Entrapment of Gas in the Spreading of a Liquid Over a Rough Surface

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Conditions for the incomplete displacement of gas from the valley between two parallel ridges by a liquid-drop front advancing over the ridges are calculated. The significant parameters are found to be the liquid density, surface tension, contact angle, and geometry of the ridges. The solution may be obtained analytically or, more conveniently, graphically. Surface roughnesses are divided into four classes, one of which can stably switch from liquid—to gas—fill, and another vice versa. This may account for some of the hysteresis effects reported in bubble nucleation. It is pointed out that surfaces consisting predominately of cavities are more likely to follow these considerations than grooved surfaces, owing to displacement of gas by advance of liquid along the grooves. An example important in boiling and cavitation theory is worked out, and qualitative agreement with the literature is shown.

In 1953 Bartell and Shepard (*2*) reported the results of an interesting series of experiments on the wetting of rough paraffin surfaces. The surfaces were machined in two directions to give pyramidal asperities of known height h and inclination to the horizontal ϕ, and the advancing and receding contact angles of large drops of various liquids on these surfaces were measured. In all cases the advancing contact angle increased with increasing ϕ. With liquids which wet the surface poorly, such as water, the hysteresis of the contact angle was almost exactly equal to the inclination ϕ. With liquids of better wetting power, such as methanol, the situation became complicated by the fact that flow through the valleys, as well as over the tops of the asperities, was an important mode of advance and recession; however, the results in general support the conclusion that would be expected from the application of Young's equation (*10*) on a microscopic scale, i.e., that the static contact angle at any point of the triple interface is a constant. The increase in advancing contact angle with increase of ϕ can be attributed to the fact that the triple interface usually comes to rest on the rear (viewed from the direction of advance) faces of the asperities, since this usually requires less contortion of the free liquid surface, and hence more nearly satisfies the minimum energy requirements.

Of equal interest was Bartell and Shepard's observation that the degree of air entrapment depended primarily on the steepness of the asperities and secondarily on their height. Large-scale entrapment was apparent in several cases where $\phi = 60$ deg. They proposed the hypothesis that the advancing liquid front contacts the forward face of the next asperity before displacing all the air from the crevice between and that the advance then proceeds from this new point of contact. The importance of this phenomenon is made apparent when it is realized that in practically all cases of ebullition, cavitation, and effervescence the appearance of bubbles is nucleated and controlled by minute quantities of gas, usually entrapped on solid surfaces. Each of these crevices where the advancing liquid front fails to displace the gaseous phase completely may therefore be a nucleus for bubble formation. Bartell and Shepard did not go into the conditions for entrapment quantitatively, and it is the purpose of this paper to set quantitative criteria for entrapment and displacement of gases from surface roughnesses. The mechanism considered by Bartell and Shepard, namely the advancement of the liquid across a valley, is alone considered. It is hoped that the advance of the liquid front along a valley will be considered at a later time. In addition to valleys, entrapment of gases in holes is also considered.

FREE LIQUID SURFACE

Before the surface geometry is considered, it is necessary to obtain the equation of the free surface of a semi-infinite sheet of liquid advancing unidirectionally. The two-dimensional problem is chosen to simplify the calculation, and since the orientation of the sheet is not specified, this does not limit the generality. The horizontal asymptote to the free liquid surface is chosen as the X axis. The location of the vertical Z axis is fixed by the condition that $X = 0$ when $Z = -2B^{1/2}$, where

$$B = \frac{\gamma}{(\rho_L - \rho_G)g} \qquad (1)$$

In this case γ is surface tension, ρ_L and ρ_G are the densities of liquid and gas, and g is the local acceleration due to gravity. Since one principal radius of curvature of the liquid surface is everywhere infinite, the Gibbs (*5*) condition for equilibrium of a curved interface reduces to

$$Z = \frac{-B}{R} \qquad (2)$$

where R is the radius of curvature. The solution of this problem yields (*1*) for a sheet advancing to the left

$$X = B^{1/2}\left[\log\left(+\sqrt{\frac{4B}{Z^2} - 1} - \frac{2B^{1/2}}{Z}\right) - 2\sqrt{B - \frac{Z^2}{4}}\right] \qquad (3)$$

The signs in front of the square-root terms would be reversed for a sheet advancing to the right. The valuable result is obtained that, for a particular liquid at a particular temperature, a single curve describes all possible surface configurations, regardless of contact angle at the solid surface, since B is the only parameter in Equation (3).

SURFACE GROOVES

Now the advance of this semiinfinite liquid sheet normally across a groove, or valley is considered. It should be noted that a system of long grooves constitutes the most common type of gross surface roughness of metals, since almost all metal-forming operations, such as machining, drawing, extruding, polishing, and even pressing, will give a grooved surface. In regard to grooves with a V-shaped profile, such that the angle of inclination of the groove walls with the horizontal is ϕ (Figure 1), the conditions for entrapment may be quite simply stated:

$$\theta > 180° - 2\phi \qquad (4)$$

This implies that no gas can be entrapped if the liquid wets the solid perfectly ($\theta = 0$). Likewise, every deep groove with vertical walls will have trapped gas, according to this mechanism. It should be emphasized at this point that we are considering displacement of gas only by travel of liquid across the grooves, and not by some other mechanism, such as travel along the grooves.

