior of a hanging, rotationally-shaped drop was analogous emerged from an experiment by Lord **Kelvin** ⁽²⁷⁾ in which a horizontal metal ring that was spanned by a thin rubber membrane was stretched into a shape similar to a drop by pouring water into it, and at a certain stage of that process, a jerky configuration of unstable equilibrium will come about.

After the drop falls off, the stretched neck will snap back into one or more smaller drops. The process would be more accessible to the observer of the formation of the drop

⁽²⁶⁾ **Fr. Neumann**, *Vorl. über Capill.*, pp. 117.

⁽²⁷⁾ **W. Thomson**, *Popular lectures and addresses* 1, London, 1889, pp. 38. – The drop forms in Fig. 8 were taken from there.

were to result in a fluid that was just a little simpler, but that has still not be subjected to a mathematical treatment ⁽²⁸⁾.

7. Rise height. – The mass of A that is found in a vessel C perpendicular beneath the separation surface F_{AB} , calculated from the level surface $z = z_{AB}$, exceeds the mass of B that it displaces by:

$$(14) \quad g(\rho_A - \rho_B) \int_{F_{AB}} (z - z_{AB}) \cos(nz) df = -T_{AB} \int_{F_{AB}} \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \cos(nz) df$$

$$= -T_{AB} \int \cos(j_{AB} z) ds,$$

in which the latter integral extends over the boundary of F_{AB} . The first conversion follows from (6), while the second one follows by an application of formula (3) to a parallel displacement of the surface in the z -direction, under which its area does not change. If the wall of the vessel is everywhere vertical at the boundary of F_{AB} then one will have $(j_{AB} z) = \pi - \omega_A$ here, in which one understands ω_A to mean the boundary angle of A , and the last expression in (14) will then be equal to $T_{AB} \cos \omega_A U$, where U means the circumference of the boundary curve, which will then be positive, zero, or negative, in particular, according to whether the angle ω_A is acute, right, or obtuse, resp.

If C represents a vertical capillary tube with a circular cross-section of radius R then an elevation or depression of the fluid in the tube will take place (here, we imagine that $\rho_A > \rho_B$, and that B lies over A) according to whether the boundary angle of A is acute or obtuse, resp., so in particular, it will rise when A wets the tube. From (14), *the mean rise height* over the cross-section of the tube *will be*:

$$h_m = \frac{2T_{AB} \cos \omega_A}{g(\rho_A - \rho_B)R} = 2 \frac{T_{BC} - T_{AC}}{g(\rho_A - \rho_B)R},$$

which is then *inversely proportional to the radius of the tube* ⁽²⁹⁾. The meniscus can be regarded as a spherical surface in the first approximation. If one approximates it more precisely as an ellipsoid of rotation around the axis of the tube ⁽³⁰⁾, which agrees with that meniscus in its boundary angle, the radius of curvature on the axis, and the weight that was raised, then it will follow, e.g., when A wets the tube, that the rise height along the axis will be:

⁽²⁸⁾ **G. Hagen**, Ann. Phys. Chem. **67** (1846), pp. 1, 157; *ibid.*, **77** (1849), pp. 449. – **C. V. Boys**, *Seifenblasen. Vorl. über Capill.*, German trans. by G. Meyer, Leipzig, 1893, pp. 33, 65. – Lord **Rayleigh** treated the relations between the diameter of a tube and the weight of a drop that falls from it in Phil. Mag. **48** (1899), pp. 321 (*Scientific Papers* 4, pp. 415), **Th. Lohnstein**, Ann. Phys. Chem. **20** (1906), pp. 237, pp. 606. – **A. M. Worthington** and **R. S. Cole**, “Impact with a liquid surface,” London Phil. Trans. **189** (1897), pp. 137.

⁽²⁹⁾ The proportionality of the rise height in a capillary tube with the reciprocal of the diameter seems to have been first established by **Borelli** (*De motionibus naturalis a gravitate pendentibus*, Reggio, 1670); many attribute the law to **Jurin** [Phil. Trans. **30** (1718)].

⁽³⁰⁾ **Mathieu**, *Capillarité*, Paris, 1883, pp. 49.

$$h = \frac{h_m}{1 + \frac{1}{3} \frac{R}{h_m}}.$$

If several fluids A, B, B^*, \dots are layered on top of each other in a capillary tube and they do not wet its wall then the total weight that rises up will be the same as if only B were found over A . An objection that **Young** believed had to be raised against this argument, and therefore against **Laplace's** theory in its own right, which was based on observations, was refuted by **Poisson** ⁽³¹⁾.

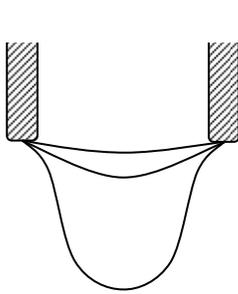


Figure 8

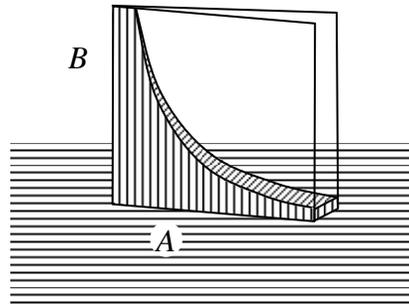


Figure 9

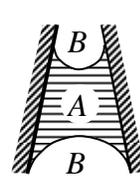


Figure 10.



Figure 11.

As a result of (14), the mean rise height between two parallel vertical plates is half as large as it would be in a capillary tube whose diameter is equal to the distance between the plates. If the two vertical plates has a narrow wedge opening between then the fluid in it will rise upward to an equilateral hyperbola (Fig. 9). Under some circumstances, a drop in a conical tube can be in equilibrium with an acute boundary angle when the tube is tapered above (Fig. 10) or an obtuse angle when it is tapered below (Fig. 11).

8. Capillary buoyancy. Adhesion. – Now, let the body C be in contact with only the fluids A and B . In order to ascertain the component $-P_w$ in an arbitrary direction w of the opposing pressure that C exerts against A and B in order to maintain equilibrium, we can displace C parallel to itself in that direction. We will then define a family of displacements of the system that depends upon one parameter w that makes C advance in that direction through the length w , so the parts F_{AC}, F_{BC} will also go along while leaving their common boundary lines unchanged, all boundary surfaces in A and B that abut in other media than C will remain fixed, and finally F_{AB} will be deformed in such a way that the volumes V_A and V_B remain unchanged. We can then pose the relation $dE / dw = 0$ for the total energy E that comes into play, including the terms $w P_w$ for the opposing pressure $-P_w$. Now, the areas of F_{AC}, F_{BC} are unchanged, the differential equation (6) is valid along F_{AB} , and to simplify, we set $z = 0$ at the level plane of A, B , so we will have $\lambda_{AB} = 0$. If we recall (3) and (5) then we will get:

⁽³¹⁾ **Poisson**, *Nouv. théorie de l'act. capill.*, pp. 141.

$$(15) \quad P_w - \int_{F_{AC}} g (\rho_A - \rho_B) z \cos(w n) df - \int_{F_{BC}} g (\rho_B - \rho_C) z \cos(w n) df - T_{AB} \int \cos(w j_{AB}) ds = 0,$$

in which the first integral refers to F_{AC} , the second, to F_{BC} , and the third, to their common boundary, and n denotes the exterior normal to C .

The vertical buoyancy that is exerted on C can be calculated from this when we take w to be the z -direction. If the separation surface F_{AB} has no boundary on C except for its boundary line – i.e., if it asymptotically approaches the level plane, moreover – then the transformation that is given by (14) will show that the last term in (15) will then be equal to $g (\rho_A - \rho_B) V_{AB}$, in which one understands V_{AB} to mean the volume under F_{AB} that reaches up to the level plane. (As long as F_{AB} exists under the level plane, the volume in V_{AB} that lies between them will be counted as negative.) Of that volume, the part V can be attributed to the medium A (Fig. 12, in which one finds \mathfrak{F}_{AB} in place of F_{AB}). On the other hand, upon continuing the level plane, C will split into a lower part of volume $V_C^{(A)}$ and an upper part of volume $V_C^{(B)}$, so the second and third terms in (16) will become:

$$- g (\rho_A - \rho_B) (V_C^{(A)} + V_{AB} - V), \quad - g (\rho_B - \rho_C) (V_C^{(B)} + V_{AB} + V),$$

resp., and it will then follow that:

$$(16) \quad P_w = g (\rho_A - \rho_C) V_C^{(A)} + g (\rho_B - \rho_C) V_C^{(B)} - g (\rho_A - \rho_B) V.$$

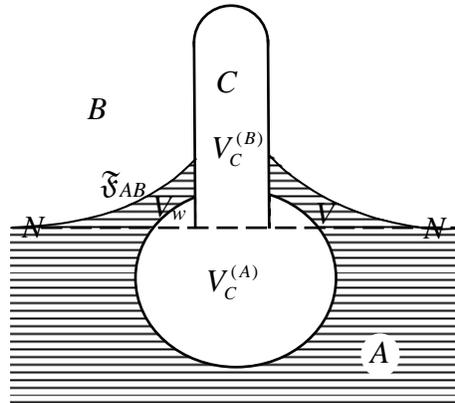


Figure 12.

The first two terms define the hydrostatic buoyancy, in case the separation surface falls in the level plane, while the third term, namely, the *capillary buoyancy* (negative downward force, resp.), is equal and opposite to the weight of the fluid that is raised above the level plane as a result of capillarity. Therefore, in some situations, a body can float on a fluid of lower specific gravity for an *obtuse* boundary angle ω_A .

If a circular disc C that lies on a wide horizontal surface between A and B (Fig. 5) and has a base that remains horizontal and is always in complete contact with A is continuously raised perpendicularly then the free surface of revolution that is located on

the boundary of the disc will once more obey equation (11). The meridian curve asymptotically approaches the level plane, while the boundary angle φ of A with respect to the horizontal base of the disc will increase continually as a result of the first inequality (9) up to the value ω_A that is determined by (8), at which point the fluid breaks off. For large areas S of the disc, the maximum height z_0 of the rise will give approximately $\varphi = \omega_A$ for $c = 1$ from (13), and indeed, independently of S , and the maximum weight of the fluid that is raised above the level plane plus the weight of the disc will then follow from (16), when one substitutes $V_C^{(A)} = -z_0 S$ in it, and $V = V_{AB}$ will be calculated from (14) by means of $(j_{AB} z) = \pi/2 + \omega_A$.

Given the adhesion of two very close equal horizontal plates (which might once more be circular of area S) by means of a thin fluid layer A of volume V_A that is found between them and *wets* them, the meridian curve of height z , which we measure from the upper surface of the layer (and thus also regard $d\varphi/ds$ as varying little), will be determined approximately from (12), and therefore that curve will approximate a semicircle of diameter V_A/S (Fig. 13). From (12), the level plane is found at a height of $z = -z_0$, which is inversely proportional to that value. Once more, (15) implies precisely the relation (16), in which one sets $V_C^{(A)} = -S z_0$, $V = 0$, and that will imply the pull that is exerted on the upper plate from above, together with its weight, which will, in fact, be proportional to S^2/V_A . For small V_A , an extremely large force will be necessary to separate the plates then.

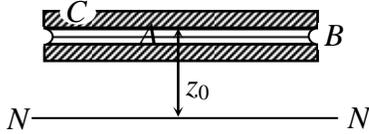


Figure 13.

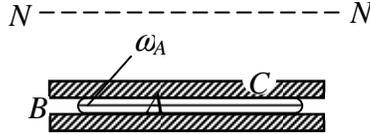


Figure 14.

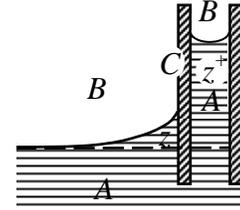


Figure 15.

By contrast, if the *boundary angle* at the plate is *obtuse* then the level plane will lie above the layer, the magnitude of the area of the surface that covers the plate will depend upon the value of V_A , and it will be necessary to exert a corresponding pressure on the plates in order to reduce the distance between them (Fig. 14).

