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ALTERNATIVE EQUILIBRIUM CONFIGURATIONS OF THE INTERFACE BETWEEN TWO FLUIDS IN CONTACT WITH SOLIDS

A cylindrically symmetric system comprising two immiscible fluids placed between two identical parallel plates is analysed for the possible equilibrium configurations of the fluid interface. The configurations include bridges, attached «drops» and isolated «drops» and multiply connected combinations of these. After determining the geometrical properties and the Helmholtz energy of each configuration, the stability of the various configurations is discussed and the transitions between them, as the stability limits are overshoot, are predicted.

1 — INTRODUCTION

The equilibrium shape of the interface between two immiscible fluids acted by externally applied fields is the solution of Young-Laplace differential equation [1,2] that satisfies the specific conditions of each particular problem. Usually these conditions are the given volume of the fluid enclosed by the interface and boundary conditions for the interface. Two types of boundary conditions can be distinguished: i) geometrical and ii) contact angle conditions. Examples of the first type are the boundary conditions at the apex and at the line of contact of a drop hanging from a tube of given radius. Contact angle conditions appear, for example, in liquid bridges between two spheres or two indefinite plates and in drops hanging from a ceiling. These latter conditions are in fact necessary for equilibrium [2] but are generally introduced as boundary conditions for the interface.

Particularly when solid bodies of a given geometry are present, there may be alternative equilibrium configurations for the fluid interface, each with specific boundary conditions. It is also possible *(e.g.,* in pendent drops [3]) that more than one equilibrium configuration is compatible with the imposed conditions (volume and boundary conditions). As the geometrical parameters of the system (that is, the position of the solid bodies or the volume of fluid, if this regarded as a variable parameter) are allowed to change, it generally happens that a particular set of boundary conditions can only be fulfilled for values of the parameters within a certain interval.

Problems on equilibrium shapes of interfaces are usually discussed for a particular type of boundary conditions, without allowance for alternative conditions (*e.g.,* [3-7]). But an actual two fluid system comprising solids of a given geometry may frequently admit multiple equilibrium configurations, each with specific boundary conditions. This possibility may change the stability limits of a particular type of configuration [8]. In addition, no attention is generally given to the change in configuration that necessarily occurs when the geometrical parameters overshoot the permissible interval for a particular set of boundary conditions. This is essentially a dynamical problem but, as will be shown, predictions on the final configuration can be made based on equilibrium properties.

This paper contains a detailed study of the alternative configurations of the interface between two fluids bounded by two identical plates symmetrically placed. To make the calculations easiest, a cylindrically symmetric geometry is assumed, in the absence of applied fields. The cross-section of the fluid interface is then circular, provided the fluid interfacial tension, γ, is independent of position in the interface [2]. The contact angle, θ_c, of fluid 1 with the plates (in presence of fluid 2) will be taken as a characteristic of the system, and is given by Young's equation [1,2]

$$\cos\theta_c = \frac{\gamma_2 - \gamma_1}{\gamma} \quad (1)$$

where γ_1, γ_2 are the solid-fluid interfacial tensions. It will be assumed that the ratio in the second term of equation (1) is in the interval [-1,1], so that $\theta_c$has a well defined value.

The system to be studied is not easy to reproduce experimentally, but the approach developed can also be applied to more common situations, particularly to axially symmetric interfaces in a gravitational field [9], and to predict the distribution of liquid in wetted powders such as those used in liquid phase sintering [10].

2 — ALTERNATIVE EQUILIBRIUM CONFIGURATIONS

The fluid enclosed by the interface and plates will be denoted by fluid 1. The other fluid, 2, is the surrounding fluid. Only configurations with fluid 2 as the surrounding fluid will be considered. The volumes of both fluids are fixed. If allowance is made for the fragmentation of fluid 1 in several non-connected volumes, a large variety of configurations will be possible. We shall consider at this stage the «elementary» configurations, which can be classified into three groups: bridges, attached drops and isolated drops or i-drops. Examples are given in fig. 1. In the first two cases, the interface may contact the plates either at their edge or within the plates. These two configurations will be termed r- and θ_c- configurations, respectively. Therefore, the elementary configurations are: r-brides, θ_c-bridges, r-drops, θ_c-drops and i-drops. We shall discuss in greater detail bridge configurations and triply connected configurations comprising two attached drops and an i-drop placed as shown in fig. 1f. Multiply connected θ_c-bridges and more complex configurations will not be treated explicity.

