## GROWING DROPS AND BUBBLES

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The deformation of the free surface is considered for a slowly growing drop or bubble with a horizontal solid wall (either continuous or having a circular hole). The volume at the instant of detachment is determined. It is assumed that the liquid is subject to surface tension and gravitational forces.

1. Consider a liquid drop (gas bubble) of axially symmetrical shape on the lower (or upper) surface of a solid horizontal plate subject to capillary forces and gravitation of strength $\mathrm{ng}\left(\mathrm{g}=9.81 \mathrm{~m} / \mathrm{sec}^{2}, \mathrm{n}\right.$ is the overload factor), the gravitational force being directed vertically downwards. The plate may be continuous or have a circular hole of radius $r_{0}$ with its center at the axis of symmetry (Fig. 1).

We assume that the volume of the drop or bubble increases slowly, e.g., due to condensation or evaporation of the liquid or forced injection of the liquid or gas through the hole in the plate. We assume that the growth rate is so small that the inertial forces can be neglected relative to gravitation and surface tension.

Under these conditions we need to determine the deformation of the free surface and the critical value $\mathrm{v}^{*}$ of the volume at which the drop or bubble is detached. The problem will be considered as aquasistatic one. It is formulated as follows: find the equilibrium shape of the drop (bubble) if the volume of liquid (gas) at a given instant is v subject to given values for the surface tension $\sigma$, density $\rho$, and wetting angle $\alpha$; find the value $\mathrm{v}=\mathrm{v}^{*}$ at which the corresponding equilibrium state becomes unstable.

The value of $v^{*}$ is the volume of the drop or bubble at the instant of detachment, not the volume detached. It is difficult to find the latter accurately without solving the dynamical problem.

This problem arises in various aspects of chemical technology [1, 2] and some aspects of space research. The solution may be of value in examining the behavior of steam bubbles in boiling [3-7].

The present study is based on the results of [8-11]. The solution can be used as an illustration of the use of the methods of [8-11] in problems on the behavior of drops (bubbles) in contact with solid surfaces of arbitrary axially symmetrical shape.

The set of all equilibrium forms for drops and gas bubbles coincides apart from mirror symmetry with respect to the horizontal plane. The stability conditions also coincide, so in what follows we will consider only a drop, although the results all apply equally well to bubbles.
2. Consider the shape of the free surface. Singly coupled axially symmetrical equilibrium surfaces for a liquid in a gravitational field have been examined previously [8, 9], and such surfaces are uniquely determined by their axial cross sections, namely, their equilibrium curves.


Fig. 1 Lines 1-6 in Fig. 2 illustrate the behavior of the families of maximum realizable parts of the equilibrium curves in terms of the dimensional variables.

$$
R=\sqrt{|b|} r, \quad Z=\sqrt{|b|} z \quad\left(b=\rho n g_{i} \sigma, \quad r^{2}=x^{2}+y^{2}\right)
$$

(see [8, 9] for more details of this family). These parts are bounded by the line 0 wEF . If the equilibrium curve is not contained completely in the region 0 wEF 0 , then the corresponding equilibrium surface is certainly unstable $[8,10]$.

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Each of the families of equilibrium curves has a corresponding value of parameter $C$ (lines 1-6 correspond to values of $C$ of $0.6,1.2,1.8,2.6,3.5,7.0$, respectively). In determining the droplet shape it is sufficient to consider the curves for which $C \geq 0$ (in determining bubble shape one can use the mirrorimages of these curves with respect to the line $Z=0$; they correspond to negative values of C ).

