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Fig. 1

Figure 1: Fig. 1

Abstract**Full Text**

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PHYSICAL CHEMISTRY

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ON THE MECHANISM OF BUBBLE DETACHMENT FROM A NONWETTABLE HORIZONTAL PLANE*(Presented by Academician A. N. Frumkin on 29 IV 1965)*

For the theory and practice of many physical and chemical processes, the mechanism of detachment of vapor or gas bubbles growing on a solid surface, as well as the size of the detaching bubbles, is of great importance. It is generally assumed that the dependence of the detachment diameter D_{\max} on the contact angle θ , the surface tension σ , and the densities of the liquid ρ and vapor ρ' is determined by Fritz' s formula ⁽¹⁾

$$D_{\max} = \varphi(\theta) \sqrt{\sigma/g(\rho - \rho')}, \quad (1)$$

where the function $\varphi(\theta)$ is usually replaced by its approximate value $\varphi \cong 0.220$. Fritz obtained this formula with the aid of tables ⁽²⁾. In doing so he assumed that the detachment volume coincides with the maximum bubble volume V_{\max} , above which mechanical equilibrium becomes impossible. Formula (1) is in satisfactory agreement with experimental data ⁽³⁻⁵⁾; however, in all these experiments the contact angles did not exceed 100° .

In reality, however, for large θ the detachment diameter is smaller than that determined by equality (1). The reason is that Fritz' s formula determines the maximum volume, whereas the detachment volume may turn out to be smaller than V_{\max} because of violation of the stability condition for the bubble shape.

Fig. 1

To determine the initial volume (diameter) of a rising bubble, it is necessary to clarify the dynamics of its growth and detachment. This problem can be solved by variational methods. From the symmetry conditions it is clear that the surface bounding the bubble is a surface of revolution; it can be determined

from the condition of a minimum of the total energy U , equal to the sum of the surface energy U_1 and the potential energy U_2 .

As is seen from Fig. 1,

$$U_1 = \pi \int_{-x}^x \left[(\sigma_{20} - \sigma_{12}) + \sigma_{10} \sqrt{1 + y'^2} \right] x dx. \quad (2)$$

Accordingly,

$$U_2 = -\frac{1}{2} g(\rho - \rho') \pi \int_{-x}^x xy^2 dx \quad (3)$$

(ρ and ρ' are the densities of the liquid and vapor).

Thus, the problem is reduced to determining the minimum of the functional

$$U = \pi \int_{-x}^x \left[\sigma_{20} - \sigma_{12} + \sigma_{10} \left(\sqrt{1 + y'^2} - \frac{y^2}{2a^2} \right) \right] x dx \quad (4)$$

with movable ends under the condition of constancy of the bubble volume

$$V = \pi \int_{-x}^x xy dy = \text{const} \quad \left(a^2 = \frac{4\sigma_{10}}{g(\rho - \rho')} \right) \quad (4')$$

The Euler equation for the conditional minimum has the form

$$-\frac{d}{dx} \frac{xy'}{\sqrt{1 + y'^2}} + \frac{yx}{a^2} - \lambda x = 0, \quad (5)$$

where λ is an undetermined Lagrange multiplier.

For large contact angles, y' is small, so that in (5) one may neglect the term $y'/\sqrt{1 + y'^2}$. As a result we obtain the equation determining the shape of the contour of the bubble section:

$$-\frac{d}{dx} \frac{y'}{\sqrt{1 - y'^2}} + \frac{y}{a^2} - \lambda = 0. \quad (6)$$