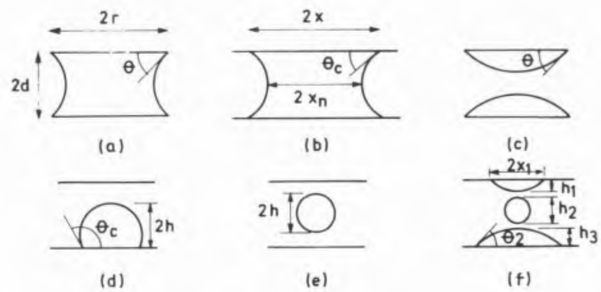

Fig. 1

Different types of equilibrium configurations with cylindrical symmetry: a) r-bridge; b) θ_c-bridge; c) two equal attached r-drops; d) one attached θ_c-drop; e) one isolated or i-drop; f) triply connected configuration with two θ_c-drops and an i-drop symmetrically placed

3 — GEOMETRICAL PARAMETERS, HELMHOLTZ ENERGY AND FORCE OF ADHESION

Let 2V be the volume of fluid 1 per unit length of the system, θ_c its contact angle with the plates, 2r and 2d, respectively, the plate width and separation. We calculate, for each of the configurations referred to above, the width 2x of the interface at the plates (in θ_c-configurations), the total heigth 2h perpendicular to the plates (for drops) and the Helmholtz energy 2A per unit length of the system. This is the sum of the energies of the fluid interface and solid interfaces [11]. Since V, r, and the γ's are fixed, it is sufficient, for comparative purposes, to compute the quantity (cf. eq. (1)

$$A^* = \frac{A}{2\gamma V^{1/2}} - \frac{\gamma_2}{\gamma}\frac{r}{V^{1/2}} = \frac{L}{2V^{1/2}} - \frac{x}{V^{1/2}}\cos\theta \quad (2)$$

where 2L is the total length of the fluid interface profile. For a given system A* increases linearly with A. In the following equations θ designates the angle between the interface and the plates measured at the line of contact. Clearly $\theta = \theta_c$ in θ_c-configurations (*e.g.* figs. 1b, d), and $x = r$ in r-configurations (fig. 1a, c).

BRIDGES

The main equations are ($2x_n$ is the neck width, fig. 1b)

$$\frac{d}{V^{1/2}} = \frac{d}{x} \cdot \frac{x}{V^{1/2}} =$$

$$= \frac{d}{x}\left[2\frac{d}{x} + \left(\frac{d}{x}\right)^2 \left(\mathrm{tg}\theta - \frac{\pi/2-\theta}{\cos^2\theta}\right)\right]^{-1/2} \quad (3)$$

$$A^* = \frac{d}{V^{1/2}}\left(\frac{\pi/2-\theta}{\cos^2\theta} - \frac{x}{d}\right)\cos\theta \quad (4)$$

$$\frac{x_n}{d} = \frac{x}{d} - \frac{1-\sin\theta}{\cos\theta} \quad (5)$$

DROP CONFIGURATIONS

θ_1,θ_2 are the angles of the attached drops with each plate and $2x_1$, $2x_2$ are their widths at the plates (fig. 1f); f_1, f_2, f_3 are the volume fractions of fluid 1 in the two attached drops and in the i-drop, respectively. In particular $f_3=1$ indicates an i-drop and $f_1=f_2=½$ two equal attached drops. The total height $2h=h_1+h_2+h_3$, see fig. 1f. The main equations are:

$$\frac{x_1}{V^{1/2}} = \sqrt{2f_1}\,\lambda(\theta_1) \qquad \frac{x_2}{V^{1/2}} = \sqrt{2f_2}\,\lambda(\theta_2) \quad (6)$$

$$\frac{h}{V^{1/2}} = \frac{1}{\sqrt{2}}\left[\sqrt{f_1}\,\Psi(\theta_1) + \sqrt{f_2}\,\Psi(\theta_2) + 2\sqrt{f_3/\pi}\right] \quad (7)$$