The shape of the free surface is uniquely determined by the coordinates $R_{A}, Z_{A}$ of the point of contact $A$ between the equilibrium curve and the solid wall or the coordinate $\mathrm{R}_{\mathrm{A}}$ of that point and the value of the parameter $C=C_{L}$ on the equilibrium curve $L$. Each point $\left(R_{A}, Z_{A}\right)$ in Fig. 2 corresponds to a certain value of the angle $\beta$ between the tangent to the equilibrium curve at point $A$ and a definite value for the dimensionless volume

$$
\pi \int_{L} R^{2} d Z=V_{1}\left(C_{L}, R_{A}\right)
$$

where the integration is performed along $L$ from point 0 to point $A$. The values of $\left(R_{A}, Z_{A}\right)$ or ( $C_{L}, R_{A}$ ) must be chosen such that the drop has the specified value for the dimensionless volume $V=|\beta|^{3 / 2} v$

$$
\begin{equation*}
V=V_{1}\left(C_{L}, R_{A}\right) \tag{2.1}
\end{equation*}
$$

and that the necessary condition for stable equilibrium is set at point A.
It is found $[8,11]$ that the stable equilibrium requires that the angle of contact equals the wetting angle along the line of contact with the smooth surface. If the line of contact runs along a ridge in the solid wall, the angle of contact should be not less than the corresponding wetting angle. In the case of a drop hanging from a plate with a hole, these conditions can be put as

$$
\begin{array}{ll}
\beta\left(C_{L}, R_{A}\right)=\alpha, & \text { if } \\
\beta\left(C_{L}, R_{A}\right) \leqslant R_{0}  \tag{2.3}\\
& \text { if } \\
R_{A}=R_{0}
\end{array}
$$

Here $R_{0}=\sqrt{|b|} x_{0}$ is the dimensionless radius of the hole.
For any given instant one can use known values for $V, \alpha$, and $R_{0}$ with (2.1) and (2.2) and (2.3) to find $C_{L}$ and $R_{A}$ and the shape of the free surface. We use the method described in [9] and the graphs given the re for $V_{1}(R)$ and $\beta(R)$ for the set of values of $C$. The known values of $\rho, \mathrm{n}, \sigma$, and $v$ are used to find $V$. Then the $V_{1}(C, R)$ curves are used to draw the horizontal straight line $V_{1}=V$, and from the values of $(C, R)$ at the points of intersection with the curves of the $V_{1}(C, R)$ family we construct the curve ( $C, R$ ). Each point ( $C, R$ ) on this curve corresponds to an equilibrium curve for some drop having the specified volume. However, such a drop, in general, will not meet condition (2.2), (2.3) on the line of contact with the solid.

We identify the ( $C, R$ ) for which (2.2) is met. For this purpose we calculate $R_{0}$, and on the $\beta(C, R)$ curves we draw horizontal straight line $\beta=\alpha, R>R_{0}$, and at the points of intersection with the $\beta(C, R)$ curves we derive a second $C(R)$ curve. If these two $C(R)$ curves have points of intersection, then each point ( $C^{*}, R^{*}$ ) corresponds to an equilibrium curve $C_{L}=C^{*}, R_{A}=R^{*}$, while the volume and angle of contact have preset values, and the line of contact encompasses the hole. To represent the shape of the equilibrium curve one has to draw in Fig. 2 the point of contact for which $R=R_{A}=R *, C=C L=C$; this point can be defined more precisely if we find the value $\mathrm{Z}=\mathrm{Z}_{\mathrm{A}}$ for it from the following equation [9]:

$$
2 R_{A} \sin \beta_{A}=-Z_{A} R_{A}^{2}+C_{L} R_{A}^{2}+\pi^{-1} V .
$$

The value $\beta_{A}=\beta\left(C^{*}, R^{*}\right)$ appearing there must be found via the $\beta(C, R)$ relationships.
Consider now condition (2.3). On the $\beta(C, R)$ curves we draw a vertical straight line $R=R_{0}, 0 \leq \beta \leq \alpha$ and use its points of intersection with the $\beta(C, R)$ curves to construct a third $C(R)$ curve. If this third curve $C(R)$ has points of intersection with the first $C(R)$ curve, then each such point corresponds to an equilibrium curve for a drop with given values for the volume and line of contact with the plate running along the edge of the hole.