Let C represent a vertical plate of very large width L that is parallel to the yz -plane and is arranged to be equal on both sides and is immersed in A and B , but in such a way that the position of the separation surface F_{AB} can have different heights on both sides of (15) (Fig. 15). One can then use (15) to calculate the sum of the two pressures P_x^- and P_x^+ in the direction of the x -axis that the plate experiences to the left and the right, on the side of smaller (larger, resp.) x . The two boundary integrals will then cancel, and all that will remain are the surface integrals for the part of the plate that is covered by A , on the one hand, and by B , on the other. If A is to the left of the plate at a height of z^- and to the right at a height of z^+ then the total pressure will be:

$$P_x = g (\rho_A - \rho_B) \frac{(z^+)^2 - (z^-)^2}{2} = T_{AB} (c^+ - c^-) L,$$

when (13) implies that the integration constant c^- for the form of the surface F_{AB} comes under consideration on the left and c^+ comes under consideration on the right.

If two plates C^- and C^+ of equal width L that are parallel to the yz -plane and very close to each other are immersed now, and if the integration constant c comes under consideration for the meniscus in the xz -plane between them, while beyond them, the surface F_{AB} might asymptotically approach the level plane, so the constant in question would have the value 1 there, then the plates would be pushed apart by a force of $T_{AB}(c - 1)L$. Now, if A defines an acute or obtuse angle with both plates then the meniscus in the xz -plane between the plates will necessarily exhibit a place where the tangent is horizontal, and from (13), one will then have $c > 1$. A apparent attraction of the plates will then take place, and indeed, since $c - 1$ is proportional to the square of the rise height at each location, from (13), it will be approximately inversely proportional to the square of the distance between the plates. If A defines an acute angle at one plate and an obtuse angle at the other one then a certain distance between the plates will correspond to an unstable equilibrium that will lead to an attraction when the plates are closer (due to the stronger curvature of the meniscus) and a repulsion when they are further apart⁽³²⁾.

9. Eliminating gravity. – According to (6), the action of gravity on the form of the separation surface between A and B seems to disappear when $\rho_A = \rho_B$, so when the two fluids have the same density. That fact, which **Segner** had already pondered⁽¹³⁾, was employed in various ways by **Plateau**⁽³³⁾ in order to study pure capillary action.

From (6), an oil drop that is brought into an equally-dense mixture of water and alcohol will assume the figure of a surface of constant mean curvature. If the drop is completely free to float then it will necessarily exhibit the form of a ball, since the sphere is the single closed surface of constant mean curvature that is free of singularities⁽³⁴⁾. If the surface of the drop is not closed on all sides, but partially leans on an immersed body of revolution, then it might define a surface of revolution around the respective axis. Now, if one has along an arbitrary normal to the meridian curve of that surface, in turn (Fig. 16), that P is the point of the curve, M is the center of curvature, N is the point at which it meets the axis (so PM , PN are the two radii of principal curvature of the surface of revolution), and finally Q is placed in such a way that $PNQM$ are four harmonic points, so one has:

$$\frac{1}{PM} + \frac{1}{PN} = \frac{2}{PQ},$$

then from (6) or (11), the length PQ must prove to be constant. The mirror image Q^* of Q along the axis will then yield a constant sum $PN + NQ^* = PQ$, while PN and NQ^* will exhibit equal and opposite inclinations with respect to the axis. If we now let P describe

⁽³²⁾ **Laplace**, *Suppl. à la théorie de l'act. capill.* (De l'attraction et de la répulsion apparente des petits corps qui nagent à la surface des fluides). – **Poisson**, *Nouv. théor. de l'act. capill.*, Chap. VI. – **W. Voigt** developed some general theorems on the attraction and repulsion of floating bodies in *Kompendium der theor. Phys.* 1, Leipzig, 1895, pp. 239.

⁽³³⁾ **Plateau**, *Mém. l'Acad. de Belgique*, 1843 to 1868; *Statique expérimentale et théorique des liquides* (Ghent, 1873).

⁽³⁴⁾ Cf., **Liebmann**, *Math. Ann.* 53, pp. 81.

the meridian curve and continually construct N , Q , Q^* in the way that was described then since PQ is constant, Q will describe a curve that is parallel to the meridian curve, so the motion of Q will always be normal to NP , and therefore the motion of Q^* , which is the mirror image of it along the axis, will always be normal to NQ^* . It is clear from this that the meridian curve of our surface of revolution will be generated by the focal point P of a certain conic section that one rolls without slipping on the axis of rotation whose other focus is Q^* and twice its major axis will be PQ ⁽³⁵⁾.

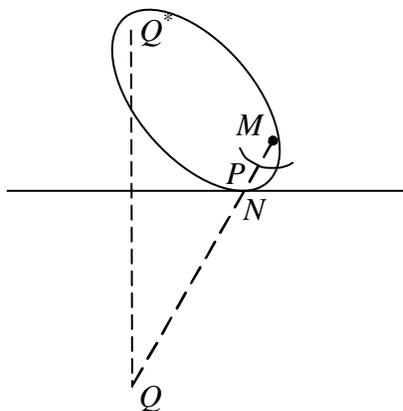


Figure 16.

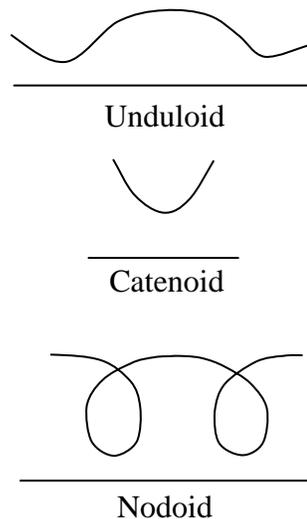


Figure 17.

If the drop is supported by two horizontal discs or rings whose centers lie vertically above each other then by changing the distance between those two supports, as well as the mass of oil that is found between them, one can generate the various forms of the surfaces of revolution of constant mean curvature, namely, the *unduloid*, which is a sphere – cylinder – catenoid in the limit, the *nodoid*, which is a catenoid – sphere in the limit, and which correspond to a rolling ellipse or hyperbola, resp., while the limiting surface will correspond to a line segment, circle, and parabola, resp. (Fig. 17). In that way, one can place spherical caps on the rings in each case that have the same mean curvature as the drop that is found between them. Here, the catenoid is a stable figure of equilibrium, namely, it is actually a surface of smallest area for a given magnitude of the volume that is contained between the two basic circular surfaces, but only as long as the tangents at the two end points to the meridian curves that generate it find their point of intersection along the axis of rotation ⁽³⁶⁾, and the cylinder surface is stable in the same sense only as long as the height of the cylinder does not attain the circumference of the cross-section ⁽³⁷⁾.

⁽³⁵⁾ Ch. Delaunay, J. de Math. (1) 6 (1841), pp. 309. – The literature about the mean curvature of surfaces up to 1869 was discussed thoroughly by Plateau (*Statique des liquides* 1, pp. 131).

⁽³⁶⁾ L. Lindelöf in Moigno-Lindelöf, *Calcul des variations*, Paris, 1861, pp. 209, 231. – Poincaré, *Capillarité*, pp. 66.

⁽³⁷⁾ Plateau. *Statique des liquides* 2, Chap. IX. – Poincaré, *Capillarité*, pp. 95.

If a freely-floating oil drop in the form of a sphere is put into uniform rotation around an axis (say, the z -axis) with the help of a disc that is immersed in the oil then increasing values of the angular velocity ω of the rotation will correspond to different forms of the drop. It will first appear ellipsoidal with flattening above and below, and finally a ring will detach from the equator that takes part in the rotation⁽³⁸⁾. If one imagines (and of course, this corresponds to experiments only inadequately) that only the drop A rotates, but not the surrounding fluid B , and one treats the motion of the co-rotating coordinate axes by introducing the potential of the centrifugal force $-\frac{\omega^2}{2}\rho_A\int_A r^2 dv$ then one will get [with the same notations as in (11)] the equation for the meridian curve of the rotating drop:

$$T_{AB} \frac{1}{r} \frac{d(r \sin \varphi)}{dr} = \lambda_{AB} - \frac{\omega^2}{2} \rho_A r^2 \quad \left(\frac{dz}{dr} = \tan \varphi \right).$$

One determines z from this as a hyperelliptic integral in r of genus 2, and one will get spheroidal or annular surfaces according to the values of ω ⁽³⁹⁾. One can, if need be, compare the figures that appear in this case with the forms of gravitating fluid masses that are found in stationary rotation when one starts with distant forces with the expression $-k \frac{e^{-cr}}{r}$ ($c \geq 0$) as a potential for two unit masses at a distance of r , which will imply gravitation, on the one hand, and surface tension, on the other, as the two limiting cases $c = 0$ and $c = \infty$, resp.

10. Fluid films. – Under some circumstances, a fluid A can exist for a long time in a medium B as a thin film with two very close surfaces that separate it from B . **Plateau**⁽⁴⁰⁾ based the permanence of such fluid films upon the gelatinous character (surface viscosity) that emerges primarily in the boundary layers. That is further explained by distributing material components in the surface layers as the interior of the film, which will make those layers have the properties of solid bodies, rather than fluids⁽⁴¹⁾. In films of very small thickness, a flow in the interior between the surface layers will then be slowed down considerably by the internal friction of the fluid⁽⁴²⁾, which will then make a variation of the mutual distance between the two separation layers more difficult. If F_{AB}^-, F_{AB}^+ are the areas of the two sides of the film then if one is to have equilibrium then one must require that the potential energy:

$$T_{AB} (F_{AB}^- + F_{AB}^+) + g (\rho_A - \rho_B) \int_A z dv + g \rho_B \int_{A+B} z dv$$

⁽³⁸⁾ **Plateau**, Mém. de l'acad. de Bruxelles **16** (1843).

⁽³⁹⁾ **Beer**, *Einl. in die math. Theorie der Elastizität u. Capillarität*, Leipzig, 1869.

⁽⁴⁰⁾ **Plateau**, *Statique des liquides* 2, Chap. VII.

⁽⁴¹⁾ **Marangoni**, *Nuov. Cim.* (2) **5**, **6** (1871/72); *ibid.* **3** (1878). – Lord **Rayleigh**, *Proc. Roy. Soc.* **48** (1890), pp. 127 (*Sci. papers* 3, pp. 363).

⁽⁴²⁾ Cf., the relevant calculation of **Gibbs**, *Equilibrium of heterogeneous substances*, pp. 475.

of the film must be a minimum under only those virtual displacements of A for which the normal distances between two separation surfaces will remain unchanged; the other displacements are then regarded as unfeasible. Now, when the thickness of the film is considered to be vanishing and one recalls (3), (4), (5), it will follow simply that $2T_{AB} F_{AB}$ – hence, F_{AB} – should be a minimum for the film, and one understands F_{AB} to mean the total area of the film. For instance, if a frame of moving filaments is constructed in some way from fixed wires to serve as the support for a fixed surface, and it is dipped into a soap solution then the soap solution will span the interior of the fixed and variable limits in the form a *minimal surface* (art. by **von Lilienthal**, III D 5, pp. 307), and one will encounter one of the rare cases in which a purely mathematical subject has been able to find a multifaceted stimulus from a relatively simple class of experiments.

One will get:

$$(17) \quad \frac{1}{R_1} + \frac{1}{R_2} = 0$$

for the differential equation for the form of the film, while the condition will result for its boundary (as long as it is not held fixed) that it must impinge perpendicularly to the surface that it spans. In that way, the prescribed boundary conditions will imply that intersections will necessarily arise during the evolution of the film. However, in stable equilibrium, one can never have more than three lamina that meet along a curve, and indeed only with equal surface angles then (so 120°), and at most four can meet at a point, and indeed with equal spatial angles⁽⁴³⁾. Hence, e.g., a frame that represents the edges of a regular tetrahedron will define a soap film that consists of six planar lamina – namely, the six triangles from the center of mass of the tetrahedron to the individual edges – while a surface will be created inside of the edge framework of a cube that does not exhibit all of the symmetries of the cube, but will favor an arbitrary pair of its sides (Fig. 18)⁽⁴⁴⁾.

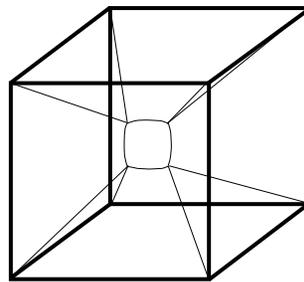


Figure 18.