$$A^* = \frac{1}{2\sqrt{2}}\Big\{\sqrt{f_1}\phi(\theta_1) + \sqrt{f_2}\phi(\theta_2) + 2\sqrt{\pi f_3} -$$

$$-2\cos\theta_c[\sqrt{f_1}\,\lambda(\theta_1) + \sqrt{f_2}\lambda(\theta_2)] \quad (8)$$

with

$$\lambda(\theta) = \left(\frac{\theta}{\sin^2\theta} - \mathrm{ctg}\theta\right)^{-1/2} \quad (9a)$$

$$\Psi(\theta) = \frac{1-\cos\theta}{\sin\theta}\lambda(\theta) \quad (9b)$$

$$\phi(\theta) = \frac{2\theta}{\sin\theta}\lambda(\theta) \quad (9c)$$

Fig. 2 shows plots of $x/V^{1/2}$ as function of $d/V^{1/2}$ in bridges, for various values of θ. Also shown (dotted lines) are curves of $x/V^{1/2}$ as a function of $h/V^{1/2}$ for one and two equal attached drops and the value of $h/V^{1/2}$ of an i-drop. Fig. 3 shows the limits of geometrical possibility of bridges and drops, as a function of θ. The limiting curves for bridges correspond to $x_n=0$ when $\theta<\pi/2$ and to $x=0$ when $\theta>\pi/2$. Bridges with a given θ are possible for values of $d/V^{1/2}$ smaller than the one given

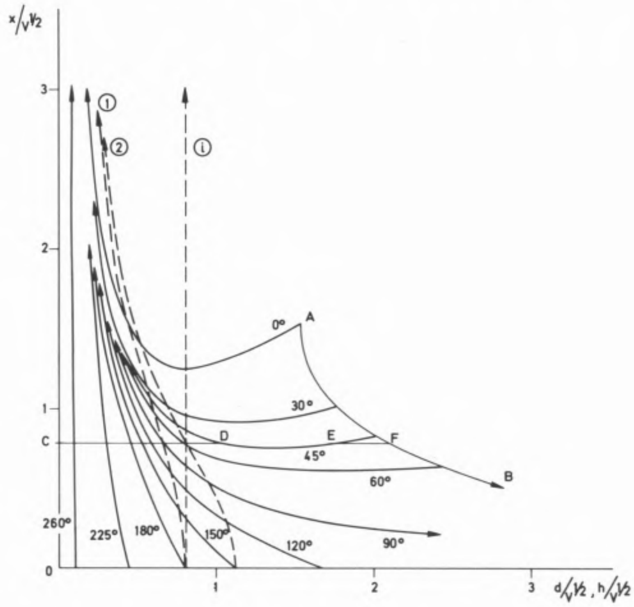

Fig. 2

Full lines give the bridge width, 2x, at the plates as a function of plate séparation, 2d, for various values of θ. Dotted lines give the width of one (1) and two (2) attached drops and of one i-drop (i) as a function of the total height 2h of the drops. The line AFB marks the limit of possible bridge configurations. CDEF indicates the path of a bridge for $r/V^{1/2}=0.78$ and and $\theta_c=45°$. An arrow means that a curve continues

by the curves. The limiting curves for drops correspond to $h=d$. Each drop configuration (one or two equal drops or one i-drop) is possible for values of $d/V^{1/2}$ larger than those given by the curves of fig. 3. All the necessary information on the geometrical parameters of the various configurations can be obtained from figs. 2 and 3.