If the first of the $C(R)$ curves does not intersect with the other two, this means that there are no stable equilibrium forms for the drop under these conditions. If the constructions give one or several equilibrium block forms, one has to verify whether these equilibrium forms are stable.


Fig. 3


Fig. 4
3. The stability conditions for equilibrium forms have previously been examined $[8,10,11]$ via the principle of minimum potential energy. These conditions may be formulated as follows for the present case:

1) the equilibrium state will be stable for $R_{A}>R_{0}$ if the point of contact A shown in Fig. 2 with the coordinates $\left(R_{A}, Z_{A}\right)$ lies below the line 0tEF; if $A$ lies above that line, the equilibrium state is unstable. The point of contact A lies on the line OtEF in critical equilibrium states, and the loss of stability occurs in an axially symmetrical fashion (the equilibrium state is always unstable with respect to unsymmetrical perturbations that displace the drop as a whole in a horizontal direction, but such perturbations do not detach the drop and so are not considered).
2) The equilibrum state of the drop will be stable for $R_{A}=R_{0}$ if the corresponding point ( $\mathrm{R}_{\mathrm{A}}, \mathrm{Z}_{A}$ ) lies below the line 0 wEF and the condition $\beta_{A}<\alpha$ is met. If point $A$ lies above $0 w E$ or if $\beta_{A}>\alpha$, then the equilibrium state is unstable. The critical equilibrium state (for $\beta_{A}<\alpha$ ) corresponds to points of contact $\left(\mathrm{R}_{\mathrm{A}}, \mathrm{Z}_{A}\right)$ that lie on the line 0 wEF ; stability is lost on the 0 WE in an axially symmetrical fashion, and on EF in an unsymmetrical fashion, and at point $e$ in either fashion.

Here we have omitted the comparatively rare cases where point $A$ lies on the curve $0 t E$ (for $R_{A}>R_{0}$ ) or on the line $0 w E F$ (if $R_{A}=R_{0}$ and $\beta_{A} \leq \alpha$ ) or as $\beta_{A}=\alpha$ (for $R_{A}=R_{0}$ ).
These stability conditions show that stable equilibrium states of a drop on a plate exist only for $\mathrm{R}_{0} \leq \mathrm{R}_{\mathrm{F}}=3.83 \ldots$
4. Consider the properties of the functions $V_{1}(R, Z), \beta(R, Z)$ and their level lines. The behavior of the surface shape in response to volume increase can be judged from the position of the point of contact $\left(\mathrm{R}_{A}, \mathrm{Z}_{A}\right)$ in Fig. 2, where the characteristic equilibrium curves 1-6 are accompanied by level lines for $\beta=$ constant (lines $7 \sim 14$, which correspond to $\beta$ of $5,15,30,45,60,75,90$, and $105^{\circ}$ ), and parts of the lines $V_{1}=$ const (broken lines $15-22$, on which $V_{1}$ takes the values $2.0,3.42,5.4,8.0,11.2,14.8,17.65$, and 18.72, respectively). The following points concern the disposition of these lines in Fig. 2.

The function $V_{1}(R, Z)$ has a maximum at point $E$ :

$$
V_{1}(R, Z)<V_{1}\left(R_{E}, Z_{E}\right)=18.96
$$

for $(R, Z)$ lying below 0 wEF ; on the $Z=0$ axis, the function $V_{1}(R, 0)=0$, and $V_{1}=\mathscr{F}_{1}(R)$ on 0 wEF is shown in Fig. 3.

Each line $V_{1}=$ constant lying on or below 0 WEF has not more than one point of intersection and one point of contact with each vertical line, and also not more than two points of intersection and one point of contact with each line $\beta=$ constant.

The points of contact of the curves $V_{1}=$ const and straight lines $R=$ const lie on the line $0 w E$. If $\left(R_{1}, Z_{1}\right)$ is one of these points, then $V_{1}\left(R_{1}, Z\right)$ as a function of $Z$ increases monotonically in the range $0 \leq$ $\mathrm{Z} \leq \mathrm{Z}_{1}$ and has a local maximum at $\mathrm{Z}=\mathrm{Z}_{1}$.