It is a characteristic property of minimal surfaces that their map by parallel normals to a conical surface is conformal when one assigns the angles. Now, should the boundary of that minimal surface be a given closed sequence of segments, or more generally, should it lie piecewise along prescribed lines or planes, then the lines would have to be asymptotic curves on the surface, and the planes would have to cut out lines of curvature from them, and that spherical map would be a polygon of circular arcs of known circumference. The

⁽⁴³⁾ **Lamarle**, Mém. de l'acad. de Belg. **35, 36**. – **Plateau**, *Statique des liquides* 1, Chap. V.

⁽⁴⁴⁾ **Plateau**, *loc. cit.*, pp. 318.

analytical determination of the minimal surface in question would require the conformal mapping of that polygon onto a half-plane, so that mapping problem would depend upon a second-order linear differential equation with rational functions for its coefficients, and ultimately one should establish a finite number of parameters that would enter into that equation and correspond to the lengths and angles of the given framework, wherein transcendental relations would lie whose theory can be brought to a satisfying conclusion only in some special cases ⁽⁴⁵⁾.

Plateau ⁽³³⁾, and later **H. A. Schwarz** ⁽⁴⁵⁾, have realized various types of minimal surfaces (e.g., the catenoid inside of two circular rings that are kept perpendicular to each other, a helicoid inside of a glass cylinder between two generators) by means of soap films, and at the same time, have established, theoretically, as well as experimentally, the limits of their character as extremals, as well as how they rearrange when instabilities enter in. Inside of a wire that is spanned by the six edges of a straight, regular, six-sided prism and the sides of it that are alternately coupled to one and the other base surface, in the event that the edges of the prism are sufficiently long in comparison to the basic sides, one will find a lamina that will lie essentially closer to one of the two base surfaces along the centerline of the prism and will skip over to the opposite image relative to the other base surface by a slight shake. However, that striking phenomenon shall be attributed entirely to just the slight imperfections that are always present in the model.

The condition for the stability of a fluid film in a fixed framework is that it is not possible to find an infinitely-close minimal surface through any closed system of curves that lie on the surface ⁽⁴⁶⁾. **Hilbert** ⁽⁴⁷⁾ gave the general criterion for the presence of an extremum, exclusive of its stability, for the case of moving boundaries.

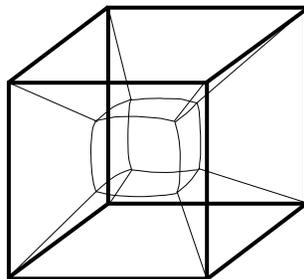


Figure 19.

When one proceeds in a suitable way, one can also span soap films inside of a fixed framework in which completely closed surfaces (viz., bubbles) will appear. [For example, one can establish a soap film inside the framework of the edges of a cube that consists of closed, outward-curving suspended surfaces with the symmetries of the cube and twelve planar trapezoidal lamina that couple their intersections with the edges of the cube (Fig. 19) ⁽⁴⁸⁾.] In that way, every closed bubble $B^{(i)}$ will contain a well-defined quantum of air for any volume $V^{(i)}$ and any pressure $p^{(i)}$, and one must accordingly add the corresponding term $-p^{(i)} V^{(i)}$ to the potential energy of the total system. It will then follow more generally, and in agreement with (10), that one will have:

⁽⁴⁵⁾ Cf., **H. A. Schwarz**, *Gesammelte math. Abh.* 1, Berlin, 1890.

⁽⁴⁶⁾ **H. A. Schwarz**, *Acta soc. scient. Fennicae* **15** (1885), pp. (*Ges. math. Abh.* 1, pp. 223).

⁽⁴⁷⁾ **Hilbert**, *Gött. Nachr.* 1905, pp. 159.

⁽⁴⁸⁾ **Plateau**, *loc. cit.*, pp. 361.

$$p^{(i)} - p^{(h)} = 2T_{AB} \left(\frac{1}{R_1} + \frac{1}{R_2} \right),$$

instead of (17), for a side surface of the bubble on whose other side a pressure $p^{(h)}$ prevails, in view of the two separation surfaces of the lamina, in which the radii of curvature are counted as positive for curvature that is convex outward. In order to fix the $p^{(i)}$, one appeals to the value of the external pressure, as well as the magnitudes of the individual quanta of air that are trapped inside. In that way, one can once more arrive at all forms of the unduloids and nodoids, e.g., with the help of two fixed rings that are closed with spherical caps. An isolated free soap bubble will necessarily have the form of a sphere, and the excess pressure inside of it will be inversely proportional to its radius, while that proportionality factor will be a multiple of the surface tension.

11. Stability of a separation surface. – For the stable equilibrium of a separation surface FAB , which already corresponds to the previously-discussed condition $dE / dw = 0$ ($w = 0$) for every one-parameter family of virtual displacements whose parameter is w , it is further necessary that the *second derivative of the potential energy with respect to the variation parameter w* must be positive-definite; i.e., one must have the inequality:

$$(18) \quad \frac{d^2 E}{dw^2} > 0 \quad \text{for } w = 0 .$$

If we assume that the boundary of F_{AB} is fixed, such that the integral over the curve in (3) drops out, then it will follow from differentiating (3), (4), (5) with respect to w and recalling (6) that:

$$\frac{d^2 E}{dw^2} = \int_{F_{AB}} N \left\{ T_{AB} \frac{\partial}{\partial w} \left(\frac{1}{R_1} + \frac{1}{R_2} \right) + g (\rho_A - \rho_B) \frac{\partial z}{\partial w} \right\} df .$$

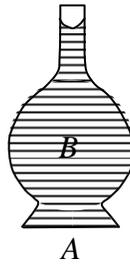


Figure 20.

Let us make a special application of that. The separation surface falls in the level plane $z = 0$. The fluid B is found above A in a vessel that is open at the bottom, but let it be denser than A , so $\rho_B > \rho_A$ (Fig. 20). We will then have:

$$z \equiv N w \pmod{w^2}, \quad \frac{\partial}{\partial w} \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \equiv - \frac{\partial^2 N}{\partial x^2} - \frac{\partial^2 N}{\partial y^2} \pmod{w}$$

for the varied surface [in which the symbol \equiv and the term (mod w^2) or (mod w), resp., shall suggest an equality up to terms of order w^2 or w , resp.], and it will emerge from the condition (18) that:

$$(19) \quad \int_{F_{AB}} N \left\{ -T_{AB} \left(\frac{\partial^2 N}{\partial x^2} + \frac{\partial^2 N}{\partial y^2} \right) - g (\rho_B - \rho_A) N \right\} df > 0,$$

while the constancy of the volume V_A will demand that the equation:

$$(20) \quad \int_{F_{AB}} N df = 0$$

must be satisfied, and N must further be zero everywhere on the boundary of F_{AB} .

In a more elementary treatment of this, **Maxwell** ⁽⁴⁹⁾ said that the integrand in (19) must be ≥ 0 everywhere, which is never achieved at all over the entire circumference for the functions N that are allowed here.

If the opening of the vessel is a circle of radius R around the zero point then one will express the condition of the vanishing of $N(x, y)$ on the boundary in the most general kind of calculation by the Ansatz:

$$N(r \cos \varphi, r \sin \varphi) = \sum_{m=0}^{\infty} \sum_{k=1}^{\infty} J_m \left(\frac{\lambda_{mk} r}{R} \right) (a_{mk} \cos m \varphi + b_{mk} \sin m \varphi),$$

in which $J_m(\lambda)$ means the **Bessel** function of the first kind of order m , and $\lambda_{m1}, \lambda_{m2}, \dots$ mean their positive roots, arranged by magnitude ⁽⁵⁰⁾. (19) then implies that:

$$\frac{\pi}{2} R^2 \sum_{m=0}^{\infty} \sum_{k=1}^{\infty} \left[\frac{m^2 \lambda_{mk}^2}{R^2} T_{AB} - g (\rho_A - \rho_B) \right] [J_{m+1}(\lambda_{mk})]^2 (a_{mk}^2 + b_{mk}^2) > 0,$$

while (20) will imply the equation:

$$2\pi R^2 \sum_{k=1}^{\infty} \frac{J_1(\lambda_{0k})}{\lambda_{0k}} a_{0k} = 0.$$

In fact, from the sequence of values of the λ_{mk} , the criterion that **Maxwell** gave for stability will imply the requirement here that one should have:

$$R < \lambda_{11} \sqrt{\frac{T_{AB}}{g(\rho_B - \rho_A)}}.$$

⁽⁴⁹⁾ **J. C. Maxwell**, *Scientific Papers* 2, pp. 585.

⁽⁵⁰⁾ Cf., *Die part. Differentialgl. d. math. Physik, nach Riemann's Vorl.*, revised by **H. Weber**, 2, pp. 262; 1, pp. 164.

If B wets the wall of the vessel then the upper limit can be described by $\frac{\lambda_{11}}{\sqrt{2}}\sqrt{h_m}$ here, if h_m is the mean rise height in a capillary tube of radius 1 (cf., no. 7) ⁽⁵¹⁾; the constant $\lambda_{11}/\sqrt{2}$ has the value 2.709...

If the opening of the vessel is a rectangle with sides a , b , and $a \geq b$ then it will be necessary for the stability of equilibrium that:

$$t^2 \left(\frac{4}{a^2} + \frac{1}{b^2} \right) T_{AB} - g (\rho_B - \rho_A) > 0,$$

from which, the corresponding condition that relates to a wide opening will be likewise clear for $a = \infty$.

12. Capillary oscillations. – In the equilibrium state, A is found completely beneath the level plane $z = 0$, while B is found above it, and its separation surface, which is thought to be *unbounded*, will exhibit surface oscillations, moreover:

$$z \equiv \varepsilon f(x, y, t) \pmod{\varepsilon^2}$$

under the influence of the surface tension and gravity, in which ε means a parameter in a certain neighborhood of 0. In A , as in B , one might find velocity potentials $\equiv \varepsilon \varphi_A$ [$\equiv \varepsilon \varphi_B$, resp.] $\pmod{\varepsilon^2}$, which satisfy the **Laplace** differential equation, and their *negative* differential quotients with respect to the coordinates will represent the respective velocity components. At the separation surface, one has, on the one hand for A and on the other for B , first of all, the kinematic demand that the relative velocity must be tangential to the surface, and secondly, that the pressure in it, namely $\equiv p_0 + \varepsilon p_A$ ($\equiv p_0 + \varepsilon p_B$, resp.) $\pmod{\varepsilon^2}$, must be the integral of *vis viva*, and thirdly, that the pressure difference, as the capillary pressure, must be $\equiv \varepsilon (p_A - p_B)$ $\pmod{\varepsilon^2}$, according to (10). For $\lim \varepsilon = 0$ (i.e., for infinite surface waves), those conditions will become:

$$-\frac{\partial f}{\partial t} = \frac{\partial \varphi_A}{\partial z} = \frac{\partial \varphi_B}{\partial z}, \quad \frac{p_A}{\rho_A} = \frac{\partial \varphi_A}{\partial t} - g f, \quad \frac{p_B}{\rho_B} = \frac{\partial \varphi_B}{\partial t} - g f \quad (z = 0),$$

$$p_A - p_B = -T_{AB} \left(\frac{\partial^2 f}{\partial x^2} + \frac{\partial^2 f}{\partial y^2} \right),$$

resp.

Should one have $\lim z = -\infty$ for A and $\lim z = +\infty$ for B then all of the stated conditions would be satisfied, in such a way that an additive construction would suffice for their general solution from the particular Ansatz:

⁽⁵¹⁾ Observations of **Duprez** [Mém. de l'Acad. de Belgique **26** (1851), *ibid.* **28** (1854)] are in agreement with that theoretical result.

$$f = \Re [e^{-i\sigma t} F(x, y)], \quad \varphi_A = \Re \left(-\frac{i\sigma}{k} e^{kz-i\sigma t} F \right), \quad \varphi_B = \Re \left(\frac{i\sigma}{k} e^{-kz-i\sigma t} F \right),$$

$$\frac{\partial^2 F}{\partial x^2} + \frac{\partial^2 F}{\partial y^2} + k^2 F = 0,$$

in which σ , k are positive real constants, \Re is the symbol for the real part of the quantity that it is applied to, and it will then follow from the last relations that one has the relation:

$$(21) \quad \left(\frac{\sigma}{k} \right)^2 = \frac{\rho_A - \rho_B}{\rho_A + \rho_B} \frac{g}{k} + \frac{T_{AB}}{\rho_A + \rho_B} k$$

between k and σ .

