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CAPILLARY FORCES IN LIQUID BRIDGES AND FLOTATION

Capillary forces can be calculated quite generally by a thermodynamic method in which the Helmholtz energy is differentiated with respect to the appropriate geometrical coordinates. Using this method, it is shown that the usual "mechanical" approach to capillary forces is valid, provided a pressure difference term is included in addition to the surface tension and buoyancy terms. Different but equivalent descriptions of the system of forces are useful when dealing with floating solids. The calculation of capillary forces in situations of complete wetting is also discussed. Finally, applications to liquid bridges and to flotation are presented.

1 — INTRODUCTION

Capillary forces play a crucial role in a variety of situations and phenomena. For example, they are responsible for the adhesion between two solid bodies connected by a a liquid bridge and for the flotation of denser particles at the free surface of a liquid, in a gravitational field.

Equations have been derived and used to calculate such forces in a variety of simple geometrical situations. However, a careful search in the literature reveals that there is not complete uniformity in the expressions in use. Sometimes different methods have been employed to derive the same equations, and, as frequently happens when dealing with surface or interfacial tensions, a physically devious argument may lead to the correct answer.

In this paper we shall first review critically the available treatments of capillary forces; then, a general thermodynamic method will be presented which is sounder than previous methods. This method will be applied to cylindrically symmetric geometries, under various types of boundary conditions as regards the contact between the liquid surface and the solids. Simple equations are obtained in this way for the resultant force and resultant moment that have to be applied to the solid bodies to keep the system at equilibrium in a given configuration.

Flotation of a particle can be regarded as a special case of a liquid bridge between the floating particle and the container, the system being in a uniform gravitational field. The two situations can therefore be treated simultaneously. There is, however, an useful classification of liquid bridges which we shall adopt here. It has to do with the boundary conditions for the liquid surface (or fluid interface) at the line of contact with the solids. There are essentially two possibilities: i) the angle of contact θ is fixed; ii) the line of contact is a fixed line in the solid. We shall distinguish these boundary conditions by the symbols θ and r. We may then consider three types of bridges between two solid bodies: θ-bridges, r-bridges and θ,r-bridges, respectively when the boundary conditions at the two solid surfaces are θ,θ; r,r; θ,r. Examples of each type are shown in fig. 1.

The two fluids will be denoted by 1 and 2. In bridges, the inner fluid is always fluid 1. It will be assumed that the contact angle, θ, of fluid 1 with the solid (in presence of fluid 2) is related to the interfa-

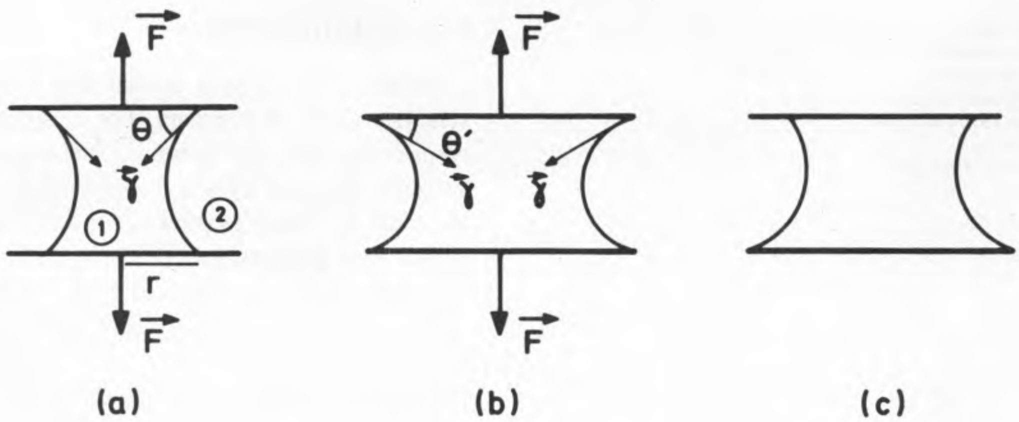

Fig. 1

Examples of bridge configurations between parallel plates, with different boundary conditions: a) θ-bridge; b) r-bridge; c) θ, r-bridge. The solids are shown in heavy lines. The figure applies both to axial and cylindrical symmetry

cial tensions γ_{S1}, γ_{S2} and to the fuid interfacial tension, γ, by Young's equation

$$\cos\theta = \xi \ ; \ \xi = \frac{\gamma_{S1}-\gamma_{S2}}{\gamma} \qquad (1)$$

provided $|\xi| < 1$. Capillary forces are frequently calculated assuming conditions of complete wetting of the solids by one of the fluids ($|\xi| > 1$) and this is taken as implying a 0 (or 180°) contact angle. Such situations of complete wetting have to be regarded carefully, however, because the equilibrium configuration of the interface will then be different from that for $|\xi| = 1$, that is, for a true 0 (or 180°) contact angle. The calculation of capillary forces in such cases will also be discussed.

2 — PREVIOUS TREATMENTS OF THE PROBLEM

Most studies of capillary forces have been made for axially symmetric bridges between two identical solids. We shall then review critically these studies by considering a θ-bridge between two identical parallel plates in the absence of gravity (fig. 1a). The shape of the fluid interface can be calculated by solving the equation of Young-Laplace subject to given conditions, namely, the volume of the inner fluid, the distance between the plates and the contact angle. When more than one solution is possible, we assume that the stable solution has been found. The bridge is in equilibrium provided equal and opposite forces $\vec{F}$ are applied to the plates, along the symmetry axis.