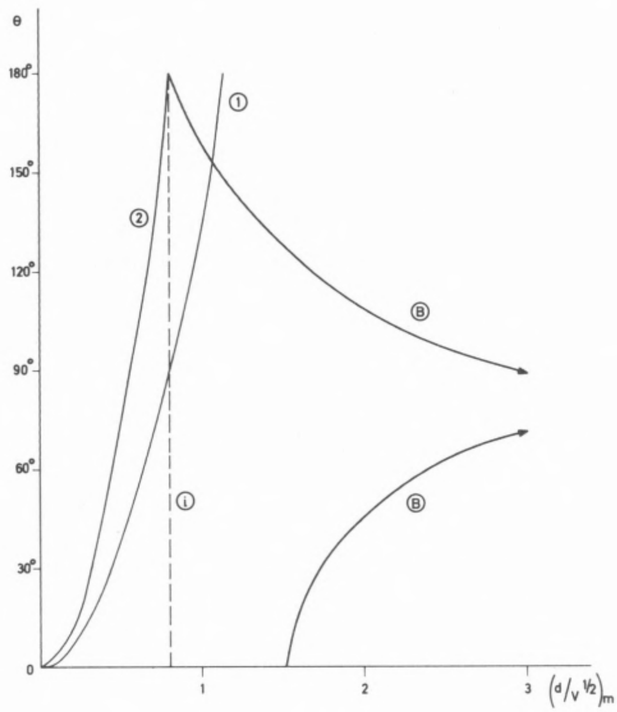

Fig. 3

Limiting values of $d/V^{1/2}$ as a function of θ for bridges (B), one attached drop (1) and two identical attached drops (2). Also marked is the limiting $d/V^{1/2}$ for one i-drop (i). Bridges and drops are possible for values of $d/V^{1/2}$ smaller and larger, respectively, than those in the limiting curves

The force of adhesion, F, due to a bridge can be determined from the rate of change of the Helmholtz energy with plate separation

$$F\delta d = \delta A \tag{10}$$

As will be shown in more detail elsewhere [12] this gives for the force the following expression

$$\frac{F}{2\gamma} = \frac{x}{d}\cos\theta + \sin\theta \tag{11}$$

or

$$\frac{F}{\gamma} = \frac{V}{d^2}\cos\theta + \sin\theta + \frac{\pi/_2 - \theta}{\cos\theta} \tag{12}$$

Equation (11) contains the usual two terms [13,14] due respectively to the pressure difference across the interface and to the fluid interfacial tension acting as a force on the plates. Fig. 4 shows examples of the variation of F with plate separation in r- and θ_c-bridges.

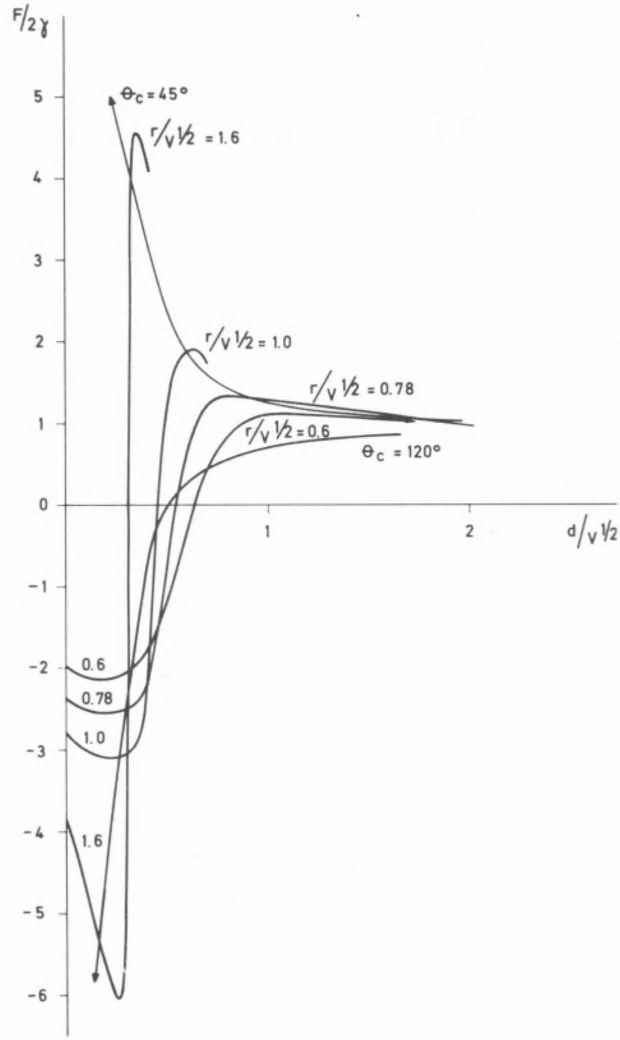

Fig. 4

The force of adhesion in θ_c-and r-bridges, as a function of plate separation, for various values of θ_c and $r/V^{1/2}$. The curves for $\theta_c = 45°$ and $r/V^{1/2} = 0.78$ intersect at two points. The curve for $r/V^{1/2} = 0.6$ is not shown complete