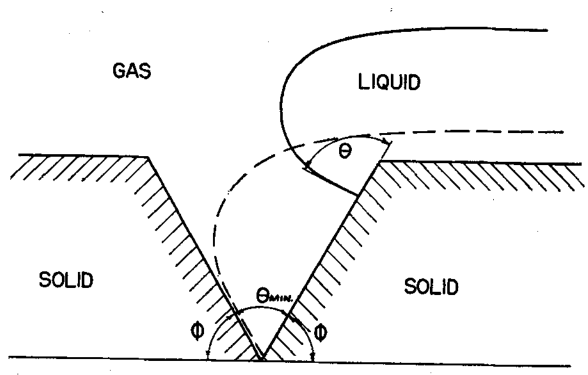

Fig. 1. Conditions for the entrapment of gas in the advance of a semiinfinite liquid sheet across a groove.

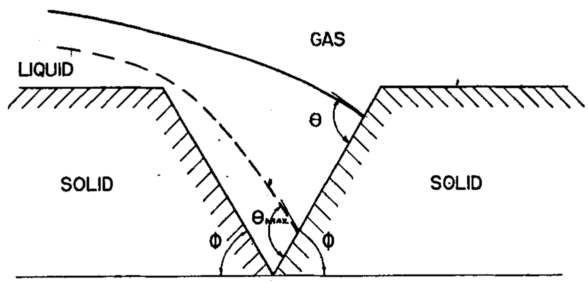

Fig. 2. Conditions for the entrapment of liquid in the recession of a semiinfinite liquid sheet across a groove.

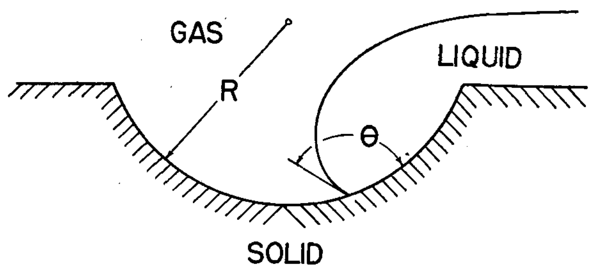

Fig. 3. Advance of a semiinfinite sheet of liquid across a rounded groove.

It is of interest to consider the displacement of liquid from the grooves by gas (Figure 2). It is assumed that the walls of the groove are perfectly smooth, and so by a microscopic force balance, there is no hysteresis of the contact angle. If the curvature of the liquid surface within these small cavities is neglected, the condition that the advancing gas-liquid interface fails to displace the liquid completely is

$$2\phi > \theta \tag{5}$$

This makes it possible to divide grooves in a particular system into four classes: (1) those that obey the first inequality, but not the second, (2) those that obey the second, but not the first, (3) those that obey both, and (4) those that obey neither. These will be examined in more detail.

The first class will exist when the liquid wets the solid poorly ($\theta \geq 90$ deg.) and when the grooves are gradually sloped ($\phi < 45$ deg.). Gas will be trapped in these shallow grooves, and even if the groove is filled with liquid, it can be completely displaced by gas. This would favor a maximum number of nucleation sites for cavitation or boiling from the surface.

The second class will exist when the liquid wets the solid well ($\theta \ll 90$ deg.) and ϕ is not nearly zero. Liquid will always eventually fill these grooves. It follows that the addition of wetting agents, sometimes used to obtain smaller bubble-release volumes in boiling, may have an unfavorable effect in reducing the number of effective nucleation sites.

The third class will exist when θ is not nearly zero, and $\phi \gg 45$ deg. Similarly, the fourth class will exist when θ is not nearly zero, and $\phi \ll 45$ deg. All very steep-walled grooves will be in the third class, from which complete displacement of either liquid or gas, once filled, is not possible. All very shallow grooves will be in the fourth class, in which entrapment is not possible.

The existence of the first and second classes of grooves, in which it is possible to switch stably from liquid to gas filled, and vice versa, may account for hysteresis phenomena observed by several investigators (*4, 9, 6*) in boiling heat transfer.

The problem becomes more complex when rounded grooves are considered. From Figure 3 it will be seen that the liquid contact angle must be considerably greater than 90 deg. in order to entrap gas if the groove is semicircular in cross section. It will be practically impossible to trap gas if the cross-sectional arc is less than a semicircle.

If the groove has any arbitrary geometry, Equation (2) must be used in either an analytical or graphical solution, the graphical solution usually being the easier method. As an example, one may wish to find the width of a groove with vertical walls which will always entrap gas when water at 100°C. is spreading over the surface with a contact angle of 60 deg. This problem is of importance in boiling heat transfer. The solution, which is given graphically in Figure 4, shows that a relatively wide groove will still entrap gas. Once again, however, only this mechanism is here being considered.