The first group of derivations of the expression for the force is based on a mechanical approach to the problem, in that $\vec{F}$ is obtained as the resultant of various "internal" forces which act on the plates. It is well known that there is a pressure difference $\Delta P = P_2 - P_1$ between the two sides 1 and 2 of the interface, given by [*e.g.*1]

$$\Delta P = \gamma\left(\frac{1}{R_1} + \frac{1}{R_2}\right) \qquad (2)$$

where R_1 and R_2 are the principal radii of curvature at any point of the interface (the average curvature is of course constant in the absence of applied fields). This pressure difference gives rise to a force $\vec{F}_1$ along the symmetry axis

$$F_1 = \Delta P.\pi r^2 \qquad (3)$$

where r is defined in fig. 1.$F_1 > 0$ indicates that the force in each plate is directed to the other plate. Some authors [*e.g.*2] have assumed that the total applied force equilibrates $\vec{F}_1$. In general, however, a second term $\vec{F}_2$ is considered, which is the resultant of the surface tension forces acting on the plates at the line of contact with the solid:

$$F_2 = 2\pi r.\gamma\sin\theta \qquad (4)$$

where θ is the contact angle. In the flotation literature [*e.g.*3,4] it is frequently assumed that the total force is simply $-\vec{F}_2$. Obviously, in general $F_1 \neq F_2$. Most authors [*e.g.*5-7] take for the total applied force the value $-(\vec{F}_1 + \vec{F}_2)$. As we will show this is cor-

rect. But the mechanical approach is weak precisely in relation to $\vec{F}_2$, because the identification of an interfacial tension with a force acting on the interface is not straightforward, as often assumed.

The second group of derivations is best illustrated by the arguments put forward by Heady and Cahn [7]. They simply note that

$$F_1 + F_2 = \text{constant} \tag{5}$$

is a first integral of the Young-Laplace equation of the interface profile, and this is indicated as a proof that $-(\vec{F}_1 + \vec{F}_2)$ is the force that must be applied to the plates. This implication is not obvious. All that can be said is that $(\vec{F}_1 + \vec{F}_2)$ is the same for all bridges which have the same profile (such bridges would of course require different liquid volumes and contact angles, and different plate separations). Heady and Chan show that eq. (5) can be obtained by imposing the stationarity of the Helmholtz energy of the bridge, with respect to variations in the interface shape. This too cannot be considered as a proof that the force is $-(\vec{F}_1 + \vec{F}_2)$, since the stationarity of the energy simply leads to the equation of Young-Laplace of wich eq. (5) is an equivalent form. Finally, this type of argument is not susceptible of generalization to non-symmetrical geometries, when the system of forces in each solid body may not be equivalent to a single force [8].

As we will show in the following section, to obtain the force by a thermodynamic argument it is necessary to consider a reversible transformation of the system in which the force performs work, that is, a transformation in which the plate separation changes. The simple consideration of the system at constant plate separation cannot give any information about the forces that have to be applied to the plates.

3 — THERMODYNAMIC TREATMENT OF CAPILLARY FORCES

The basis of the approach is as follows. We define a closed system in equilibrium, comprising the two solid bodies and fixed volumes of the two fluids. The shape of the fluid interface is obtained from Young-Laplace equation (satisfying the particular boundary conditions of the problem), as a function of the relative position of the two solid bodies (*e.g.*, as a function of plate separation in the examples of fig. 1). The Helmholtz energy, A, of the system is then calculated as a function of the relative position of the solids. Finally, the resultant force and the torque in the solids are obtained by differentiating the Helmholtz energy with respect to the appropriate coordinates used to define the relative position. In the example of fig. 1a,

$$F = \frac{\delta A}{\delta d}\,(\delta V = 0\,;\, \delta\theta = 0) \tag{6}$$

where d is the plate separation, gives the force perpendicular to the plates, which in this case is the only force required for equilibrium. The difficulty of the method is in the final operation of simplifying the derivatives of A in an attempt to give a simple form to F. For example, this is already very difficult for axisymmetric bridges, mainly because the shape of the profile cannot be written in closed form. However, it is always possible to use numerical methods to obtain the force from $\delta A/\delta d$. This has been done [9] for axisymmetric θ- and r-bridges between two identical plates, leading to the conclusion that the force $F = \delta A/\delta d$ coincides with $(F_1 + F_2)$:

$$F = \frac{\delta A}{\delta d} = (F_1 + F_2) = \pi r^2 . \Delta P + 2\pi r \gamma \sin\theta. \tag{7}$$

Note that in the case of r-bridges, θ is not the angle of contact.

The calculations are considerably simpler for cylindrically symmetric bridges, in the absence of gravity, because the cross section of the interface then includes two circles of the same radius. In Appendix 1 we give an example of the calculation of the force from eq. (6) for a θ-bridge between two identical wedge shaped solids, which shows that the applied force in each solid equilibrates the pressure (F_1) and surface tension (F_2) forces, which, per unit length of the bridge are given by (see fig. 9)

$$F_1 = 2r . \Delta P = 2\gamma r/R \tag{8a}$$

$$F_2 = 2\gamma \cos\alpha \tag{8b}$$

where R is the radius of the cylindrical interface and 2r is the width of the interface at the wedges. Other types of cylindrically symmetric bridges, shown in fig. 2, have been studied in the same way, leading to