Waves that do not depend upon y follow from the Ansatz $F = C e^{ik(x-x_0)}$, and therefore $\lambda = 2\pi/k$ will be the horizontal-cylindrical length when they travel in some direction, or one can also have standing waves of oscillation number $\sigma/2\pi$. Lord **Kelvin** ⁽⁵²⁾, and later **Kolaček** ⁽⁵³⁾, gave that relation. It finds application to the propagation of waves in an unbounded water surface that is under the common action of gravity and capillarity, but not wind, and furthermore to those forced standing capillary oscillations for which the nodal lines can be parallel lines ⁽⁵⁴⁾.

When one assumes that $\rho_A > \rho_B$, equation (21) will have the consequence that the speed of propagation $c = s/k$ is a *minimum* c_m for a certain wave length λ_m , and with those quantities, (21) will be written:

$$(21a) \quad \frac{c^2}{c_m^2} = \frac{1}{2} \left(\frac{\lambda}{\lambda_m} + \frac{\lambda_m}{\lambda} \right).$$

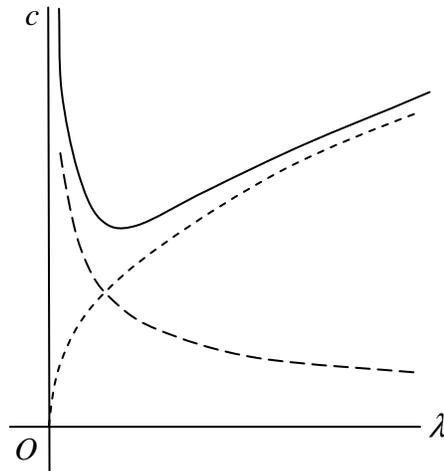


Figure 21.

⁽⁵²⁾ **W. Thomson**, Phil. Mag. (4) **42** (1871), pp. 368; Proc. Roy. Soc. Edinburgh (1870/71), pp. 374.

⁽⁵³⁾ **Kolaček**, Ann. Phys. Chem. **5** (1878), pp. 425; *ibid.* **6** (1879), pp. 616.

⁽⁵⁴⁾ Cf., the extended series of experiments by **L. Grunmach**, Wiss. Abh. d. kais. Normalaichungskommission, Berlin (1902), pp. 101.

(The curve in λ and c that is determined in that way is depicted in Fig. 21, along with the curves $c^2 / c_m^2 = \frac{1}{2} \lambda / \lambda_m$ and $c^2 / c_m^2 = \frac{1}{2} \lambda_m / \lambda$, in order to compare the effects of gravity and capillarity.) Each value of $c > c_m$ will then be associated with two types of wave length, a short one $\lambda_1 < \lambda_m$ and a long one $\lambda_2 > \lambda_m$, which will make the quotients λ_1 / λ_m and λ_2 / λ_m reciprocal. Lord **Kelvin** referred to the waves with $\lambda < \lambda_m$, for which the term T_{AB} in (21) exceeds the one with g , as “ripples.” For water waves in air, one will have, say, $\lambda_m = 1.75$ cm, $c_m = 23.2$ cm / s.

Lord **Kelvin** further discussed the influence of wind on the velocity of water waves. In that way, one makes the assumption that the upper fluid B advances with a given velocity u in the direction of the x -axis for $\lim z = \infty$. Two propagation speeds are then possible for the wave length λ :

$$c_u = \frac{\rho}{1 + \rho} u \pm \sqrt{c^2 - \frac{\rho}{(1 + \rho)^2} u^2} \quad \left(\rho = \frac{\rho_B}{\rho_A} \right),$$

in which c is the velocity for $u = 0$ that is determined by (21a). Here, an imaginary value of the square root would mean that the real part of the unvaried complex particular solution that is taken to be the starting point represents waves with continually-increasing amplitudes. That instability will not come into question for any wave length when one has $u < [(1 + \rho) / \rho^{1/2}] c_m$.

If one again imagines a motion in A that is horizontally-cylindrical, so it does not depend upon y , and that deviates only slightly from $z = 0$, but has an otherwise-arbitrary wave profile, that advances uniformly through A in the x -direction with the velocity c , and if, on the other hand, A is at rest for $z = -\infty$ then one will arrive at an integral equation (viz., a **Fourier** integral) from the integral of *vis viva* on the surface of A and, on the other hand, the capillary pressure that will allow one to adapt the wave profile to precisely any distribution of external pressure p_B that one might assume to exist on the surface. In particular, if a line that is parallel to the y -axis floats in the x -direction with a velocity $c > c_m$, which increases the total magnitude of the pressure per unit length at its location by P , while the pressure p_B is otherwise constant, precisely like a jump increase in the direction coefficients dz / dx of the wave profile by an amount $2P / T_{AB}$, and creates simply-harmonic waves of length $\lambda_1 (< \lambda_m)$ at some distance in front of it and ones of length $\lambda_2 (> \lambda_m)$ behind it. A pressure line that defines an angle of $\pi / 2 - \theta$ with its direction of advance will then act as if it had a velocity of $c \cos \theta$ perpendicular to it, and by integrating over θ , one can calculate the effect of a point that floats uniformly with the velocity c and increases the pressure, and in particular, one can show that such a wedge-shaped wave front (think of the waves from a ship) will be driven forward with an opening angle $2 \left(\frac{\pi}{2} - \theta \right)$ that is determined from $c \cos \theta = c_m$.

The consideration of *internal friction* for surface waves that advance in some direction on a *pure* water surface will have to involve assuming that the shear stress is zero on the surface, while the tension is correspondingly calculated from the capillary

pressure⁽⁵⁵⁾. If μ is the coefficient of friction and $\nu = \mu / \rho_A$ then one will find that for a given wave length λ , as long as $\vartheta = 2\pi\nu / c\lambda$ proves to be small (for water waves $2\pi\nu / c_m = 0.0048$ cm), one will find a modified wave velocity $= c (1 - \sqrt{2} \vartheta^{3/2})$ instead of the previous speed of propagation c , while at the same time, the amplitudes will then include a damping factor of $e^{-\frac{8\pi^2\nu}{\lambda^2}t}$, and therefore a relaxation time of:

$$\frac{\lambda^2}{8\pi^2\nu} \quad (= 0.712 \lambda^2 \text{ sec for water}).$$

The soothing effect of oil on water waves is then explained⁽⁵⁶⁾⁽⁵⁷⁾ by first saying that as a result of the excess of surface tension of water on oil over the sum of the two surface tensions of oil on water and air on oil, an extremely thin film will be removed from the water, and the surface layer with the added oil will exhibit elastic properties. Its tension will no longer remain constant, but will grow when one further seeks to reduce the thickness by stretching. In that way, it behaves just like a flexible and barely extensible membrane and will hinder the free unfolding and propagation of the waves that are found beneath it by its tension. As a result of that, when one would like to ascertain the influence of internal friction, no longer by assuming that the shear stress is zero on the surface as a limiting condition, as in the case of a pure water surface, but rather with the other one that the horizontal component of the velocity is zero there⁽⁵⁸⁾. That other extreme case has a relaxation time that is small by the ratio $4\sqrt{2}\vartheta : 1$ in comparison to the previously-considered situation.

Lord **Rayleigh**⁽⁵⁹⁾ treated the small oscillations of a separation surface with the form of a *circular cylinder* in order to be able to assess the stability of fluid jets from that. Gravity was not considered. Let A be found insides of the cylinder, while B is found outside of it, let R be the radius of the cylinder, while its axis is the z -axis, and:

$$r \equiv R + \varepsilon f(z, q, t) \pmod{\varepsilon^2} \quad (x + iy = r e^{i\theta})$$

is its equation of oscillation in the limit of $\varepsilon = 0$. If the external pressure in B is assumed to be constant (which is equivalent to taking $\rho_B = 0$) then one can make the particular Ansatz that the velocity potential in A is:

$$\varepsilon \Re [C e^{i(kz - \sigma t + m\theta)} J_m(ikr)] \pmod{\varepsilon^2},$$

in which J_m means the **Bessel** function of the first kind of order m , and one will arrive at the relation:

⁽⁵⁵⁾ Cf., **H. Lamb**, *Hydrodynamics*, 3rd ed., Cambridge, 1906, pp. 563.

⁽⁵⁶⁾ **Reynolds**, Brit. Assoc. Rep., 1880 (*Sc. papers* 1, pp. 409).

⁽⁵⁷⁾ **Aitken**, Edinburgh Roy. Soc. Proc. **12** (1883), pp. 56.

⁽⁵⁸⁾ **H. Lamb**, *Hydrodynamics*, 3rd ed., Cambridge, 1906, pp. 370.

⁽⁵⁹⁾ Lord **Rayleigh**, Proc. Roy. Math. Soc. London **10** (1878), pp. 4; proc. Roy. Soc. **29** (1879), pp. 71 (*Sc. papers* 1, pp. 361, 377; *Theory of Sound*, 2nd ed., Chap. XX); the influence of internal friction in the fluid was brought into consideration in Phil. Mag. **34** (1892), pp. 145 (*Sc. papers* 3, pp. 585).

$$\sigma^2 = \frac{ikR J'_m(ikR)}{J_m(ikR)} (k^2 R + m^2 - 1) \frac{T_{AB}}{\rho_A R^3}$$

by the kinematical condition, along with the pressure equation on the surface.

For $m = 0$, one will have $\sigma^2 < 0$, in the event that $kR < 1$, which implies the unstable character of perturbations whose wave lengths $2\pi/k$ exceed the circumference of the cylinder. As a result of the factor $e^{|\sigma|t}$ in the amplitude, the instability will then be greatest when $|\sigma|$ itself is greatest, which leads to $2\pi/k = 4.51 \times 2R$, such that the tendency of the jet A to decompose into drops will be strongest when that wave length swells and contracts.

Lord **Rayleigh** ⁽⁶⁰⁾ treated the case of $\rho_A = 0$, $\rho_B > 0$ on the basis of similar principles, which gave the wave length of greatest instability as $2\pi/k = 6.48 \times 2R$.

The first result can be applied to the decomposition of a jet of water in air, while the second one can be applied to the tearing of a jet of air that goes through water. The oscillations for $m = 2, 3, 4$ come about predominantly when the jet emerges from an opening of elliptic, triangular, or quadratic form, resp.

The small oscillations of a separation surface of the form of a *sphere* are obtained by starting from the simultaneous Ansatz ⁽⁶¹⁾ ⁽⁶²⁾:

$$\varphi_A = \Re \left(\frac{-C}{m} \frac{r^m}{R^m} Y_m(\theta, \psi) e^{-i\sigma t} \right), \quad \varphi_B = \Re \left(\frac{-C}{m+1} \frac{R^{m+1}}{r^{m+1}} Y_m(\theta, \psi) e^{-i\sigma t} \right),$$

in which one takes into account the kinematical condition that $\frac{d\varphi_A}{dr} = \frac{d\varphi_B}{dr}$. The r, θ, ψ in this are polar coordinates from the center of the sphere, $Y_m(\theta, \psi)$ is the spherical function of order m , and R is the radius of the sphere. It then turns out that:

$$\sigma^2 = m(m+1)(m-1)(m+2) \frac{T_{AB}}{[(m+1)\rho_A + m\rho_B]R^3}.$$

That result can be applied to the oscillations of a drop of water in air and an air bubble in water. For falling drops, oscillations of order 3 ($m = 3$) will emerge as a consequence of the tearing ⁽⁶³⁾.

⁽⁶⁰⁾ Lord **Rayleigh**, Phil. Mag. (5) **34** (1892), pp. 177 (*Sc. papers* 3, pp. 594).

⁽⁶¹⁾ Lord **Rayleigh**, Proc. Roy. Soc. **29** (1879), pp. 71 (*Sc. papers* 1, pp. 377).

⁽⁶²⁾ **Webb**, Mess. of Math. **9** (1880), pp. 177.