Each line $\beta=$ constant lying below 0 wEF has not more than two points of intersection and one point of contact with each vertical line. The line $\beta=0$ is the broken line 0 FE . The $\beta=\mathrm{f}_{1}(\mathrm{R})$ relation is shown by curve 1 of Fig. 4 for the points of contact of the $\beta=$ constant curve and $R=$ constant straight lines.

At such points ( $\mathrm{R}_{2}, \mathrm{Z}_{2}$ ) we have

$$
\beta\left(R_{2}, Z_{2}\right)>\beta\left(R_{2}, Z\right)
$$

for $Z \neq Z_{2}$ and ( $\mathrm{R}_{2}, \mathrm{Z}$ ) lying below 0 WEF .
The points of contact of the $\beta=$ constant curves with the $V_{1}=$ const curves lie on the line $0 t E$; curve 2 of Fig. 4 shows $\beta=f_{2}(\mathrm{R})$ for these, while Fig. 5 shows $V_{1}=\mathscr{F}_{2}(\beta)$.

Numerical calculation confirms that $\left.V_{1}(R, Z)\right|_{\beta=c o n s t}$ and $\left.V_{1}(R, Z)\right|_{R=\text { const }}$ have local minima, respectively, at points on the curves $0 t E$ and 0 wE , and this can be seen if one bears in mind that attainment of the first local maximum and stability loss with respect to axially symmetrical perturbations will coin-

cide in the corresponding problems. This was incorporated in [12], where $\mathrm{V}^{*}$ was determined for a solid plate as the first maximum value of $\mathrm{V}_{1} \mid \beta=\mathrm{const}$, using the tables [13] to construct $\mathrm{V}^{*}(\beta)$ for $0 \leq \beta \leq 121^{\circ}$. This relationship (Fig. 5) for the complete range in $\beta$ was constructed by another method in [8] (a misprint was made in formulating the graph of $\mathrm{V}^{*}(\beta)$ in [8]: it in fact shows $\pi^{-1} \mathrm{~V}^{*}(\beta)$ ):

The detachment of a drop from the edge of a hole in a plate [2] also gave the critical volume as the first maximum value of $V_{1}$ for $R=$ constant, together with the $V^{*}\left(R_{0}\right)$ relationship for $R_{0} \leq 2.5$ (Fig. 3). This approach is correct only for $R_{0} \leq R_{E}=3.22$, where the loss of stability has axial symmetry; if $3.22<R_{0}<3.83$, unsymmetrical perturbations are more hazardous, and stability is lost before the local maximum in $V_{1}(R, Z) \mid R=$ const is reached.
5. We now describe the behavior of the drop shape and the critical volume in relation to the physical parameters.

Consider the case where the plate has no hole ( $\mathrm{R}_{0}=0$ ); in that case, condition (2.2) must be met at point A , so the set of possible positions for point A in Fig. 2 will be the curve $\beta(\mathbf{R}, \mathrm{Z})=\alpha$. Let the initial volume of the drop be zero. As the volume increases gradually, the point of contact $\left(R_{A}, Z_{A}\right)$ will move in Fig. 2 from the origin along the line $\beta(\mathrm{R}, \mathrm{Z})=\alpha$ until this line meets the curve 0 tE . Here the dimensionless volume reaches its maximum possible value for a given $\alpha$, i.e., the critical value, and the drop becomes unstable [8] and part falls away. Then for a plate without a hole, the points of contact $\left(R_{A}, Z_{A}\right)$ lie on the line $0 t E$ for critical equilibrium states. As $\beta_{\mathrm{A}}=\alpha$, the critical dimensionless volume as a function of wetting angle takes the form