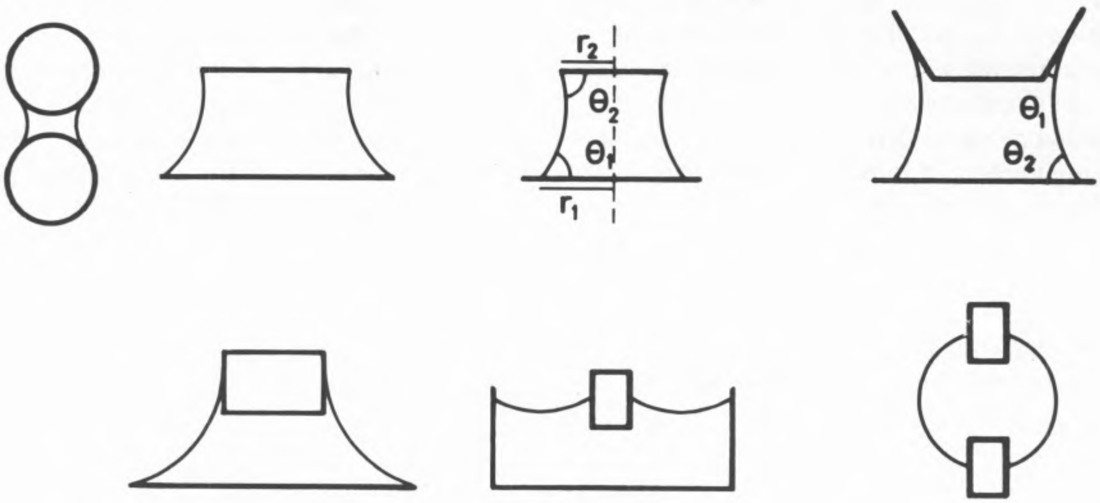

Fig. 2
Cylindrically symmetric bridge profiles which were analysed for the calculation of the capillary forces. The solid surfaces are shown in heavy lines

the same expression for the force on each plate. These bridges all have a plane of symmetry along the cylindrical axis, so that the applied forces are in that plane and form a system equivalent to zero. This is a consequence of the relation (see fig. 2)

$$\frac{r_1}{R} + \sin\theta_1 = \frac{r_2}{R} + \sin\theta_2 \tag{9}$$

which is analogous to eq. (5), and can also be regarded as a first integral of Young-Laplace equation for cylindrically symmetric bridges.

A more complicated cylindrical geometry is shown in fig. 3. For this asymmetric r-bridge we have calculated the force components along two perpendicular directions and the moment of these forces in relation to the extremity of one of the plates. This has been done by differentiating the Helmholtz energy with respect to d, b and ϵ, respectively, while keeping the two other parameters and the volume constant. Again, the results obtained show that the system of applied forces on each plate equilibrates the pressure force (acting on the centre of the plate) and the surface tension forces (acting on the edge of the plate). Furthermore, the system of applied forces on the two plates is equivalent to zero. These conclusions are a direct consequence of simple geometrical relations that can be written by taking into account the constant radius of curvature, R, of the interface, such as (see fig. 3)

$$\begin{aligned} b &= R(\sin\theta_1' - \sin\theta_2') \\ d &= R(\cos\theta_1' + \cos\theta_2') \\ c &= R(\cos\theta_1 + \cos\theta_2 - \cos\theta_1' - \cos\theta_2'). \end{aligned} \tag{10}$$

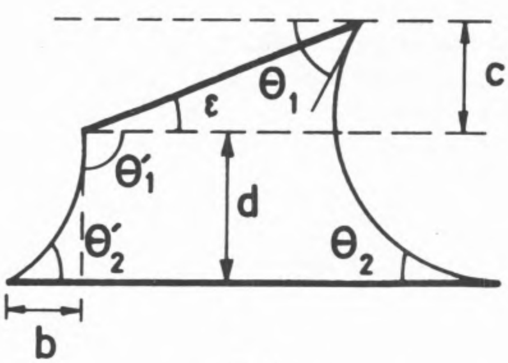

Fig. 3
Cylindrically symmetric liquid bridge (r-type) between two non--parallel plates

The calculation of the force due to a cylindrically symmetric bridge between two solids of arbitrary shape is difficult to undertake, but the previous results strongly suggest that in all such cases the applied forces in each solid equilibrate the pressure and surface tension "internal forces". Since the same is truth in the case of axially symmetric bridges between two parallel plates [9], we may confidently conclude that the forces in each solid can always be obtained in that way, whatever the shape of the solids.

4 — EFFECT OF A GRAVITATIONAL FIELD. FLOTATION

In a gravitational field, $\vec{g}$, the pressure in each fuid is not constant, and additional buoyancy terms appear in the equation for the capillary forces. The exact form of these terms, and an eventual alteration of the others that already appear for $\vec{g}=0$ can be investigated by the method described in the previous section. The Helmholtz energy now includes the potential energies of the solids and fluids. An example of the application of the method to a floating prismatic rod is given in Appendix 2. The final expression obtained shows that the total applied force in the floating rod includes, in addition to the weight of the floating solid, a pressure difference term due to the curvature of the interface, a surface tension term and buoyancy terms. The buoyancies correspond to the volumes of the prisms immersed in each fluid.

When the dimensions of the container are very large, so that the radius of curvature at the apex of the interface is infinite, the suface tension term is numerically equal to $\Delta\varrho.g.V_m$ where V_m is the volume of the meniscus above or below the free level up to the vertical plane through the line of contact (see Appendix 1).

To generalize these results we denote by Γ the line of contact of the interface with the floating solid and by Σ a surface bounded by this curve (fig. 4). Σ divides the solid into two parts, V_1 and V_2, immersed in each fluid. Let $\vec{I}_1$ and $\vec{I}_2$ be the vertical upthrusts of each volume in the corresponding fluid.