⁽⁶³⁾ **Lenard**, Ann. Phys. Chem. **30** (1887), pp. 209.

II. – Capillarity as spatially-distributed energy.

13. The hypothesis of cohesion forces. – Capillary phenomena prove to be necessary consequences of the hypothesis that, along with gravitation, yet another force of attraction acts between two material particles of the same or different substances that depends upon only the distance and which one calls the *force of cohesion*. Its law might take any form, except that it must drop rapidly with increasing distance in such a way that it will not be considered outside of an extremely small, microscopically imperceptible distance.

Initially, the rise of a fluid in a capillary tube was explained using only an attraction that the tube exerts upon the fluid, which could exist between the wall of the tube and the closest particles to it, due to the independence of the phenomena on the thickness of the tube ⁽⁶⁴⁾. **Clairaut** ⁽⁶⁵⁾ saw that it would be necessary for one to also consider an attraction of the fluid particles to each other. **Laplace** ⁽⁶⁶⁾ could then construct a complete theory of capillarity that was based solely upon the hypotheses on the force of cohesion that were just sketched out.

Laplace calculated the potential of the cohesion forces for a fluid mass whose parts cohere according that hypothesis for a position of the surface and found that it was a linear function of the mean curvature of that surface. He then considered the potential of a ball at a location on the surface, went from there to the potential of a wedge that was formed from two infinitely-close meridian sections of the ball, and finally approximated an arbitrary fluid surface in the neighborhood of a point by the surface that was generated by the curvature circles of the normal sections; i.e., roughly the osculating paraboloid. He further obtained the differential equation of a free surface from the laws of hydrostatics, whereby it would be a surface of constant potential of all forces that were acting under constant external pressure ^(66a).

Laplace ⁽⁶⁷⁾ used the second representation to calculate the tangential component of the total force of cohesion that is exerted upon the fluid surface at a location on it, in which the surface equation at that location was developed up to and including third-order quantities, and obtained the equation of the free surface from the condition that the resultant of cohesion and gravity would always be normal to the surface on it. However, **Laplace** had no proof of the constancy of the boundary angle between the fluid and a solid body, but only showed that when the body has the form of a vertical cylinder of any cross-section, the mean value of the cosine of that angle along the entire boundary curve must always lead to that constant.

Gauss ⁽⁶⁸⁾ narrowed that gap in **Laplace**'s theory. Starting from the principle of virtual displacements for an equilibrium state, **Gauss** converted that principle into the

⁽⁶⁴⁾ **Hawkesbee**, *Trans. Roy. Soc. London* **26, 27** (1709-1713).

⁽⁶⁵⁾ **Clairaut**, *Traité sur la figure de la terre*, Paris, 1743, Chap. X.

⁽⁶⁶⁾ **Laplace**, *Théorie de l'action capillaire*.

^(66a) More precisely, **Laplace** proceeded as follows: He imagined that an infinitely-narrow channel was laid in the fluid whose beginning and end joined the surface perpendicularly, calculated the pressure on a cross-section of the channel that would come about from forces of cohesion, and finally applied the "principle of equilibrium in the channel."

⁽⁶⁷⁾ **Laplace**, *Suppl. à théorie de l'act. capill.*

⁽⁶⁸⁾ **Gauss**, *Principia generalia*, Göttingen, 1830. – Self-published treatise: *Gött. gel. Anz.* 1829 (*Werke* 5, pp. 287).

requirement of a minimum of the potential energy and then considered the total potential energy of the cohesion forces that came into play. That energy took the form of a double space integral. For every space integration, a linear integration could be carried out, whereby one term that was proportional to the volume and a second one that was proportional to the area of the surface would appear, in particular, and of the remaining double surface integral, **Gauss** knew that under **Laplace's** assumption on the decrease in the force of cohesion, it would be necessary to neglect it, insofar as the radii of curvature of the surface are infinitely large compared to the distance at which the forces of cohesion become considerable, so the surface would prove to be almost planar. Using the methods of the calculus of variations (which were sketched out in nos. **3** and **4** above), **Gauss** then inferred the differential equation of the free surface from the extremal character of the potential energy, but then he also inferred the proof of **Laplace's** law of a constant boundary angle.

14. Potential energy of cohesion in a medium. – The transformation of energy of cohesion forces (⁶⁹) that **Gauss** performed can presently be represented as a double application of **Green's** theorem.

We next consider the cohesion energy inside of a single homogeneous medium A . Call its thickness ρ . A force of attraction equal to $\rho^2 dv dv' \varphi(r)$ acts between any two volume elements dv, dv' of A at the locations x, y, z and x', y', z' , resp., at a distance of r apart, where $\varphi(r)$ shall drop to zero rapidly with increasing r in a manner that will be established more precisely later. If one introduces:

$$\int_r^\infty \varphi(r) dr = \psi(r), \quad \int_r^\infty r^2 \psi(r) dr = \chi(r)$$

then the total potential energy of those forces of cohesion in A can be written:

$$(22) \quad -\frac{1}{2} \rho^2 \iint \psi(r) dv dv' = -\frac{1}{2} \rho^2 \iint \left(\frac{\partial \chi}{\partial x'} \frac{\partial \frac{1}{r}}{\partial x'} + \frac{\partial \chi}{\partial y'} \frac{\partial \frac{1}{r}}{\partial y'} + \frac{\partial \chi}{\partial z'} \frac{\partial \frac{1}{r}}{\partial z'} \right) dv dv',$$

in which dv , on the one hand, and dv' , on the other, run through all volumes in A , and the factor $\frac{1}{2}$ is assumed because in that way, every pair of elements dv, dv' will be considered twice. If we next focus on the integration over dv' for a fixed dv then we can convert the second expression in (22) using **Green's** theorem, in which we employ the **Laplace** differential equation for $1/r$, but as a result of the discontinuity of $1/r$ at the location of dv , one must remove a small ball around dv from the integration space for dv' , whose radius can ultimately allowed to converge to zero. If we denote a surface element of A by df'

⁶⁹ Simplified presentations of that transformation were given by **Bertrand**, Jour. de math. (1) **13** (1848), pp. 185; **Weinstein**, Ann. Phys. Chem. **27** (1886), pp. 544. – **L. Boltzmann**, Ann. Phys. Chem. **141** (1870), pp. 582 replaced the integrations with summations over molecules.

(and also by df , later on) and the external normal there by n' (and n), then (22) will transform into:

$$-2\pi\rho^2\chi(0)\int dv - \frac{1}{2}\rho^2\int dv\int\chi(r)\frac{\partial}{\partial n'}\frac{1}{r}df'.$$

In the first term of this, $\int dv = V_A$ is the total volume of A . We invert the order of integrations in the second term, introduce:

$$\int_r^\infty\chi(r)dr = \vartheta(r),$$

and observe that r depends upon only the differences $x - x'$, $y - y'$, $z - z'$, and that we further have:

$$\frac{\partial}{\partial n'}\left[\left(\frac{\partial r}{\partial x}\right)^2 + \left(\frac{\partial r}{\partial y}\right)^2 + \left(\frac{\partial r}{\partial z}\right)^2\right] = 0.$$

We can then write that second term as:

$$\frac{1}{2}\rho^2\int df'\int\left(\frac{\partial\vartheta(r)}{\partial x}\frac{\partial r}{\partial n'}\frac{\partial}{\partial x}\frac{1}{r} + \frac{\partial\vartheta(r)}{\partial y}\frac{\partial r}{\partial n'}\frac{\partial}{\partial y}\frac{1}{r} + \frac{\partial\vartheta(r)}{\partial z}\frac{\partial r}{\partial n'}\frac{\partial}{\partial z}\frac{1}{r}\right)dv$$

and make it possible to apply the formula for product integration (viz., **Green's** theorem) in the integration over dv a second time. Now, the discontinuity in $1/r$ lies at a location df' on the surface, this time, and for that reason, a small ball must be removed from the integration space for dv , but only from part that lies in the region of A ; i.e., afterwards, the ball will become essentially a half-ball with decreasing radius, except for the locations where a cut is present in the surface of A . In that way, the last expression, in which $\int\frac{\partial r}{\partial n'}df$ represents the projection of that expression onto the tangent plane at df' over the half-ball, will be transformed into:

$$\frac{1}{2}\pi\rho^2\vartheta(0)\int df' - \frac{1}{2}\rho^2\iint\frac{1}{r^2}\frac{\partial r}{\partial n}\frac{\partial r}{\partial n'}\vartheta(r)dfdf',$$

in which $\int df' = F$ defines the area of the surface of A . If we write:

$$(23) \quad K = 2\pi\rho^2\chi(0), \quad H = \pi\rho^2\vartheta(0)$$

then the following expression for the energy of the cohesion forces inside of A will ultimately result:

$$(24) \quad E = -KV + \frac{1}{2}HF - \frac{1}{2}\rho^2 \iint \frac{1}{r^2} \frac{\partial r}{\partial n} \frac{\partial r}{\partial n'} \vartheta(r) df df'.$$

In order for the integrals to make sense for $\vartheta(r)$, $\chi(r)$, $\psi(r)$, we assume that $r\chi(r)$, as well as $r^4\chi(r)$, $r^5\chi(r)$, converge sufficiently strongly to zero with increasing r . Furthermore, we assume that $\varphi(r)$, $\psi(r)$, $\chi(r)$, $\vartheta(r)$ drop out for microscopically-measurable r , and it is only with stronger approximations of r at zero that $\chi(r)$ and $\vartheta(r)$ will become finite quantities, and we then strive to determine upper limits on $\chi(0)$ and $\vartheta(0)$. In order to do that, it would be necessary and sufficient that $r^3\psi(r)$ should converge to zero in the limit as r goes to zero. If we refers to a quantity r_0 for which we can first neglect $\vartheta(r_0)$ in comparison to $\vartheta(0)$ as the *radius of activity* for the forces of cohesion then we will see from the fact that:

$$\vartheta(0) - \vartheta(r_0) = \int_0^{r_0} \chi(r) dr < \chi(0) r_0$$

that $\vartheta(0) / \chi(0)$ will be an extremely small length that will have the same order as r_0 , at best.

In order to estimate the double surface integral in (24), we introduce the solid angle that the element df' subtends at the location of df by way of $\frac{df'}{r^2} \frac{\partial r}{\partial n'} = do'$. That integral will then be written:

$$(25) \quad -\frac{1}{2}\rho^2 \int df \int \frac{\partial r}{\partial n} \vartheta(r) do'.$$

Now, the factor $\vartheta(r)$ has a noticeable magnitude for small r ($< r_0$), and on the other hand, $\partial r / \partial n$ is approximately equal to r / R for such $r < r_0$, in which one understands R to mean the radius of curvature of the normal section at the location df that goes through df' . If the radii of curvature of the surface of A are then considered to be extremely large compared to r_0 then neglecting the integral will seem necessary here, which will then reduce the expression (24) to:

$$(26) \quad E = -KV + \frac{1}{2}HF.$$

An exceptional case will come about when the surface of A exhibits a subset \mathfrak{S} of finite size to which another subset \mathfrak{S}' of it is continually proceeding at an extremely-small distance from it, such as, e.g., when the fluid carries a solid body along with it in an extremely-thin layer. The radii of curvature along \mathfrak{S} and \mathfrak{S}' might not drop below a limit that is extremely-large compared to r_0 , either. If one takes an element df in the integral (25) inside of \mathfrak{S} , together with all of \mathfrak{S}' , and drops an altitude from df to \mathfrak{S}' whose length

is s then within the same limits of error that were valid up to now, \mathfrak{S}' can be considered to be a plane of unbounded extent that is perpendicular to that altitude, and when one introduces $\frac{\partial r}{\partial n'} = \frac{s}{r} = \cos \gamma$, that plane can be constructed from concentric rings around the altitude that subtend solid angles of $2\pi \sin \gamma d\gamma$ at df . Due to the approximate parallelism between df and \mathfrak{S}' , the factor $\partial r / \partial n$ in (25) can then be replaced with $\partial r / \partial n'$, which will give:

$$-\frac{1}{2}\rho^2 df \int_0^{\pi/2} 2\pi \sin \gamma \cos \gamma \vartheta(r) d\gamma = -\pi\rho^2 df \int_s^{\infty} \frac{s^2}{r^3} \vartheta(r) dr$$

for the relevant part of (25). Now, when one introduces:

$$\theta(r) = 2r^2 \int_s^{\infty} \frac{\vartheta(r)}{r^3} dr = \vartheta(r) + r^2 \int_r^{\infty} \frac{\chi(r)}{r^2} dr,$$

in which it is clear that $\theta(0) = \vartheta(0)$, and one observes that the combination \mathfrak{S} , \mathfrak{S}' , as well as \mathfrak{S}' , \mathfrak{S} , appears in the double integral (25), ultimately, the supplementary term:

$$(27) \quad -\pi\rho^2 \int_{\mathfrak{S}} \vartheta(s) df,$$

which is extended over an entire side \mathfrak{S} of the layer, will be added to the expression (25) for the energy, due to the fluid layer between \mathfrak{S} and \mathfrak{S}' .