4 — STABILITY

Each type of configuration has a range of geometrical possibility which can be determined from the equations of the previous section. It is now necessary to find out whether each configuration is stable or unstable. As will be shown, some r-configurations are unstable relative to θ_c-configurations. We discuss first the stability of bridge configurations. For given $r/V^{1/3}$ and θ_c there may be, as fig. 2 shows, intervals of $d/V^{1/3}$ where r- and θ_c-bridges are both possible. In these intervals it is $x < r$ for θ_c-bridges and $\theta < \theta_c$ for r-bridges. For example, for $r/V^{1/3} = 0.78$ and $\theta_c = 45°$ both bridges are possible in the interval of $d/V^{1/3}$ between D and E in fig. 2. Outside this interval only the r- configuration is geometrically possible.

In the intervals of $d/V^{1/3}$ where the two bridge configurations are geometrically possible, calculation of A* shows that the θ_c-bridge always has a smaller Helmholtz energy than the r-bridge. This can also be seen in the examples of fig. 4. The force F is always larger for the r-bridge in the interval of coexistence: equation (10) then shows that its energy is larger. Consider now a r-bridge for a value of $d/V^{1/3}$ just above the smallest value for which the two configurations occur. If the r- bridge is slightly perturbed so as to produce a θ_c-bridge, the Helmholtz energy decreases. The r- bridge is therefore unstable.

If $d/V^{1/3}$ is increased from a value small enough for the bridge to be of the r-type, three possibilities can be distinguished: a) the bridge remains in the r- configuration until it breaks; b) the bridge changes to a θ_c- bridge at a critical separation and remains in this configuration until it breaks; c) the bridge changes to a θ_c-bridge and then again to the r- configuration. For example, for $\theta_c = 30°$ the three cases occur respectively for $r/V^{1/3} < 0.92$, for $r/V^{1/3}$ in the interval 0.92 -1.00 and for $r/V^{1/3} > 1.00$. For $\theta_c > 90°$ it is always case b) that occurs.

Similar conclusions can be drawn as regards the stability of attached drops. When both r- and θ_c- -drop configurations are possible, it is always the r-configuration that has larger A* and is therefore unstable. All other drop configurations are likely to be stable. In conclusion, all geometrically possible configurations (including those with any number of θ_c-bridges, θ_c-drops and i-drops) are stable, except the r-configurations when an alternative θ_c-configuration of the same type can occur.

We end this section with a brief discussion of the configurations that may be expected when $\zeta = (\gamma_2 - \gamma_1)/\gamma$ is not the interval [-1,1]. In such cases no θ_c-configurations are possible, but r-configurations can occur. For $\zeta > 1$, a geometrically possible r-configuration will always be stable. In the case of r-bridges, as the value $\theta = 0$ is reached and d is further increased, it is expected that a special type of θ-bridge will take its place. This bridge ends within the plates with $\theta = 0$ but is prolonged to the edge of the plates by a thin layer of fluid. For this configuration there is no solid-fluid 2 interface. It is easily shown that in this case the force of adhesion has the same value as for a true θ_c-bridge with $\theta_c = 0$. For $\zeta < -1$, r-drops are likely to be unstable. Stable configurations that may occur in this case are r-drops and r-bridges with $\theta > 180°$. For separations larger than the one corresponding to $\theta = 180°$, a special type of θ_c-bridge, analogous to the one described above but without solid-fluid 1 interface, may be a stable configuration.

5 — TRANSITIONS BETWEEN EQUILIBRIUM CONFIGURATIONS

When the limit of existence of any of the stable configurations is reached and the plate separation is slightly changed to a value outside the range of stability, the system will irreversibly change to another equilibrium configuration. Note that the variable parameter is $d/V^{1/3}$ so that the discussion also applies to transitions due to volume variations. Kinetic energy is produced in the transition, and the problem is essentially a dynamical one. If the transition is at constant temperature (in addition to constant volume) and if a negligeable amount of mechanical work is put on the system to cause the transition, the final configuration must have a smaller A* thant the original one.