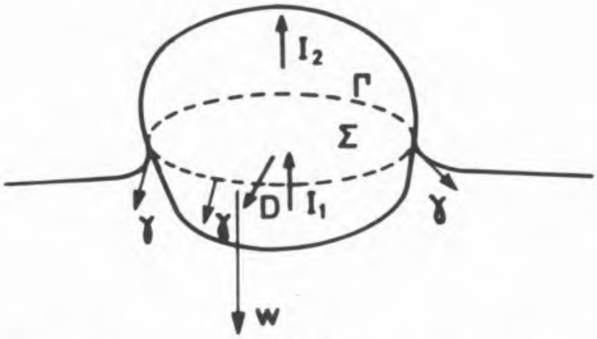

Fig. 4

Solid of arbitrary shape in flotation at an interface. Γ is the line of contact of the three interfaces and Σ a surface bounded by Γ. The system of forces that has to be applied equilibrates $\vec{I_1}$, $\vec{I_2}$, $\vec{W}$, the $\vec{\gamma}$'s, and a pressure difference force $\vec{D}$ acting on Σ

These forces are given by $I_i = \varrho_i V_i$, and are applied at the mass centre of each volume assumed homogeneous. The system of pressure difference forces on Σ can be determined as follows. Let ΔP_0 be the pressure difference at a point 0 of Γ (or Σ) which we take for origin, and z the vertical coordinate of any other point of Σ relative to 0. The system of forces

$$\Delta P = \Delta P_0 + \Delta\varrho g.z \tag{11}$$

acting perpendicularly on Σ is not in general equivalent to a single force. The horizontal and vertical resultants $\vec{H}$ and $\vec{V}$ can be determined by well known equations of hydrostatics [10]. If Σ is a planar surface, the pressure difference forces are equivalent to a resultant $\vec{D}$ applied at the pressure centre of Σ [10]. Finally let $\vec{\gamma}$ be the surface tension force at a point of Γ. $\vec{\gamma}$ is a force per unit length, normal to Γ and tangent to the interface.

The applied system of forces required to keep the floating body in equilibrium must then equilibrate the system of forces $\vec{W}$ (weight of the solid), $\vec{I}_1$, $\vec{I}_2$, $\vec{H}$, $\vec{V}$ and the forces $\vec{\gamma}$ acting on Γ. These forces are shown in fig. 4, where it was assumed that $\vec{H}$ and $\vec{V}$ are equivalent to a resultant $\vec{D}$. The complete determination of these forces requires the calculation of the interface shape by solving the equation of Young-Laplace with the appropriate boundary conditions.

If the container is very large, and the system has axial symmetry, the surface tension forces can again be interpreted in terms of the weight of the meniscus above or below the free level and up to a vertical cylinder through the line of contact Γ. This is readily concluded from a first integration of Laplace equation for axial symmetry.

The value of ΔP at any point of the line of contact of a solid placed at an interface of infinite radius of curvature at large distances from the solid is directly related to height h of the meniscus at that point, measured in relation to the free level

$$\Delta P = \Delta\varrho .\ g.h. \tag{12}$$

When the interface is flat at large distances from the solid and the system has either axial or cylindrical symmetry (with a vertical plane of symmetry in the latter case) it is possible, by combining the properties discussed above, to give a further interpretation to the flotation force $\vec{F}$, which is then vertical. Let

$\vec{W}_0$ be the weight, of the solid in the top fluid. Then $\vec{F}$ must equilibrate $\vec{W}_0$ plus the weight, in the top fluid, of the volume of bottom fluid above the general level and up to the solid surface (if the interface near the solid is below the general level the corresponding force is directed upwards) plus the upthrust in the bottom fluid of that part of the solid below the general level. This latter term may be absent when the interface is above the general level. Expressions based on this interpretation of the flotation force have been used by various authors [11--14] but generally without a formal justification. Free flotation of a denser particle is therefore possible only if the solid produces a depression of the meniscus below the free level (and vice-versa for a particle lighter than both fluids).

5 — SITUATIONS OF COMPLETE WETTING

When the surface tension ratio ξ, defined by eq. 1, is not in the interval $[-1, +1]$, the contact angle cannot be defined. Since the contact angle condition is a necessary one for equilibrium when the fluid interface ends within the solid surface [15], it can be concluded that true θ-configurations are impossible in this case. Clearly, r-configurations, if they are geometrically possible, can still occur, and for these the capillary forces are calculated in the same way as for $|\xi| < 1$.

For $|\xi| > 1$, what can be termed a pseudo θ-configuration is likely to be the actual equilibrium configuration. Examples are shown in fig. 5. For a bridge, the pseudo θ-configuration is a θ-bridge (with $\theta = 0$ or 180° according to the case) between the two solids, which is prolonged by a thin film of the wetting fluid that completely covers the solids (fig. 5a). The other fluid-solid interface is thus absent. If the surface tension of the fluid in the film is the same as in the bridge, the variable terms in the Helmholtz energy are the same as for $|\xi| = 1$ (see Appendix 1), so that the force can be calculated from the same equation with $\theta = 0$ or 180°.

Similar conclusions can be drawn for the configuration and force in the case of a floating particle with $|\xi| > 1$. In the example of fig. 5b, the film continues the fluid interface up to the edge of the prismatic rod, and in fig. 5c it "protects" the circular rod from the contact with the non-wetting fluid. In both cases the capillary forces can be calculated exactly as if $\theta = 0$, 180°.

(a) (b) (c)

Fig. 5

Examples of configurations expected when one of the fluids wets the solids: a) bridge; b, c) floating solids

6 — APPLICATIONS

6.1 — *FORCE OF ADHESION DUE TO CYLINDRICALLY SYMMETRIC θ-BRIDGE BETWEEN PARALLEL IDENTICAL PLATES*

Using the equations of Appendix 1, we have studied the effect of ξ (eq. 1) on the force of adhesion due to the bridge. The results are shown in fig. 6, which is a plot of $F/2\gamma$ as a function of ξ, for various constant values of V/d^2. V is the volume of inner fluid and d is the plate separation. We remind that for $|\xi| < 1$, it is $\cos\theta = \xi$ where θ is the contact angle with the plates; and for $|\xi| > 1$ the configuration is a pseudo θ-bridge with $\theta = 0$ or 180°.The configurations in the dotted regions of the curves of