For the law of attraction with the following expression for the potential ⁽⁷⁰⁾:

$$(28) \quad -\psi(r) = -k \frac{e^{-cr}}{r},$$

in which k and c are positive constants, one will get:

$$\varphi(r) = k \frac{e^{-cr}}{r^2} (1 + cr),$$

$$\chi(r) = \frac{k}{c^2} e^{-cr} (1 + cr), \quad \vartheta(r) = \frac{2k}{c^3} e^{-cr} (1 + \frac{1}{2} cr), \quad \theta(r) = \frac{2k}{c^3} e^{-cr},$$

$$\chi(0) = \frac{k}{c^2}, \quad \vartheta(0) = \theta(0) = \frac{2k}{c^3}, \quad c = \frac{2\chi(0)}{\vartheta(0)} = \frac{K}{H}.$$

⁽⁷⁰⁾ Van der Waals, Zeit. phys. Chem. **13** (1894), pp. 657.

We now compute the *virial of the cohesion forces*. (As is known, we understand the “virial” of a force to mean one-half the work done by the force when we displace its point of application from the coordinate origin.) The sum of the virials for the two forces that two volume elements dv , dv' mutually exert on each other is $\rho^2 \varphi(r) r dv dv'$. The total virial over the fluid itself will then be:

$$\frac{1}{4} \rho^2 \iint r \varphi(r) dv dv',$$

and it would emerge from the expression (22) for the energy when one replaces the $\psi(r)$ in it with $-\frac{1}{2} r \varphi(r)$. In that way, the function:

$$-\frac{1}{2} \int_r^\infty r^3 \varphi(r) dr = -\frac{1}{2} r^3 \psi(r) - \frac{3}{2} \int_r^\infty r^2 \psi(r) dr = -\frac{1}{2} r^3 \psi(r) - \frac{3}{2} \chi(r)$$

would have to enter in place of $\chi(r)$, and furthermore, the function:

$$-\frac{1}{2} \int_r^\infty r^3 \psi(r) dr - \frac{3}{2} \int_r^\infty \chi(r) dr = -\frac{1}{2} r \vartheta(r) - 2 \vartheta(r)$$

would have to enter in place of $\vartheta(r)$, and therefore the roles of the constants $\chi(0)$, $\vartheta(0)$ would have to be taken over by $-\frac{3}{2} \chi(0)$, $-2 \vartheta(0)$, resp. Corresponding to formula (26), it will then result that the expression for that total virial is:

$$(29) \quad \frac{3}{2} K V - H F.$$

15. Potential energy of adhesion between two media. – If one medium A is bounded by a second medium B then forces of attraction might acts between the particles of A and B whose character in regard to their decrease with distance would be analogous to that of the forces of cohesion inside of A , and which one would probably also refer to as *forces of adhesion* here in the case of different substances. The functions that correspond to the functions $\varphi(r)$, $\psi(r)$, $\chi(r)$, $\vartheta(r)$, $\theta(r)$ above for the new law of attraction might be denoted in the same way by appending lower indices AB , while the previous functions might have contained the index A . The total energy of adhesion between B and A is calculated analogously from formula (22) to be:

$$(30) \quad -\rho_A \rho_B \int_B dv' \int_A \psi_{AB}(r) dv,$$

in which dv runs through the volume elements of A , while dv' runs through those of B . A factor of $\frac{1}{2}$ has not been included now, since the spaces A and B are completely separate now. The expression here once more admits the two corresponding conversions by means of **Green's** theorem. However, in the first conversion, in which one might operate

with fixed dv , no particular spatial integral will emerge, because now $1/r$ has no discontinuities in the integration space B , so a discontinuity in $1/r$ will come under consideration in the integration space A for fixed surface elements df' in B only for those elements df' that belong to exactly the separation surface between A and B , and therefore for the small half-ball that is removed from the integration space A around df' , the integral $\int \frac{\partial r}{\partial n} df$ will have the opposite value to the one above, due to the normal n' pointing in a different direction. As a result of that situation, after neglecting the potential energy of adhesion of B to A , as above, one will finally arrive at the expression:

$$(31) \quad -\pi \rho_A \rho_B v_{AB}(0) F_{AB} = -H_{AB} F_{AB},$$

in which F_{AB} denotes the area of the separation surface of A and B .

If we now take the typical case of three media A , B , C that come together and denote their volumes by V and their constants by K and H with the corresponding single indices, while the areas of their separation surfaces and its constant H have the corresponding two indices, and further boundary surfaces with other media shall not come into question as variable here, then we will have the following expression for the variable part of the potential energy of the forces of attraction that act in them:

$$(32) \quad \left(\frac{1}{2}H_A + \frac{1}{2}H_B - H_{AB}\right)F_{AB} + \left(\frac{1}{2}H_A + \frac{1}{2}H_C - H_{AC}\right)F_{AC} + \left(\frac{1}{2}H_B + \frac{1}{2}H_C - H_{BC}\right)F_{BC} \\ - K_A V_A - K_B V_B - K_C V_C.$$

As long as the volume does not change, we will then come back to the Ansatz in no. 2, whereby the surface tension between two media seems to be given by:

$$(33) \quad T_{AB} = \frac{1}{2}H_A + \frac{1}{2}H_B - H_{AB}.$$

In the case where one can set $\rho_B = 0$, it will follow that one simply has:

$$T_{AB} = \frac{1}{2}H_A.$$

If C represents a solid body and if one can set $\rho_B = 0$ then it will follow from eq. (8) that the boundary angle ω_A of A with the body is:

$$(34) \quad \cos \omega_A = \frac{2H_{AC} - H_A}{H_A}.$$

In the event that C is a vertical cylinder, the angle ω_A can be acute or obtuse according to whether a rise or a depression, resp., of A on C relative to the level plane exists, so according to whether $2H_{AC} > H_A$ or $< H_A$, resp. [i.e., one might say, when the meniscus experiences an attraction to the body that is more or less than twice as strong as its attraction to the fluid]⁽⁶⁵⁾.

The relation (34) will be impossible to satisfy when $H_{AC} > H_A$. However, if we assume that the fluid A is drawn along in an extremely-thin layer in some part \mathfrak{S} of the wall of C , and we now understand F_{AB} , F_{AC} to mean only the areas of the separation surface in question if we ignore that layer, then if we recall (27) and the relation $\vartheta(0) = \theta(0)$, a term:

$$- \int_{\mathfrak{S}} \left[H_{AC} \left(1 - \frac{\theta_{AC}(s)}{\theta_{AC}(0)} \right) - H_A \left(1 - \frac{\theta_A(s)}{\theta_A(0)} \right) \right] df$$

will be added to the expression (32) for the total energy, which is extended over the surface \mathfrak{S} , in which s denotes the thickness of the layer at the element df of \mathfrak{S} . For a suitable force law – e.g., the one in (28) – the possibility of reducing the potential energy by means of the layer would then exist. Hence, such a layer (viz., wetting of the wall) must actually come about, and in that way, a boundary angle of zero will then arise on the boundary of the perceptible separation surface ⁽⁷¹⁾.

16. Introduction of cohesion into the relation between density and pressure. –

From hydrodynamical principles, the appearance of the term $-KV$ in the energy of a fluid A is equivalent to the assumption that a further constant pressure K exists in the interior of A , in addition to the so-called hydrostatic pressure. If one writes $K = a\rho_A^2$ then a will depend upon only the force law $\varphi(r)$, but not upon the density ρ_A . If one represents the saturated vapor of the fluid A by B then the energy in a subset M of the substance [assuming a homogeneous, continuous distribution of mass up to the boundary, along with the independence of the law of cohesion on temperature (for a more general presentation, see the article V 10 by **Kamerlingh Onnes**), and assuming that, say, F/V does not come under consideration in comparison to $1/r_0$] will be $-K \frac{M}{\rho_A} = -a \rho_A M$ in

the fluid phase and $-K \rho_B^2 \frac{M}{\rho_B} = -a \rho_B M$ in the vapor phase, and for that reason $a(\rho_A - \rho_B)$ is referred to as *the internal latent specific heat of vaporization* (see V 10 for this, as well) ⁽⁷²⁾. (The additive constant in the energy was fixed in such a way that the value zero would arise as an upper limit for the energy when one resolves the medium into nothing but volume elements that are infinitely-distant from each other.)

For the phenomena that take place for constant volumes, the quantity K does not apply at all, while the first term $-KV$ in the energy will greatly exceed the other one $\frac{1}{2}HF$. For that reason, one can expect to get information about the magnitude of K only in processes that are connected with changes in the density, and that is why **van der Waals** ⁽⁷³⁾ first had the idea of theoretically investigating the introduction of that quantity into the relationship between pressure and density at constant temperature. **Van der**

⁽⁷¹⁾ **Gauss**, *Principia generalia*, art. 32.

⁽⁷²⁾ **Dupré**, *Théorie mécanique de la chaleur*, 1869, pp. 152.

⁽⁷³⁾ **Van der Waals**, *Die continuität des gasf. u. flüss. Zustandes*, Leipzig, 1881.

Waals based the derivation of the relation on the virial theorem of **Clausius** ⁽⁷⁴⁾. The law comes about from the following intuitions: Matter is not distributed continuously, but consists of molecules. In addition to **Laplace**'s forces of cohesion, they are subject to further repulsive forces (mutual repulsions), and in that way, they are not realized by visible motions, and indeed, such that when one compares their states of motion at any two moments t and $t + \tau$, one can say approximately that only the relative positions and motions of the particles have changed. In any event, when one takes the mean value of the kinetic energy of the progressive motion of the molecule over the time interval from t to $t + \tau$, the difference quotient:

$$\frac{1}{\tau} \left[\frac{1}{4} \frac{d \sum m(x^2 + y^2 + z^2)}{dt} \right]_t^{t+\tau}$$

can already be neglected in comparison to that mean value for a relatively small τ . The sum in this extends over all molecules, and m means the mass, while x, y, z are the coordinates of the center of mass of a molecule. When one makes the approximations that were just given, a partial integration will transform that mean value of the energy directly into the mean virial of the forces that act upon the molecules over the time interval from t to $t + \tau$. Now, from the principles of the theory of gases, that mean energy of the progressive motion is $\frac{3}{2} \frac{R}{M} \rho VT$, where R represents the universal gas constant, M

is the molecular weight, ρV is the total mass, and T is the absolute temperature of the fluid. The virial of the forces of cohesion is calculated under the assumption that the radius of activity is much large than the size of the molecules, as it would be for continuous, homogeneously-distributed masses, and therefore, from (29), it can be set equal to $\frac{3}{2} a \rho^2 V$. The mean virial of the constant force p that acts on the surface is found by decomposing the volume into elementary pyramids with the zero-point as their vertices and the surface elements as the base surfaces, and is immediately found to be equal to $\frac{3}{2} pV$. The mean virial of the repulsive forces is calculated by the methods of the

theory of gases, can be written as a fraction $\frac{b\rho}{1-b\rho}$ of the mean energy of the progressive

motion, in which b is approximately constant and is connected with the molecules in a space that possesses a mass unit. (For the dependency of the quantity b on volume and temperature, again see the article by **Kammerlingh Onnes** V 10.) What finally results then is the **van der Waals** state equation in the form:

$$(35) \quad p + a \rho^2 = \frac{RT}{M} \frac{\rho}{1-b\rho}.$$

From the observed data, one can use this relation to compute $K = 10,500$ Atm. for water at 0° and 1 Atm. pressure and $K = 1430$ Atm. for ether, while the quotient H / K ,

⁽⁷⁴⁾ Cf., also **Maxwell**, *Sc. Papers* 2, pp. 407, 418; **H. A. Lorentz**, *Boltzmann-Festschrift*, 1904, pp. 721 [reprinted in *Abh. über theor. Phys.* 1 (1906)]

which serves as a measure of the radius of activity of the forces of cohesion, amounts to 15×10^{-9} cm for water and 29×10^{-9} cm for ether.