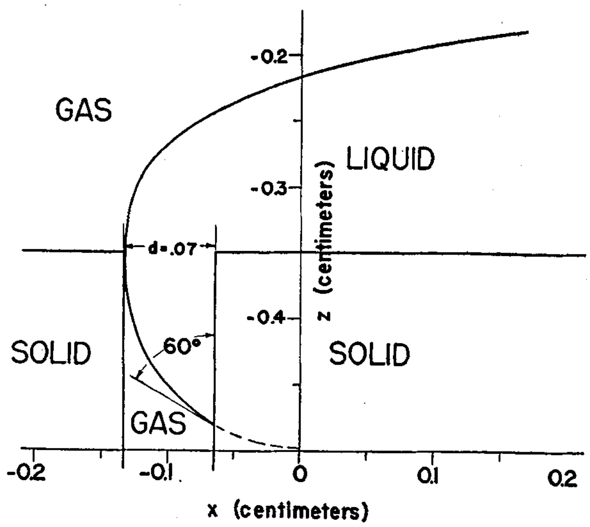

Fig. 4. Solution of problem of width of rectangular groove which will always entrap gas in the advance of a semiinfinite sheet of liquid ($\theta = 60$ deg.).

CAVITIES

Conical cavities will obey approximately the same considerations as V-shaped grooves, and cylindrical or rectangular cavities approximately the same as rectangular grooves. In fact, it is more likely that the postulated mechanism will be the determining factor in gas entrapment and therefore that these considerations will be valid, for cavities rather than for long grooves, where advance of the liquid along the grooves is an important consideration.

DISCUSSION

It is of interest to compare this theory with the large quantity of experimental data available on superheating and tensile strength of liquids. From the preceding example, the critical width of the vertical groove for the entrapment of gas in a system with water boiling at 1 atm. is about 0.07 cm. Hence the radius of curvature of the entrapped gas bubble would be about half this figure, or 0.04 cm., if such grooves exist on the surface. This would represent an extremely rough surface. Most experimenters have dealt with much smoother surfaces and have obtained critical nuclei radii, calculated from the Gibbs equation, several orders of magnitude smaller. It should also be noted that the elements of surface roughness should be cavities, rather than grooves, for the mechanism of gas entrapment by the advance of a liquid front to be controlling. As pointed out previously, most polished or machined surfaces do not obey this condition.

Two rather diverse investigations involving the cavity type of surface have been found in the literature. Jakob and Fritz (*7*) compared ebullition of water from a horizontal heating plate fitted with smooth (chromium plated and polished) surfaces and also a "screen" surface, fitted with square cavities, with lengths, depths, and spacings of about 0.025 cm. On the basis of the change of slope of the curve of heat flux vs. temperature excess, it is estimated that bubbles began forming in sizable quantities on the screen surface at a temperature excess of about 1°C. This corresponds to a critical bubble radius of about 0.0035 cm., about one-fourth the maximum that could be expected from the cavity dimensions. From the previous discussion it is seen that the liquid would probably displace some of the gas from each cavity; moreover, the thermal resistance of the entrapped gas is relatively large, thereby tending to increase the necessary temperature excess. In view of these uncertainties, this is a reasonably good order-of-magnitude check with the theory. Bubble initiation superheats of about 4° and 9°C. were found respectively for freshly formed sand-blasted and smooth surfaces, corresponding to bubble radii of about 9×10^{-4} and 4×10^{-4} cm. On any of these surfaces being allowed to remain in contact with water for a number of hours, the temperature excess required to initiate ebullition appeared to be unchanged; however, the temperature excess for a given flux was increased, possibly because some of the larger cavities had stably switched from gas-fill to liquid-fill, as described above. On allowing the surfaces to lie in contact with air again, the previous temperature excesses were restored.

Kermeen, McGraw, and Parkin (*8*) studied the inception of cavitation on various surfaces of revolution in water-tunnel experiments. Using an anodized aluminum surface, which may be considered to be a cavity type of surface, they found incipient cavitation to occur at local pressures 80 to 90 mm. Hg below the vapor pressure of water. This corresponds to a critical bubble radius of about 0.014 cm., considerably larger than the radii of 10^{-5} cm. and smaller observed in various measurements of the tensile strength of pure liquids by static, dynamic, and acoustic methods (*3*).

CONCLUSIONS

1. A quantitative procedure is given for determining whether a surface cavity of known shape and size will entrap gas or vapor in contact with a given liquid with a specified contact angle.
2. Four classes of cavities are shown to exist: those which are always liquid or gas filled; those in which complete displacement of gas by liquid is possible, but not vice versa; and those in which complete displacement of liquid by gas or vapor is possible, but not vice versa. The existence of the last two classes may account for some hysteresis effects in ebullition.
3. The primary roughness elements of most surfaces are grooves, which are relatively poor vapor traps and hence are relatively ineffective in initiating ebullition or cavitation. Two examples of the cavity type of surface, resulting in fracture of the liquid under low stresses, are adduced.

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