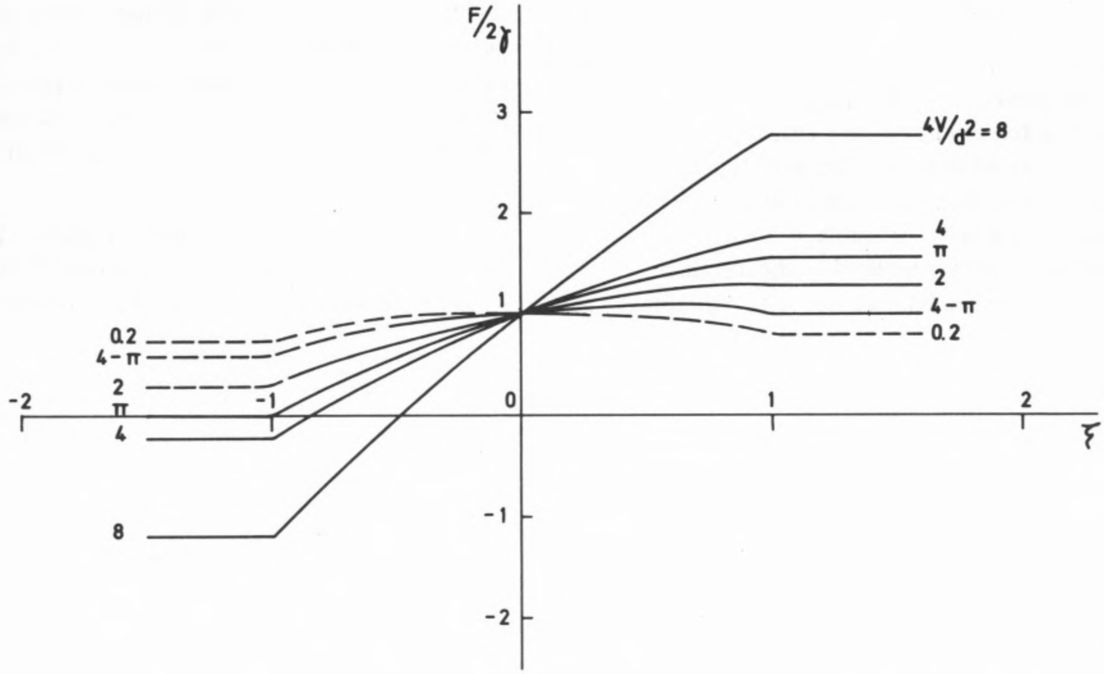

Fig. 6

Force of adhesion, $F/2\gamma$, due to a cylindrically symmetric θ-bridge between two parallel plates, as a function of contact angle ($\xi = \cos\theta$), for various values of V/d^2. V is the volume and d the plate separation. The dotted regions correspond to geometrically impossible configurations

fig. 6 are not physically possible (either $r<0$ or negative neck radius). The bridges are attractive for all values of V/d^2 when $\xi \geq 0$. For each $\xi < 0$ there is a value of V/d^2 above which the bridge is repulsive; this value is $\pi/4$ for $\xi \leq -1$.

6.2 — *MAXIMUM DIMENSION OF A FLOATABLE SQUARE PRISMATIC ROD*

The limiting floating position is the one shown in fig. 7. The angle contact is necessarily obtuse, if the density ϱ_s of the rod is larger than the density of the fluids. We shall admit that the radius R of the meniscus is infinity. In this case, the height h_o of the line of contact relative to the horizontal liquid surface is given by (see Appendix 2, eq. A2.13)

$$h_o = \frac{2\gamma^{1/2}}{\Delta\varrho.g}(1\text{-}\sin\theta)^{1/2} \tag{13}$$

Let H be the side of the square section. We assume that $\Delta\varrho \simeq \varrho$, where ϱ is the density of the liquid, and

$$\varrho_s = K.\Delta\varrho \qquad (K>1) \tag{14}$$

Using eq. A2.9 with $F=0$ we obtain for the maximum size H

$$\frac{H}{a} = [(\frac{1\text{-}\sin\theta}{2})^{1/2} + (\frac{1\text{-}\sin\theta}{2} - 2(K\text{-}1)\cos\theta)^{1/2}](K\text{-}1)^{-1} \tag{15}$$

where

$$a^2 = \frac{\Delta\varrho g}{\gamma} \tag{16}$$

Eq. 15 also applies, with $\theta = 180°$, for $\xi < -1$.

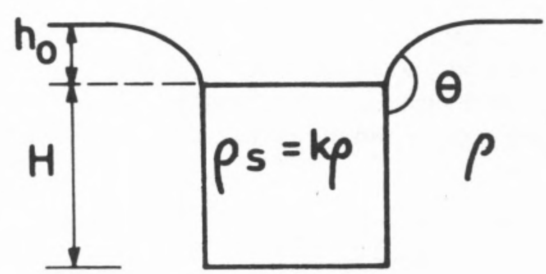

Fig. 7

Extreme floating configuration of a prismatic rod of density $\varrho_s = K\varrho$; $K>1$ and ϱ is the density of the bottom fluid. Note that the interface is in a θ-configuration

In fig. 8 we plot $\frac{H}{a}$ as a function of ξ for various values of K. Also shown is the maximum size, for $K=2$, calculated on the assumption that the pressure difference term does not enter in eq. A2.9. It can be concluded that this term is of the same order of magnitude as the surface tension term. Flotation of denser particles is possible if their dimensions perpendicular to the free level of the interface are of the order of the capillary constant, a (eq. 16).

