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Heterogeneous Nucleation

As mentioned earlier heterogeneous nucleation is a process in which bubbles nucleate at the imperfections on the surface submerged in liquid These imperfections are the scratches, pits and grooves commonly called cavities which form on the surface during its preparation. **The early work of Bankoff (1958)** indicated that the superheats associated with heterogeneous nucleation were much lower than those obtained in experiments, in which the test surface was submerged in a pool of liquid maintained at a constant temperature while the system pressure was gradually decreased until a bubble nucleated at the surface.

In these experiments the liquid superheat corresponding to the system pressure at which the first bubble nucleated was noted.

The reason for lower inception superheat can be easily rationalized if we consider that the cavities generally trap air or other noncondensibles and have radii which are much larger than those given by **equation (8.7)**.

The amount of air that is trapped in the cavity depends on the surface tension, the contact angle and the shape of the cavity as the liquid is heated. With heating , the gas expands and pushes the interface outwards.**(see figure 8.4)**

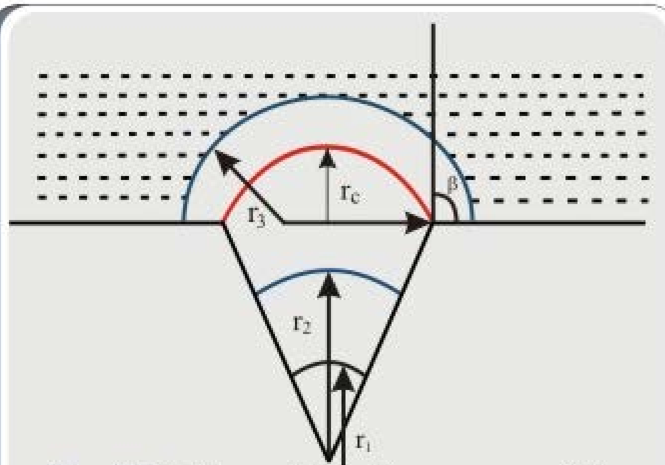

Figure 8.4: Bubble growth in a uniform temperature field

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During this process, the radius of curvature decreases and becomes smallest $(r = r_c)$ when the bubble nucleus just covers the mouth of the cavity $(\beta = 90^o)$. As the bubble grows further the radius of curvature begins to increase. Since the liquid superheat required for thermal equilibrium increases with reduction in the radius of the bubble, the highest superheat is needed when the bubble radius is equal to the cavity radius. Thus the bubble inception is controlled by the size of the cavity.

For commercial surfaces the size of the cavities is several orders of magnitudes larger than the critical cluster radius, hence lower is the observed superheat.

The precise value of the nucleation superheat strongly depends on the availability of unflooded cavities. As these cavities become fewer and fewer and their size decreases, the observed nucleation temperatures approach the homogeneous nucleation temperature.The trapped gas not only promotes nucleation but it also reduces the vapor pressure in the bubble.Using **Dalton's law of partial pressures**, the pressure in the nucleus can be written as.

$$P_b = P_v + P_g \qquad \textbf{(8.19)}$$

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Since the vapor pressure difference across the interface is reduced by P_g, the liquid superheat for thermal equilibrium is also reduced accordingly, such that

$$T_l - T_{sat} = \frac{\left(\frac{2\sigma}{R} - P_g\right)}{\rho_v h_{fg}} T_{sat} \qquad \textbf{(8.20)}$$

Next let us look at the conditions under which cavities will trap gas. **Figure 8.5** shows the advance of liquid and gas fronts over poorly conical wetted cavities.If the contact angle, β is greater than the cavity angle Φ , the advancing liquid front will fill the upper portion of the cavity while trapping gas underneath. Such a cavity will trigger early and should serve as a favored nucleation site. An advancing gas or vapor front however will not be able to displace the liquid if $\pi - \beta > \phi$. A liquid filled cavity will not be conducive to nucleation. Table 2 lists the trapping abilities of various cavities.

Type of Cavity	*Condition*	*Contact angle*	*Trapping Ability*
Steep	Poorly wetted	$\beta > \frac{\pi}{2}$	Traps gas or vapor only
Shallow			Traps liquid only
Steep	well wetted	$\beta < \frac{\pi}{2}$	Traps neither
Shallow			Traps gas or vapor and liquid

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The extent to which an advancing liquid front will penetrate into a cavity, not only depends on the contact angle and size and shape of the cavity but also on the pressure in the liquid and the temperature. The higher the liquid pressure and lower the temperature deeper will be the penetration of the liquid. The sketch on the left in **Figure 8.6** shows the shape of the liquid gas/ vapor interface after the penetration is over.