17. Theories on the avoidance of discontinuities in density. – Laplace's theory of capillarity was based upon the assumption of homogeneous fluids throughout. **Poisson** ⁽⁷⁵⁾ proceeded from the idea that a rapid change in density must take place at the boundary surface of a fluid, and took that fact into account with the intention of easing the complications that lay in the assumption of pressure discontinuities at the separation surface. In **Poisson's** theory, one does not modify the equations for the capillary phenomena, but only the meaning of the two constants K and H for the law of cohesion forces.

Maxwell ⁽⁷⁶⁾, Lord **Rayleigh** ⁽⁷⁷⁾, **van der Waals** ⁽⁷⁸⁾ pursued the further consequences of the assumption of a continuous variation of density at the separation surface. As the simplest case, one treats the equilibrium of a fluid A in contact with its saturated vapor B . Gravity shall be ignored. The entire space of fluid and vapor will be divided by surfaces on which the density is constant each time. Transverse to them, the value of the density varies rapidly inside of an extremely-thin layer and very soon comes close to well-defined limiting values ρ_A (ρ_B , resp.) on one side of it and the other.

For the complete implementation of the Ansatz that is implied by hydrodynamical (or thermodynamic) principles, one particular force law for cohesion has proved to be especially suitable ⁽⁷⁹⁾, which shall likewise be used here, namely, the one that was stated in (28), which represents the potential function for two unit masses at a distance of r by:

$$-k \frac{e^{-cr}}{r},$$

and k , as well as c , are positive constants. The potential that is due to the total mass of the substances (A and B) on a unit mass at a location x, y, z is then:

$$\Psi(x, y, z) = -k \int \rho' \frac{e^{-cr}}{r} dv',$$

in which the integral extends over all volume elements dv' in the substance, and r denotes the distance from the reference point x, y, z to the element dv' . Now, that function $\Psi(x, y, z)$ satisfies the differential equation:

⁽⁷⁵⁾ **Poisson**, *Nouvelle théorie de l'action capillaire*. – Critiques of **Poisson's** theory were given by **Minding**, Dove's Repert. d. Phys. Bd. 5; **J. Stahl**, Ann. Phys. Chem. **139** (1870), pp. 239; **B. Weinstein**, Ann. Phys. Chem. **27** (1886), pp. 544.

⁽⁷⁶⁾ **Maxwell**, "Capillary action" (*Sc. Papers*, pp. 541).

⁽⁷⁷⁾ Lord **Rayleigh**, Phil. Mag. **33** (1892), pp. 209 (*Sc. Papers* 3, pp. 513).

⁽⁷⁸⁾ **Van der Waals**, Zeit. phys. Chem. **13** (1894), pp. 657; **H. Hulshof**, Ann. Phys. Chem. (4) **4** (1901), pp. 165.

⁽⁷⁹⁾ **Van der Waals**, *loc. cit.*, pp. 706.

$$(36) \quad \Delta\Psi = \frac{\partial^2\Psi}{\partial x^2} + \frac{\partial^2\Psi}{\partial y^2} + \frac{\partial^2\Psi}{\partial z^2} = c^2 \Psi + 4\pi k \rho$$

everywhere in the space of the substance, and on the basis of that relation, the force field that is present can be described as an initially-given state of tension in the substance, instead of stemming from forces at a distance, in the following way ⁽⁸⁰⁾: One sets:

$$\left(\frac{\partial\Psi}{\partial x}\right)^2 + \left(\frac{\partial\Psi}{\partial y}\right)^2 + \left(\frac{\partial\Psi}{\partial z}\right)^2 = \Phi^2,$$

$$\frac{1}{8\pi k} (c^2 \Psi^2 - \Phi^2) = \Sigma_1, \quad \frac{1}{8\pi k} (c^2 \Psi^2 + \Phi^2) = \Sigma_2.$$

The substance appears to be threaded with directed “lines of force” that are perpendicular to the surfaces $\Psi = \text{const.}$ and lead from larger to smaller values of Ψ . A tension Σ_1 prevails at each location in the direction of the force line that goes through it, as well as the opposite direction, and in all directions that are perpendicular to it, there is a tension Σ_2 such that for every closed part I of the substance, the components and rotational moments of the cohesions that are exerted from the remaining part II on I are calculated in precisely the same way as the distribution of those tensions on the surface of I.

At a very slight distance from the transition layer, Ψ is already almost constant, Φ is almost zero, and $\Sigma_1 = \Sigma_2$, so the phenomena of surface tension can be explained by the previous cohesion K in the transition layer as something that results from the difference $\Sigma_1 - \Sigma_2$.

From hydrodynamical principles, in order for there to be equilibrium in the fluid-vapor system at equal temperature, it is necessary that the complete differential:

$$(37) \quad d\Psi = -\frac{d\Pi}{\rho},$$

where the Π in this is a function that depends upon only density and temperature at the location that is referred to as the *thermal pressure* ⁽⁸¹⁾. If we write $2\pi k / c^2 = a$ then from (36), at a distance from the transition layer where the fluid appears homogeneous, one will have $\Psi = -2a \rho_A$, and where the vapor seems homogeneous, one will have $\Psi = -2a \rho_B$. We set $\Pi = p + a \rho^2$, in general, and call p the *hydrostatic pressure*. p will then approach the same constant p_0 on both sides of the layer, namely, the external pressure or saturation vapor pressure. When one recalls (37), equation (36) will be written:

⁽⁸⁰⁾ **G. Bakker**, Zeit. phys. Chem. **48** (1904), pp. 17.

⁽⁸¹⁾ **Van der Waals** used that terminology; **H. A. Lorentz** referred to the same concept as “kinetic pressure” in Zeit. phys. Chem. **7**.

$$(38) \quad \Delta\Psi = - c^2 \int_{p_0, \rho_A}^{p, \rho} \frac{dp}{\rho}.$$

From now on, it will be assumed that the dependency of p on ρ and temperature can be represented in the transition layer by the same **van der Waals** formula (35) as it is in the homogeneous phases, which admittedly finds its support in one's the power to believe in that formula more than in its derivation. The curve for p as a function of the increasing argument $1/\rho$ (see the article by **Kammerlingh Onnes**, V 10) that is given in that way varies between the two points $p_0, 1/\rho_A$ and $p_0, 1/\rho_B$ within the interval from $1/\rho_A$ to $1/\rho_B$ by falling, rising, and falling again, initially below the line $p = p_0$, then up to a certain point of intersection with it, then above it, and along its first segment that lies below $p = p_0$, it must obviously exhibit a well-defined point $p_1, 1/\rho_1$ for which the integral over that curve segment is:

$$- \int_{p_0, \rho_A}^{p_1, \rho_1} \frac{dp}{\rho} = 0.$$

(Fig. 22). From (38), one will then have $\Delta\Psi = 0$ at that location on the curve.

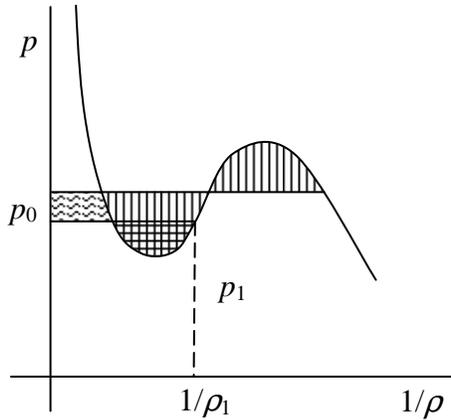


Figure 22.

The combinations $p, 1/\rho$ that correspond to the wavy lines ($\rho_A > \rho > \rho_B$) are unstable for homogeneous phases, and **van der Waals** found that they were stable in the transition layer. If (37) were integrated along a path that goes from the homogeneous interior of the fluid to the homogeneous interior of the vapor then that would give:

$$\int_{p_0, \rho_A}^{p_0, \rho_B} \frac{dp}{\rho} = 0$$

over those wavy lines, which is precisely the formula that **Clausius** and **Maxwell** presented for the determination of the pressure p_0 of the saturated vapor by means of isotherms by applying the second law of thermodynamics to unstable states.

Now, the surfaces of constant density might be assumed to a family of parallel planes $z = \text{const.}$, in particular. The differential equation (37) would then be written:

$$\frac{d^2\Psi}{dz^2} = c^2 \Psi + 4\pi k \rho = c^2 \Psi - 4\pi k \frac{d\Pi}{d\Psi},$$

and integration would yield:

$$\left(\frac{d\Psi}{dz}\right)^2 = c^2 \Psi - 8\pi k (p + a \rho^2 - p_0).$$

For $\rho = \rho_1, p = p_1$, $\frac{d^2\Psi}{dz^2}$ will increase through zero and then $\frac{d\Psi}{dz} = \Phi(z)$ will achieve its greatest value $\Phi_1 = \sqrt{8\pi k(p_0 - p_1)}$; one will have $z = 0$ there. In place of the previous surface tension, one will now have:

$$\frac{1}{2}\bar{H} = \int (\Sigma_2 - \Sigma_1) dz = \frac{1}{4\pi k} \int [\Phi(z)]^2 dz,$$

when taken along the z -axis from the homogeneous fluid to the homogeneous vapor.

The curve for $\Phi(z)$ as a function of z very soon becomes asymptotic to the z -axis on both sides of $z = 0$. If the piece of it that lies above the z -axis were replaced approximately by a parabola $\Phi_1 - \Phi = \Phi_1 \left(\frac{z}{z_0}\right)^2$ that contacts it at the vertex and the pieces $z \leq -z_0$ and $z_0 \leq z$ of the z -axis that are placed to the left and right of it were replaced approximately by an equal area over the z -axis then it would follow that:

$$\frac{1}{2}\bar{H} = \frac{8}{5} \frac{\sqrt{2\pi k(p_0 - p_1)}}{c^2},$$

in which, at the same time, $2z_0 = \frac{15}{16} \frac{\frac{1}{2}\bar{H}}{p_0 - p_1}$ is regarded as roughly the density of the transition layer inside of which the inhomogeneous behavior would take place.

In a recent paper, **Bakker** ⁽⁸²⁾ sought to give a theory that would explain the observations of **Reinhold** and **Rücker** ⁽⁸³⁾, who found that soap films at their thinnest locations, which are characterized by the discontinuous appearance of black flecks, have a thickness around 10^{-6} cm, and immediately next to them they suddenly jump to a density around 5×10^{-6} cm.

⁽⁸²⁾ **G. Bakker**, Zeit. phys. Chem. **51** (1905), pp. 344.

⁽⁸³⁾ Proc. Roy. Soc. **26** (1878), pp. 334; Phil. Trans. **172** (1882), pp. 447; Phil. Trans. **174** (1884), pp. 645; Ann. Phys. Chem. **44** (1891), pp. 778.