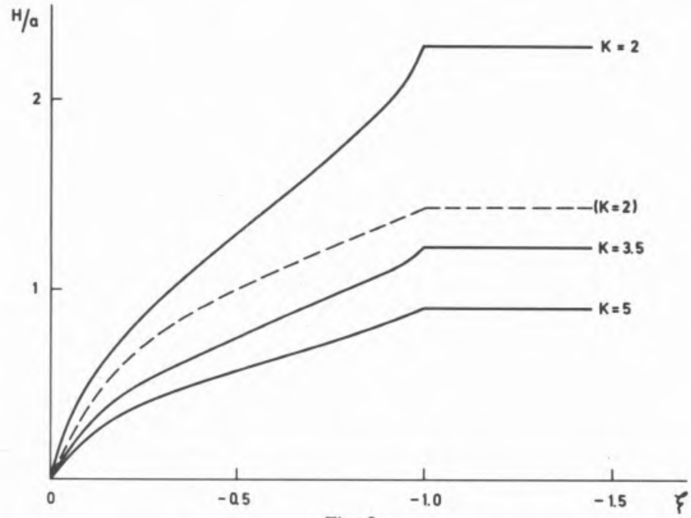

Fig. 8

Maximum reduced size H/a of a floatable square prismatic rod as a function of contact angle ($\xi = \cos\theta$), for various densities of the rod ($\varrho_s = K\varrho$). The dotted curve was obtained by neglecting the pressure difference term in eq. A2.9

7 — CONCLUSIONS

The main conclusions of the present work can be summarized in the following points:

1 — The system of forces that must be applied to solid bodies connected by a liquid bridge (or to a floating solid) to keep equilibrium can be calculated by differentiating the Helmholtz energy with respect to the coordinates that define the relative position of the solids, at constant volume of the fluids, and with the interface always satisfying the equation of Young-Laplace and the appropriate boundary conditions.

2 — In r-bridges and in θ- or r, θ-bridges, when the quantity ξ defined by eq. 1 is such that $|\xi| < 1$, the system of applied forces is one that equilibrates the weight of the solids and the "internal forces" in the bridge. These include the surface tension forces at the line of contact with the solid, and the pressure forces normal to the solid surface with a discontinuity across the curved fluid interface. The pressure forces are equivalent to two buoyancy forces and a pressure difference system of forces acting on a dividing surface Σ through the solid and bounded by the line of contact Γ.

3 — The same conclusions apply to floating bodies. If the solid body is axially or cylindrically symmetric, the vertical resultant of the surface tension forces is equal to the weight of the meniscus displaced by the solid.

4 — The system of forces that must be applied to each solid is not in general equivalent to a single force. The system that includes the pressure difference forces on Σ and the surface tension forces on Γ for the two solids is equivalent to zero. This can be regarded as a general property of a curved interface in a external field: if we take a closed line Γ on the interface and a surface Σ bounded by Γ, the system of forces on Γ and Σ defined above is independent of the choice of Γ and Σ.

5 — In conditions of complete wetting, $|\xi| > 1$, the equilibrium configurations are different, but the force can still be calculated from the same equations using the values 0 or 180° for the contact angle. For example, there is no improvement on flotation from an increase in the repellency of the liquid behyond the value for which $\theta = 180°$.

APPENDIX 1 — *FORCE OF ADHESION BETWEEN TWO WEDGES*

We shall assume that the two solid surfaces are identical wedges placed symmetrically (fig. 9). In the absence of external fields, the fluid interface is a circular cylinder. The volumes of the fluids are fixed. We distinguish between two types of boundary conditions. In θ-bridges, the interface ends within the solid surfaces at a constant angle θ (the contact angle). In r-bridges, the interface is forced to end at a particular line in the solid surfaces; the angle between the interface and the wedge is now θ'. In all cases the force will be calculated by differentiating the Helmholtz energy with respect to the distance between the solid surfaces.

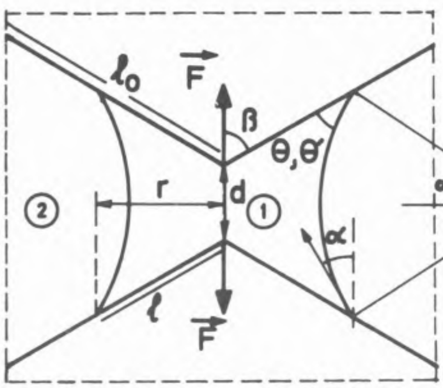

Fig. 9
θ-bridge betwwen two wedges. The dotted line indicates the boundary of a closed system

The wedge angle is 2β ($0<2\beta\leq 2\pi$). The radius R and the angle α will be taken as positive when the centre of curvature 0 is the surrounding fluid, as in fig. 9. In the other case R and α are taken as negative. In both cases $|\alpha|\leq\pi$. The total Helmholtz energy A of a closed system comprising the entire fluid and solid-inner fluid interfaces can be put in the form [16]:

$$A = \sum_i \gamma_i \Omega_i \tag{A1.1}$$

where Ω_i is the area of interface i with surface tension γ_i. This equation is appropriate for comparing Helmholtz energies of equilibrium configurations at constant volume and temperature, in the absence of external fields. Introducing the contact angle θ

$$\cos\theta = \frac{\gamma_{S2}-\gamma_{S1}}{\gamma} \tag{A1.2}$$

we obtain

$$\frac{A}{4\gamma} = R\alpha - \ell\cos\theta + \text{const.} \tag{A1.3}$$

The volume of the inner fluid is

$$V = 4(rR\sin\alpha - \frac{r^2}{2}\text{ctg}\beta - \\ - \frac{\alpha}{2}R^2 + \frac{R^2}{2}\sin\alpha\cos\alpha). \tag{A1.4}$$

We have the additional geometrical relations

$$\alpha + \theta' = \beta \tag{A1.5a}$$

$$r = \ell\sin\beta \tag{A1.5b}$$

$$\frac{d}{2} + r\,\text{ctg}\beta = R\sin\alpha. \tag{A1.5c}$$

We now differentiate A with respect to the distance d at constant volume, assuming either that $\theta'=\theta$ is a constant or r is a constant.
In the first case we have

$$\frac{F}{2\gamma} = \frac{\delta(A/\gamma)}{2\delta d} = \frac{\delta(A/2\gamma)}{\delta R}\cdot\frac{\delta R}{\delta d} = \\ = 2\;(\alpha\text{-}\cos\theta\,\text{cosec}\beta\frac{\delta r}{\delta R})\cdot\frac{\delta R}{\delta d} \tag{A1.6}$$