In fig. 5 are compared the Helmholtz energies, A*, of the following configurations: r- and θ_c-bridges, one and two equal attached drops and one i-drop. Only the stable bridge configurations are represented in fig. 5, but both r and θ_c-attached drops are considered, although r-drops are unstable relative to θ_c-drops. Other configurations have also been studied and their A* values calculated, but they are not indicated in fig. 5. The following conclusions can be drawn from these results.

i) Simply connected configurations of a given type (*i.e.*, bridges, attached drops and i-drops) always have a smaller A* than multiply connected configurations of the same type.

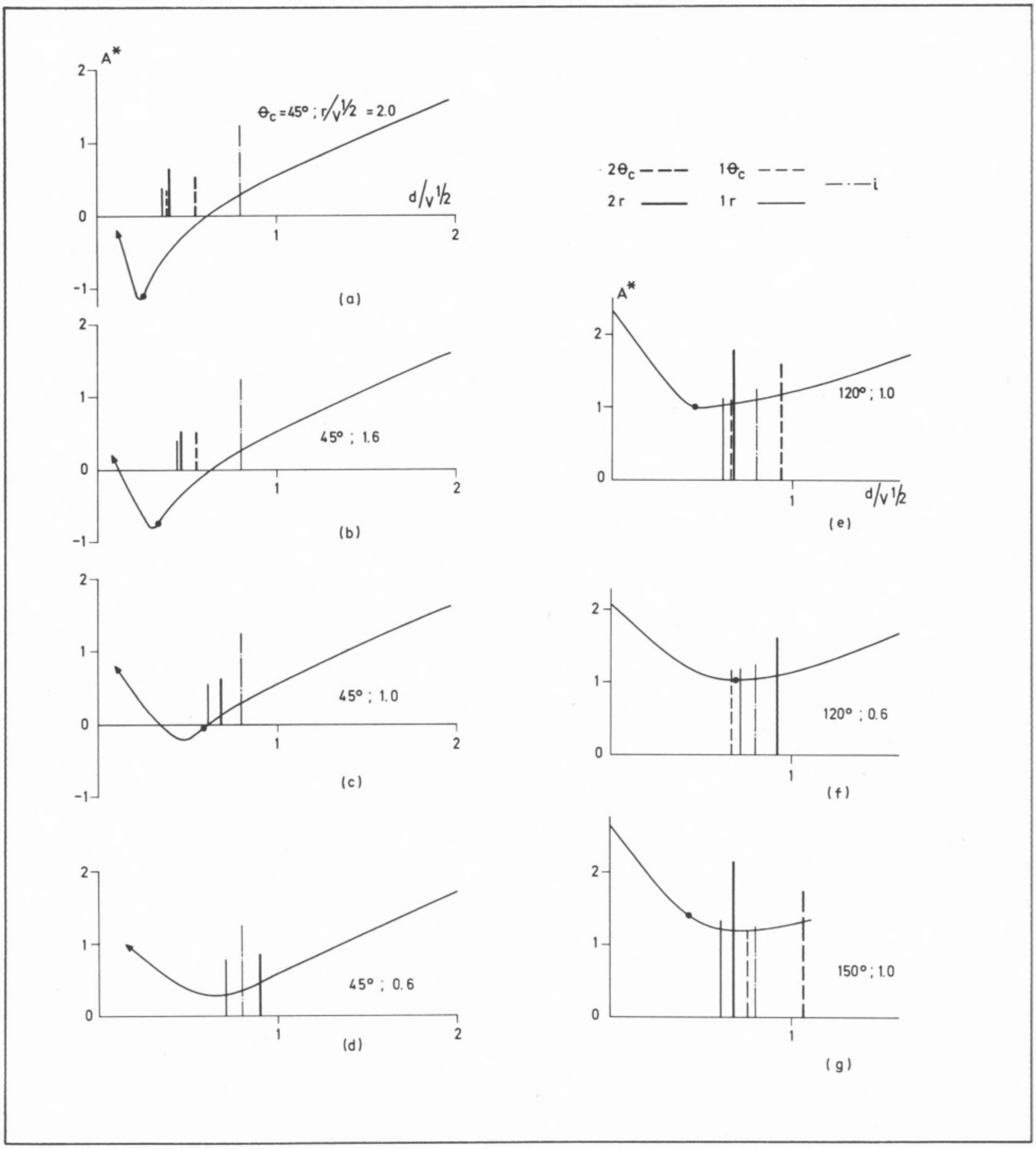

Fig. 5

Helmoltz energy, A^*, as a function of plate separation, $d/V^{1/2}$, for various configurations and different values of contact angle, θ_c, and plate width, $r/V^{1/2}$. The curves give A^* for bridges. The dot indicates the transition between r-and θ_c-bridge configurations. In (d) only the r-bridge occurs. The other configurations included are: one r-drop (——); two equal r-drops (**—**); one θ_c--drop (---); two equal θ_c-drops(**———**); one i-drop (—.—.). Some of these configurations cannot occur in specific cases

ii) Considering only simply connected configurations (*i.e.*, one bridge, one attached drop, one i-drop) and values of $d/V^{1/2}$ for which two or three of such configurations are possible, the A* for one attached drop is always smaller than that for an i-drop; the A* for the bridge may be larger or smaller than the A* for any of the two other configurations.

iii) The A* for two equal attached drops is larger than the A* for one i-drop when $\theta_c > 90°$ and *vice-versa.*

When the limiting $d/V^{1/2}$ for a stable configuration of the types considered in fig. 5 is slightly overshoot, the new configuration cannot be predicted from the values of A* exclusively, since there are in general various alternative possibilities. However, some final configurations can be rulled out. For example, a θ_c-bridge with $\theta_c \lesssim 130°$ cannot give two attached drops (cf. fig. 4g).