$$
V^{*}=\mathscr{F}_{2}(\alpha),
$$

and Fig. 5 shows the curve, where one puts $\mathrm{V}_{1}=\mathrm{V}^{*}$ and $\beta=\alpha$.
We now consider the case where the plate has a hole $\mathrm{R}_{0}<\mathrm{R}_{\mathrm{F}}=3.83 \ldots$ (see Sec. 3). Initially, the free surface is flat, and the line of contact with the plate runs along the edge of the hole. The point of contact $A$ will have the coordinates $R_{A}=R_{0}, Z_{A}=0$. As $\beta_{A}=0$, we have for any $0<\alpha<\pi$ that $\beta_{A}<\alpha$, and Sec. 3 indicates that the initial equilibrium state will be stable. This equilibrium state corresponds to a drop of zero volume. As the volume increases, point $A$ in Fig. 2 begins to move upwards along the line $R=R_{0}$, while (2.3) is obeyed: $\beta_{A} \leq \alpha$. Various cases can arise:

$$
\text { I. } R_{0} \leqslant R_{E}=3.22
$$

a) $\mathrm{f}_{1}\left(\mathrm{R}_{0}\right) \leq \alpha<\pi$; as $\beta\left(\mathrm{R}_{0}, \mathrm{Z}\right) \leq \mathrm{f}_{1}\left(\mathrm{R}_{0}\right)$, the condition $\beta_{\mathrm{A}} \leq \alpha$ cannot be violated, and so $A$ will move upward along the line $R=R_{0}$ until it reaches the curve $0 w E$. Then Secs. 3 and 4 indicate that the drop reaches its maximum possible volume (for stable axially symmetrical equilibrium states) of $V=\mathscr{F}_{1}\left(R_{0}\right)$, and stability is lost when this is exceeded. The resulting motion of the liquid may cause part of the drop to break away or the entire drop to transfer to a new equilibrium state. As the loss of stability has axial symmetry, the resulting motions also must have axial symmetry, and the new stable equilibrium state will be of the same type. However, for $V>\mathcal{F}_{1}\left(R_{0}\right)$ such equilibrium states do not exist (see Sec. 4). Consequently, the drop must break away, and hence, in this case the $\mathrm{V}^{*}\left(\mathrm{R}_{0}\right)$ relationship takes the form

$$
V^{*}=\mathscr{F}_{1}\left(R_{0}\right)
$$

Figure 3 shows the curve, where one puts $V_{1}=V^{*}$ and $R=R_{0}$.
b) $f_{2}\left(R_{0}\right) \leq \alpha \leq f_{1}\left(R_{0}\right)$; in this case the line $R=R_{0}$ and the curve $\beta(R, Z)=\alpha$ have two points of intersection, which lie below 0tE. Point A will move along the line $R=R_{0}$ up to the first of these points, and then along the curve $\beta(R, Z)=\alpha$ (to the right of the vertical line $R=R_{0}$ ) to meet the vertical line $R=R_{0}$, and then again vertically upwards along this line to meet the line 0wE, where stability is lost and the drop falls away. The critical volume is as in case a), i.e., $V^{*}=\mathcal{F}_{1}\left(R_{0}\right)$.
c) $0<\alpha<f_{2}\left(R_{0}\right)$; the straight line $R=R_{0}$ and the curve $\beta(R, Z)=\alpha$ have either one or two points of intersection. The first of these lies below 0tE, while the second lies above it. Point A will move vertically upwards along $R=R_{0}$ to the first point of intersection, and then along the curve $\beta(R, Z)=\alpha$ (to the right of $R=R_{0}$ ) until it reaches curve $0 t E$. Then Sec. 3 indicates that the volume $V=\mathscr{F}_{2}(\alpha)$ is reached, and the drop loses stability. It is shown that the stability loss produces an axially symmetrical motion such that the radius $R_{A}$ of the line of contact falls. In such motion, this line may sit on the edge of the hole, and the drop (after the transient) can take up a new equilibrium state. In Fig. 2 this state will correspond to a
point A lying on the intersection of the curve $V_{1}(R, Z)=\mathscr{F}_{2}(\alpha)$ with the straight line $\mathrm{R}=\mathrm{R}_{0}$. If $\mathscr{F}_{2}(\alpha)>\mathscr{F}_{\mathrm{i}}\left(R_{0}\right)$, there is no such point of intersection (see Sec. 4). Therefore, the drop breaks away when the volume passes through the value $V=\mathscr{F}_{2}(\alpha)$. If $\mathscr{F}_{2}(\alpha)<\mathscr{F}_{1}\left(R_{0}\right)$ one cannot rule out in advance the possibility that the drop will transfer to a new stable equilibrium state. The question can be decided by calculating the observed stability of the equilibrium state, or else by examining the dynamical problem. If such a transition occurs, the shape change will proceed as in case b), i.e., $V^{*}=\mathscr{F}_{1}\left(R_{0}\right)$.