Differentiating A1.5c and A1.4 we obtain respectively

$$\frac{1}{2}\frac{\delta d}{\delta R} + \text{ctg}\beta\frac{\delta r}{\delta R} = \sin\alpha \tag{A1.7a}$$

$$\frac{\delta r}{\delta R}(R\sin\alpha - r\,\text{ctg}\beta) = \\ = \alpha R\text{-}R\sin\theta\cos\alpha - r\sin\alpha\,. \tag{A1.7b}$$

Eliminating $\frac{\delta r}{\delta R}$ and $\frac{\delta R}{\delta d}$ between eqs. A1.6 and A1.7 we obtain upon simplification

$$\frac{F}{2\gamma} = \frac{r}{R} + \cos\alpha = \frac{r}{R} + \cos(\theta\text{-}\beta)\,. \tag{A1.8}$$

If, instead of a constant θ, the differentiations are at constant r the same final result is obtained.
Suppose now that $\xi>1$. The θ-bridge contacts the wedge at 0° and is continued to the edge of the plates by a film of the inner fluid. The Helmholtz energy is now (ℓ_o is the length of half-wedge)

$$\frac{A}{4\gamma} = R\alpha + (\ell_o\text{-}\ell)$$

and only differs by a constant from the value A1.3 for $\theta=0$. The force of adhesion is therefore given by the same expression.

APPENDIX 2 — *FLOTATION OF A PRISMATIC ROD*

We consider a prismatic rod of weight 2w per unit length, symmetrically placed at the interface between two fluids in a closed container of width 2(L + M), 2M being the width of the rod and H_o its height (fig. 10). The system is indefinite in the direction perpendicular to the figure. The two fluids are denoted by B and T (respectively from bottom and top), with densities ϱ_B and ϱ_T. Their volumes are fixed. The contact angles of fluid B with the container and rod are, respectively, θ_2 and θ_1. For the rod to be in equilibrium at some distance d from a reference level, which can be taken as the base of the container, it is necessary to apply a vertical force $\vec{F}$ to the rod which can be calculated by derivation of the Helmholtz energy of the system with respect to d. Clearly an equal and opposite force has to be applied to the container.

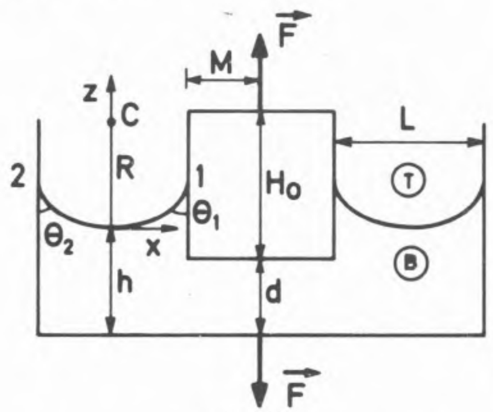

Fig. 10
Primatic rod at the interface between fluid B and fluid T

We choose x, z axes as in fig. 10 with z antiparallel to $\vec{g}$ and with origin at the point where $z' = 0$. The equation z(x) of the interface is a solution of Young-Laplace equation

$$\frac{z''}{(1+z'^2)^{3/2}} = \frac{1}{R} + \frac{\Delta\varrho . gz}{\gamma} \quad \text{(A2.1)}$$

where γ is the interfacial tension, $\Delta\varrho = \varrho_B - \varrho_T > 0$ and R is the radius of curvature at the origin. R is positive or negative according to whether the centre of curvature at the origin is in fluid T or in fluid B. Since

$$\frac{z''}{(1+z'^2)^{3/2}} = \frac{\delta}{\delta x}\left(\frac{z'}{(1+z'^2)^{1/2}}\right) \quad \text{(A2.2)}$$

we can integrate eq. A2.1 between point 2 at the container surface ($x_2<0, z_2>0, z_2'>0$ in fig. 10) and point 1 at the rod surface ($x_1>0, z_1>0, z_1'>0$) obtaining

$$\cos\theta_1 + \cos\theta_2 = \frac{\Delta\varrho g}{\gamma}\int_{x_2}^{x_1} z dx + \frac{L}{R} \quad \text{(A2.3)}$$

because $L = x_1 - x_2$.

The Helmholtz energy per unit length, 2A, includes the interfacial energies and the potential energy of the rod and fluids. Neglecting those terms that do not change when d changes we have (for convenience the potential energy zero will be taken at the base of the container)

$$A = wd - \gamma(h + z_2)\cos\theta_2 - - \gamma(h + z_1 - d)\cos\theta_1 + E_p \quad \text{(A2.4)}$$

where $2E_p$ is the potential energy of the fluids per unit length of the system. When d changes by δd, the shape of the interface does not vary, so that z_1, z_2 are constants, and the constancy of volumes implies that

$$L\delta h + M\delta d = 0. \quad \text{(A2.5)}$$

We therefore have for the force

$$\frac{F}{2} = \frac{\delta A}{\delta d} = w + \gamma\cos\theta_1 + + \gamma(\cos\theta_1 + \cos\theta_2)\frac{M}{L} + \frac{\delta E_p}{\delta d}. \quad \text{(A2.6)}$$