Bakker computed the constant k for that:

$$\begin{array}{ll} \text{For water:} & k = 7.53 \times 10^{23} \\ \text{For ether:} & k = 1.54 \times 10^{23} \end{array} \quad \begin{array}{ll} \text{for} & T = 325^\circ, \\ \text{for} & T = 125^\circ. \end{array}$$

18. Entropy and mass density of a dividing surface. – When two fluids A and B that bound each other are found to be in equilibrium, both thermally and chemically, and they also seem to be homogeneous at a very slight distance from the separation surface, nonetheless, each of them will be altered by the influence of the other one in the immediate neighborhood of the boundary. **Gibbs** ⁽⁸⁴⁾ has developed an Ansatz for including that influence in the calculations without making any hypothesis in regard to the molecular forces of attraction. The inhomogeneous transition layer between A and B has a very narrow thickness, from experiments. One chooses any point on that layer and lays a surface through it and all points in the layer that lie correspondingly in regard to the immediately bounding matter; that surface is called the *dividing surface*. The choice of that surface is arbitrary to some extent. One can assume that one can select it arbitrarily from a family of very-close-lying parallel surfaces that fill up the entire layer. The matter couplings that come under consideration in A , B , and the transition layer might be constructed from the materials a , b , ..., which are considered to be *independent* components. For the total structure that consists of A , B , and the transition layer, let U be the total internal energy, let S be the total entropy, and let M_a , M_b , ... be the total masses of a , b , ... We let V' , V'' denote the volumes of A and B , measured up to the dividing surface, and let F denote the area of the dividing surface. Furthermore, let u' , s' , ρ'_a , ρ'_b , ... be the spatial densities of energy, entropy, ... of the components a , b , ..., resp., of the space A , where A appears homogeneous, and let u'' , s'' , ρ''_a , ρ''_b , ... be the corresponding densities for B , where B appears homogeneous. Finally, we write the quotients of the differences:

$$U - V'u' - V''u'', \quad S - V's' - V''s'', \quad M_a - V'\rho'_a - V''\rho''_a, \dots$$

by the areas F by u , s , ω_a , ω_b , ...; those quotients are called the *surface densities of the energy, entropy, and mass components* for the dividing surface between A and B .

It will be assumed that u' is a function of the arguments s' , ρ'_a , ρ'_b , ..., just as u'' is a function of the arguments s'' , ρ''_a , ρ''_b , ..., and one will further introduce the assumption that u is also only a function of the arguments s , ω_a , ω_b , ... (Cf., on this, the general conception of spatial energy density that was touched upon in the beginning of no. 5.) Consequently, one will succeed in characterizing the equilibrium state by means of the thermodynamic principle that U is a minimum for constant values of S , M_a , M_b , ... To the extent that one is dealing with homogeneous masses, that Ansatz was also spoken of in the article by **Bryan**, V 3, no. 26. Only the special consequences of it that flow out of the new assumption in the transition layer shall be pursued here.

If one develops the complete differential:

⁽⁸⁴⁾ **Gibbs**, *Equilibrium of heterogeneous substances*, pp. 380.

$$(39) \quad du = T ds + \mu_a d\omega_a + \mu_b d\omega_b + \dots$$

then T will be the temperature, and μ_a, μ_b, \dots are called the *potentials* for the component of the transition layer. In order for there to be equilibrium, it would be necessary that the temperature in the bounding homogeneous masses should be the same, and furthermore that the potential should be the same for each component of the layer that is found in a bounding homogeneous mass. If a component is found in only the layer then, by contrast, its surface density in the layer would have to be specified from the outset.

It follows from (39) that:

$$d(Fu) = T d(Fs) + \sigma dF + \mu_a d(F\omega_a) + \mu_b d(F\omega_b) + \dots,$$

in which one sets:

$$(40) \quad \sigma = u - T s - \mu_a \omega_a - \mu_b \omega_b - \dots$$

From now on, σ will be referred to as the *surface tension* in the dividing surface, and that will imply that:

$$(41) \quad d\sigma = -s dT - \omega_a d\mu_a - \omega_b d\mu_b - \dots$$

A relation that gives u as a function of $s, \omega_a, \omega_b, \dots$ or s as a function of $s, \omega_a, \omega_b, \dots$ will be referred to as a *fundamental equation* for the dividing surface.

Analogously, one will have:

$$(42) \quad \begin{aligned} d(V'u') &= T d(V'u') - p dV + \mu_a d(V'\rho'_a) + \mu_b d(V'\rho'_b) + \dots \\ -p' &= u - T s' - \mu_a \rho'_a - \mu_b \rho'_b - \dots \end{aligned}$$

in the homogeneous mass A (and indeed with the same values of T and μ_a, μ_b, \dots as long as the component in question actually exists in A), with corresponding relations in the homogeneous mass B . In that way, p' and p'' then mean the hydrostatic pressure in A (B , resp.). As was shown in (10), it will follow that:

$$(43) \quad p' - p'' = \sigma \left(\frac{1}{R_1} + \frac{1}{R_2} \right)$$

for the form of the dividing surface. The densities $u, s, \omega_a, \omega_b, \dots$ generally still depend upon the choice of the dividing surface in the layer; however, in the case of a planar dividing surface, the value σ will be independent of that choice, which is easy to see on the basis of (43).

If the independent components a, b, \dots are fixed in such a way that one cannot have $\rho'_a < 0$, and if only ρ'_a is changed in the homogeneous phase A , while keeping T, p', ρ'_b, \dots constant, then the behavior of ideal gases and dilute solutions will suggest that when

ρ'_a decreases to zero, $\rho'_a \frac{d\mu_a}{d\rho_a}$ will approach a well-defined positive (which is necessary from stability considerations) limiting value, so for very small values of ρ'_a , the potential μ_a can be represented essentially by an expression $K_a \log \rho'_a$, in which K_a means a positive function of T, p', ρ'_b, \dots (⁸⁵). The total quantity of a will then be:

$$M_a = V' \rho'_a + V'' \rho''_a + F \omega_a .$$

Now, if neither M_a nor ρ'_a, ρ''_a can be negative then for small values of the spatial densities ρ'_a, ρ''_a , the surface density ω_a can have arbitrarily large positive values, but only small negative values. Moreover, on the basis of what was just done, the relation (41) will show that a slight addition of matter can very strongly reduce the surface tension that exists between two media, but it cannot increase it appreciably. As a rule, surfaces that were quite freshly made cannot see a change in their surface tension, insofar as it takes time to establish the static surface density (⁸⁶).

If one places small pieces of camphor on a pure water surface then the camphor will dissolve in the water at the contact locations, and the surface tension will be lowered there. The camphor particles go into a lively state of motion in such a way that this change in surface tension will take place at different places in different degrees (⁸⁷). Lord **Rayleigh** (⁸⁸) found that the motion of the camphor will come to an end when the water surface is contaminated by an oil layer of any sort to the extent that the tension drops down to just the value that it would achieve for water that is saturated with camphor, namely, 53 erg/cm²; i.e., 72% of the value 74 for pure water. That “camphor point” brings about a layer of roughly 2×10^{-7} cm in thickness for olive oil. Lord **Rayleigh** (⁸⁹) has measured the influence of even more minor impurities in the water on the surface tension and found that the drop in tension will first begin to be more discontinuous for an oil layer of, say, 1×10^{-7} cm, and will again become more sluggish when the camphor point is exceeded.

The Ansatz (39) gave **Gibbs**, in particular, an opportunity to carry out many investigations into the behavior of fluid films.

Gibbs also applied the same principles to the separation surfaces between a fluid and a fixed amorphous or crystalline body. For crystalline ones, the tension σ in the bounding surface would be a function of the location of the surface in the crystal, and the form of very small crystals that are in equilibrium with the surrounding solution would be determined essentially by the condition that the sum $\sum \sigma F$ of the surface energies over all surfaces must be a minimum relative to the volume that is present.

(⁸⁵) **Gibbs**. *loc. cit.*, pp. 194.

(⁸⁶) **A. Dupré**, *Théorie mécanique de la chaleur*, Paris, 1869, pp. 377; Lord **Rayleigh**, Proc. Roy. Soc. **47** (1890), pp. 281 (*Sc. Papers* 3, pp. 341).

(⁸⁷) **Van der Mensbrughe**, Mém. couronnés de l'acad. de Belg. **34** (1869).

(⁸⁸) Lord **Rayleigh**, Phil. Mag. **30** (1890) (*Sc. Papers* 3, pp. 383).

(⁸⁹) Lord **Rayleigh**, Proc. Roy. Soc. **47** (1890), pp. 364 (*Sc. Papers* 3, pp. 347); **A. Pockels**, Nature **43** (1891), pp. 437; *ibid.*, **48** (1893), pp. 153.

When one considers gravity, as a result of the Ansatz (41), the previous condition for the form of the separation surface will be modified into the equations:

$$p' - p'' = \sigma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) + g \omega \cos(nz), \quad \frac{d\sigma}{dz} = g \omega$$

in which n is the normal that points to B , $\frac{1}{R_1} + \frac{1}{R_2}$ is the mean curvature towards B , and $\omega = \omega_a + \omega_b + \dots$ means the total mass density at the variable locations on the dividing surface.

The thermal relationships to which the Ansatz (41) would lead were already deduced by **W. Thomson** ⁽⁹⁰⁾ by considering certain cyclic processes. In order to give an example, suppose that a planar fluid lamina A is found in a saturated vapor B . Let the dividing surface be laid on each side of the lamina in such a way that the surface density of the single component a that is present will be zero, so it will then follow from (41) that $d\sigma = -s dT$. If the lamina are pulled apart, and one carries out the process isothermally and without condensation, then the total heat that must be supplied in order to maintain the unity of the resulting surface will be:

$$Q = T s = -T \frac{d\sigma}{dT} = -\frac{d\sigma}{d \log T}.$$

By contrast, if one carries out the process adiabatically and at constant external pressure p then a fixed evaporation temperature T will belong to p as the saturated vapor pressure, and in order to obtain that properly, in order to maintain the unity of the resulting surface, an amount δ_a of vapor must condense whose magnitude will be given by the condition for the zero of supplied heat:

$$s - \delta_a (s'' - s') = 0.$$

That would correspond to an increase in volume of δ_a / ρ'_a in the fluid and a decrease in volume of δ_a / ρ''_a in the vapor, and while maintaining the external pressure, one must then do an amount of work:

$$W = p s \left[\frac{1}{s'' - s'} \left(\frac{1}{\rho''_a} - \frac{1}{\rho'_a} \right) \right]$$

in order to maintain the unity of the resulting surface. The expression in square brackets here follows from the dependency between temperature and pressure of the saturated vapor as the differential quotient dT / dp [cf., the article by **Bryan**, V 3 eq. (138)], and that will imply that:

⁽⁹⁰⁾ **W. Thomson**, Proc. Roy. Soc. **9**(1858), pp. 255 or Phil. Mag. (4) **17** (1859), pp. 61; **van der Mensbrughe**, Bull. de l'acad. de Bruxelles **51** (1876), pp. 769, *ibid.*, **52** (1876), pp. 21; **P. Duhem**, Ann. de l'éc. norm. sup. (3) **2** (1885), pp. 207.

$$W = -p \frac{d\sigma}{dT} \frac{dT}{dp} = -\frac{d\sigma}{d \log p}.$$

Ostwald called the product of σ with the $2/3$ power of the molecular volume M_v of the fluid (i.e., the volume of M grams, when M denotes the molecular weight) the *molecular surface energy* of the fluid. The differential quotient $-d(M_v^{2/3} \sigma)/dT$ (one could call it the *molecular surface entropy*) lies close to the value $2.1 \text{ erg / cm}^2 \text{ grad}$ for a large number of fluids ⁽⁹¹⁾. That remarkable law, which was established experimentally by **Eötvös** ⁽⁹²⁾ and **Ramsay and Shields** ⁽⁹³⁾ (see the article by **Kammerlingh Onnes** for this) offers a method for ascertaining the molecular weight of fluids on the basis of capillary constants.

Finally, those capillarity phenomena whose theory can be based upon the **Gibbs Ansatz** (41) include the dependency of surface tension of a molten metal electrode in an electrolyte on the electromotive force of its polarization ⁽⁹⁴⁾.

(Completed in the Fall of 1906)

⁽⁹¹⁾ For water, which belongs to the exceptions here, the molecular entropy lies between 0.9 and 1.2. Hence, for a water layer, the aforementioned latent heat of expansion will be almost equal to one-half of the work that must be done ($Q = \frac{1}{2} \sigma$) in order to create against surface tension.

⁽⁹²⁾ **Eötvös**, Ann. phys. Chem. **27** (1886), pp. 452.

⁽⁹³⁾ **Ramsay and Shields**, Zeit. phys. Chem. **12** (1893), pp. 433.

⁽⁹⁴⁾ For the theories in this experimentally richly-explored chapter in electro-capillarity, cf., **F. Krüger**, Gött. Nach. (1904), pp. 33; Jahrbuch d. Radioaktivität und Elektronik **2** (1904).