$$
\text { II. } R_{0}>R_{E}=3.22
$$

a) $\mathrm{f}_{1}\left(\mathrm{R}_{0}\right) \leq \alpha<\pi$; in that case, as in Ta , the condition $\beta_{\mathrm{A}} \leq \alpha$ cannot be violated, and the point A will move upwards along the straight line $R=R_{0}$ until it meets the curve $E F$. Here the drop volume is largest (for stable axially symmetrical equilibrium states corresponding to $R_{A}=R_{0}$ ). The value of the volume is

$$
V=\mathscr{F}_{1}\left(R_{0}\right)
$$

Then the stability loss occurs in an unsymmetrical fashion on line EF, so for given $V>\mathscr{F}_{1}\left(R_{0}\right)$ the drop may take a distorted stable form, which for $V \rightarrow \mathscr{F}_{1}\left(R_{0}\right)$ goes over continuously to the critical axially symmetrical form. However, a discussion of the branching of the equilibrium surfaces on the line EF (subject to the condition that the line of contact persists) indicates that this is not possible, so attainment of the volume $V=\mathscr{F}_{1}\left(R_{0}\right)$ will mean detachment of the drop in whole or in part, or else jump to some comparatively remote unsymmetrical stable state. By virtue of the latter possibility, we can merely assume that $V^{*}=\mathscr{F}_{1}\left(R_{0}\right)$ in this case.
b) $0<\alpha<\mathrm{f}_{1}\left(\mathrm{R}_{0}\right)$; the initial stage of behavior is as in case Ib , while the final state is as in case IIa.

Consideration of the shape behavior of the free surface for a drop sitting on a circular hole shows that:

1) in the case $R_{0} \leq R_{E}$

$$
\begin{aligned}
& V^{*}=\mathscr{F}_{1}\left(R_{0}\right), \quad \text { if } \quad f_{2}\left(R_{0}\right) \leqslant \alpha<\pi ; \\
& \text { while if } 0<\alpha<f_{2}\left(R_{0}\right), \text { then } \\
& V^{*}=\mathscr{F}_{2}(\alpha) \text { for } \mathscr{F}_{2}(\alpha) \geqslant \mathscr{F}_{1}\left(R_{0}\right) \\
& \text { and } \mathscr{F}_{2}(\alpha) \leqslant V^{*} \leqslant \mathscr{F}_{1}\left(R_{0}\right) \text { for } \mathscr{F}_{g}(\alpha)<\mathscr{F}_{1}\left(R_{0}\right)
\end{aligned}
$$

2) in the case $R_{0}>R_{E}$

$$
V^{*}=\mathscr{F}_{\mathrm{i}}\left(R_{0}\right)
$$

We have $V^{*}=\mathscr{F}_{2}(\alpha)$ if the drop hangs on a continuous plate.
For the gas bubble in a liquid with wetting angle $\alpha_{1}=\pi-\alpha$ the shape behavior will be as above for a liquid with a wetting angle of $\alpha$.

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