As shown in [6], the first integral of this equation can be represented in the form

$$\sin^2 \frac{\alpha}{2} = \frac{1}{a^2} (h^2 - y^2) + \lambda(y - h), \quad (7)$$

where α is the angle of inclination of the tangent to the contour at the point with ordinate y ; $h = y_{\max}$ is the height of the contour at the center of the bubble. To eliminate λ , we take into account that for the boundary points ($y = 0$)

$$\sin^2 \frac{\alpha_0}{2} = \frac{h}{a^2} - \lambda h, \quad (8)$$

with $\alpha_0 = 180^\circ - \theta$. Consequently,

$$\lambda = \frac{h}{a^2} - \frac{1}{h} \sin^2 \frac{\alpha_0}{2}. \quad (8')$$

Substituting (8') into (7), we obtain

$$\sin^2 \frac{\alpha}{2} = \frac{1}{a^2} (h - y)y + \left(1 - \frac{y}{h}\right) \sin^2 \frac{2\alpha_0}{2}. \quad (9)$$

It is easy to see that, as y changes from 0 to h , the angle α changes from α_0 to 0. To determine the character of the variation of the angle α , we find the maximum of the function $\sin^2 \alpha/2 = f(y)$, corresponding to the point of inflection on the bubble contour. For the relative height of the inflection points we obtain

$$\frac{y_1}{h} = \frac{1}{2} - \frac{1}{2h^2} a^2 \sin^2 \frac{\alpha_0}{2}. \quad (10)$$

It follows from this that, as long as the height of the bubble has not reached the value

$$h^* = a \sin \frac{\alpha_0}{2} a \cos \frac{\theta}{2}, \quad (11)$$

there is no inflection on the contour.

Since h^* decreases, while the maximum height h_{\max} increases with the angle θ , there exists a certain critical angle θ^* . If $\theta < \theta^*$, a neck cannot form in the bubble. In the case $\theta > \theta^*$, such a neck appears in sufficiently large bubbles. For small θ , the bubble height h

is close to its diameter D . Therefore one may assume that $h_{\max} = 0.011\theta a$, and since $h_{\max}(\theta^*) = h^*(\theta^*)$, then $0.011\theta^* = \cos \theta^*/2$. Hence $\theta^* \approx 73^\circ$.

It is clear that for $\theta < 73^\circ$ the bubble can detach only as a whole, but for $\theta > 73^\circ$ another type of detachment is also possible—along a neck. The condition for detachment of the bubble along the neck is equality of the angle α_{\max} at the inflection point to 180° (see Fig. 2). Substituting (10) into (11), after simple transformations we obtain

$$\sin \frac{\alpha_{\max}}{2} = \frac{1}{2ah} \left(h^2 + a^2 \sin^2 \frac{\alpha_0}{2} \right), \quad (12)$$

whence follows the monotonic increase of α_{\max} with the bubble height h .

Fig. 2

Fig. 2

Finally, at a certain h_0 the angle α_{\max} reaches 180° , and the upper spherical part separates from the base of the bubble.

Thus, it remains to determine the conditions under which one or the other detachment mechanism occurs. If in (12) we put $\alpha_{\max} = 180^\circ$, then for h_0 we obtain $h_0 = a(1 + \sin \theta/2)$. Correspondingly, the height of the neck will be equal to (Fig. 3)

$$y_{10} = \frac{1}{2} \left(h_0 - \frac{1}{h_0} a^2 \sin^2 \frac{\alpha_0}{2} \right), \quad (13)$$

so that the diameter of the upper spherical part of the bubble

$$D_0 = h_0 - y_{10} = a = 2\sqrt{\sigma/g(\rho - \rho')} \quad (14)$$

does not depend on the angle θ .

Fig. 3

Fig. 3

Obviously, the mechanism of detachment along the neck will begin to act from the moment when the total volume of the spherical part V_0 and of the base of the bubble V becomes equal to the maximum V_{\max} determined by equality (1). It can be shown that always $V < V_0$. Therefore bubbles will evidently detach along the neck from the moment when $V_0 = V_{\max}/2$. Substituting, instead of V_0, V_{\max} , the expressions D_{\max} and D_0 from equalities (1) and (14), we obtain for the limiting angle $\theta_0 \approx 100^\circ$.

Thus, for contact angles $\theta < 100^\circ$ Fritz' s formula is valid, while for $\theta > 100^\circ$ the size of the detaching bubbles does not depend on the angle θ and is determined by formula (14).

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