To evaluate the last term, suppose that d changes by $\delta d(>0)$ so that h changes by $\delta h(<0)$. A volume of fluid B is then transferred from the interface, where its potential energy was $\delta h . \varrho_B g \int_{x_2}^{x_1}(h+z)\delta x$, to underneath the rod, where its potential energy is $\varrho_B g M d \delta d$. Similarly, the same volume of fluid T is transferred from the top of the rod (potential energy $\varrho_T g M(H_o + d)\delta d$) to the interface (potential energy $-\delta h \varrho_T g \int_{x_2}^{x_1}(h+z)\delta x$). Therefore

$$\delta E_p = \varrho_B g M d \delta d + \delta h \varrho_B g \int_{x_2}^{x_1}(h+z)dx - - \delta h \varrho_T g \int_{x_2}^{x_1}(h+z)\delta x - \varrho_T g M(H_o + d)\delta d \quad \text{(A2.7)}$$

We use eq. A2.5 to evaluate $\frac{\delta E_p}{\delta d}$, insert this in eq. A2.6 and combine with A2.3 to obtain

$$\frac{F}{2} = w + \gamma\cos\theta_1 + \gamma\frac{M}{R} - \varrho_B g M(h - d) - - g\varrho_T(H_o - h + d). \quad \text{(A2.8)}$$

This can be written as

$$\frac{F}{2} = w + \gamma\cos\theta_1 - \varrho_B gM(h - d + z_1) - \\ - \varrho_T gM(H_o - h + d - z_1) + M\Delta P_o \qquad (A2.9)$$

where

$$\Delta P_o = P_{1T} - P_{1B} = \frac{\gamma}{R} + \Delta\varrho g z_1 \qquad (A2.10)$$

is the pressure difference between two points, one in fluid T, the other in fluid B, in the vicinity of the line of contact of the interface with the rod. The second and third terms in eq. A2.9 are the vertical upthrusts, I_B and I_T, on the rod portions immersed in each fluid:

$$\frac{F}{2} = w + \gamma\cos\theta_1 - I_T - I_B + M.\Delta P_o \quad . \qquad (A2.11)$$

The same expression applies if $\theta_1 > \pi/_2$, in which case all terms in eq. A2.11, except w, will be negative.

When $R = \infty$, the heigth z_1 of the meniscus can be calculated from eq. A2.1 noting that

$$\frac{z''}{(1 + z'^2)^{3/2}} = -\frac{\delta}{\delta z}\left(\frac{x'}{(1 + x'^2)^{1/2}}\right). \qquad (A2.12)$$

Integration between $z = 0$ and z_1 gives immediately

$$1 - \sin\theta_1 = \frac{\Delta\varrho.g}{\gamma}\frac{z_1^2}{2}. \qquad (A2.13)$$

Finally, for $R = \infty$, eq. A2.3 gives

$$\gamma\cos\theta_1 = \Delta\varrho.gV_m \qquad (A2.14)$$

where V_m is the volume of the meniscus above or below the free level. The surface tension term in the expression for the force is then equal to the weight of the meniscus produced by the rod.

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NOTATION

A — Helmholtz energy
$\vec{D}$ — resultant of pressure forces on Σ
$2E_p$ — potential energy per unit lenght
$\vec{F}, \vec{F}_1, \vec{F}_2$ — forces acting on solids connected by liquid bridge
$\vec{H}$ — horizontal resultant of pressure forces on Σ
H, H_o — side of section of prismatic rod
$\vec{I}$ — vertical upthrust
K — ratio of solid to liquid densities
L — half-width of meniscus
M — half-width of rod
P — pressure
R — radius of curvature of cylindrically symmetric bridge; radius of curvature at apex of meniscus
R_1, R_2 — principal radii of curvature
$\vec{V}$ — vertical resultant of pressure forces on Σ
V — volume of inner fluid in bridge
V_1, V_2 — volumes of solid separated by Σ
V_m — volume of meniscus above or below free level
a — capillary constant
b — geometrical parameter (fig. 3)
c — geometrical parameter (fig. 3)
d — bridge width; distance between solid bodies connected by liquid bridge
g — acceleration due to gravity
h — height of point meniscus relative to a fixed level
ℓ, ℓ_o — length of wetted region in wedge; length of wedge
r — linear dimension (*e.g.* radius half-width) of line of contact of fluid interface with solid
$2w$ — weight per unit length
x — horizontal coordinate
z — vertical coordinate
$z' = \frac{\delta z}{\delta x}$

Greek symbols

ΔP — pressure difference across a curved interface
$\Delta\varrho$ — difference between densities of two fluids separated by an interface
Γ — line of contact between fluid interface and solid
Σ — surface bounded by Γ
α — angle (fig. 9)
β — half-angle of wedge
δ — differentation symbol
ϵ — angle (fig. 3)
γ — interfacial tension
$\vec{\gamma}$ — fluid interfacial tension regarded as a force per unit legth
θ, θ' — contact angle; angle between fluid interface and solid in r-bridges
$\theta_1, \theta_2, \theta_1', \theta_2'$ — angle between fluid interface at solid and fixed direction (figs. 2, 3)
ϱ — density
ξ — relation between fluid interfacial tensions (eq. 1)

Subscripts

1, 2 — denote the two fluids (1 is the inner fluid, 2 is the surronding fluid); denote the two solids in a bridge
B, T — bottom and top fluids in a gravitational field
S — solid

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RESUMO

Forças de capilaridade em pontes líquidas e em flutuação

As forças de capilaridade podem ser calculadas, em todos os casos, por via termodinâmica, diferenciando a energia de Helmholtz em ordem às coordenadas geométricas de cada problema. Com base neste método, mostra-se a validade da interpretação "mecânica" das forças capilares, desde que se inclua um termo associado à diferença de pressão, além dos termos relativos à força de tensão suprficial e às impulsões em cada fluído. São apresentadas outras descrições equivalentes do sistema de forças, as quais podem ser preferíveis em problemas de flutuação. Discute-se o cálculo das forças de capilaridade em situações em que um dos fluídos molha perfeitamente o sólido. Finalmente apresentam-se exemplos de aplicação a pontes líquidas e a sólidos em flutuação.