The final configurations may even depend on the way $d/V^{1/2}$ is changed from its limiting value. If the two plates are moved in the same way, it is expected that a symmetric configuration will give rise to another symmetric configuration. However, if only one plate is displaced, for example, the final configuration may not be the same. A θ_c-bridge with $\theta_c > 90°$ illustrates this point. Depending on the way d is increased behyond the limiting value, either an i-drop or one attached drop may result.

Expected transitions for a symmetrical displacement of the plates are schematically shown in fig. 6. The following are the main conclusions.

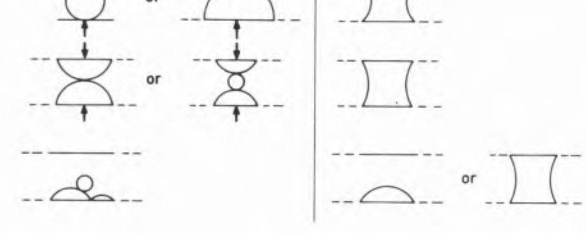

Fig. 6

Examples of irreversible transitions at the limit of stability of various initial configurations. The plates are moved in the same way, indicated by the arrows, to produce the transitions. The dotted lines indicate that either r- or θ_c-configurations may be considered

i) For bridges with $\theta_c < 90°$, two equal attached drops will result (either r- or θ_c-drops); if $\theta_c > 90°$, an i-drop will result.

ii) For one or two attached drops, or for an i-drop (or other conbinations such as in fig. 6), a bridge (r or θ_c) is expected to form.

Finally, when two volumes in a multiply connected configuration come in contact as a result of a displacement of the volumes, not necessarily associated with a displacement of the plates, they coalesce to produce a simply connected volume.

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RESUMO

Configurações alternativas da interface entre dois fluidos em contacto com sólidos.

Faz-se um estudo comparativo das diversas configurações de equilíbrio (com simetria axial) que pode assumir a interface entre dois fluidos imiscíveis, colocados entre duas placas paralelas e idênticas. As configurações possíveis são: pontes líquidas, «gotas» cativas e «gotas» isoladas e combinações não-conexas destas. Com base em cálculos das propriedades geométricas e da energia de Helmholtz, discute-se a estabilidade de cada configuração e prevê-se as transições que ocorrem quando o limite de estabilidade de uma delas é ultrapassado.