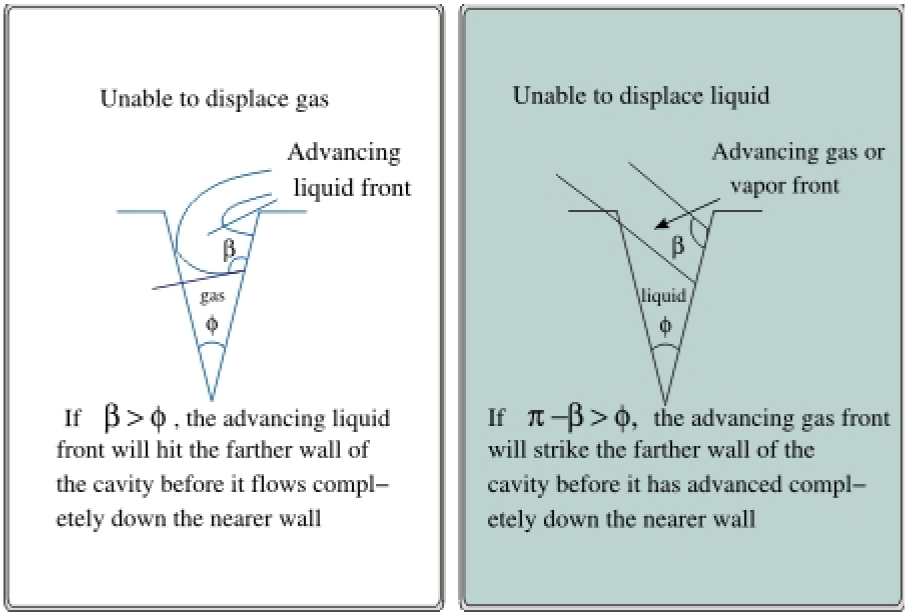

Figure 8.5: Vapor or gas trapping behavior of cavities (adopted from Cole)

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The interface is concave upward indicating that the pressure in the gas or vapor is lower than that in the liquid. After heating of the wall is initiated or the liquid chemically interacts with the cavity surface such that the surface becomes wettable **(e.g. reaction of liquid metals with oxides)** the interface turns over and becomes convex upward.This is shown in the right hand sketch in **Figure 8.6**.

For prediction of heterogeneous nucleation the criterion developed by **Hsu (1962)** has

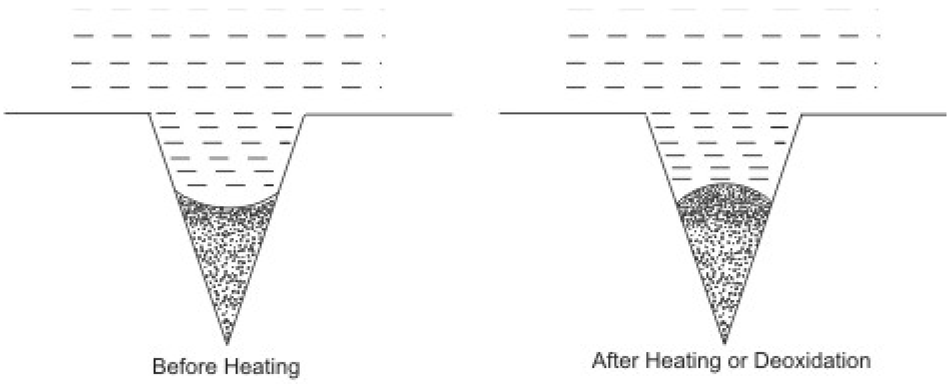

Fig 8.6 : Liquid- Gas Interface Shape Before Heating and After Heating and/or Deoxidation of Cavity Wall

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been found to be quite successful. This criterion does a fairly good job in predicting the wall superheat necessary for nucleation. The criterion requires that the top of a bubble embryo be covered with warm liquid before it can grow. Since the bubble embryo must be at saturation temperature corresponding to the vapor pressure which is higher than the pool pressure by $2\sigma/r_c$, the liquid surrounding the bubble must be superheated. If the required superheat does not exist, the heat transfer into colder liquid will cause the bubble to collapse.Because the heat is transferred from the wall, the liquid temperature decreases with distance from the wall and Hsu's criterion is satised everywhere if the liquid at the tip of the bubble has the required superheat

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Figure 8.7 shows as to how Hsu's criterion could be satisfied for a bubble embryo when the wall heat flux is gradually increased. In plotting the temperature a fictitious film thickness δ, is defined which with a linear temperature profile gives the same heat flux at the wall as the actual thermal layer,δ_{th}. Also, it is assumed that δ is independent of the temperature difference across the layer. During natural convection this is not a correct assumption. However in natural convection, the dependence of film thickness on temperature difference is weak. The temperature profile traced in the solid line indicates the wall heat flux at which Hsu's criteria is just satisfied. If the cavity for which the criterion is satisfied is available on the surface **(i.e. is not completely filled with liquid)**, this cavity will be the first one to nucleate. The lowest superheat at which nucleation is possible, can be determined from the expressions for the temperature distribution in the film and the liquid temperature dictated by the equilibrium considerations. If the bulk liquid is saturated, the temperature prole in the liquid film is given by.

$$T - T_{sat} = (T_w - T_{sat})(1 - y/\delta) \qquad \textbf{(8.21)}$$

The vapor bubble thermal equilibrium condition **equation (8.6)** is written as

$$(T_l - T_{sat}) = \frac{2\sigma T_{sat}}{R\rho_v h_{fg}}$$

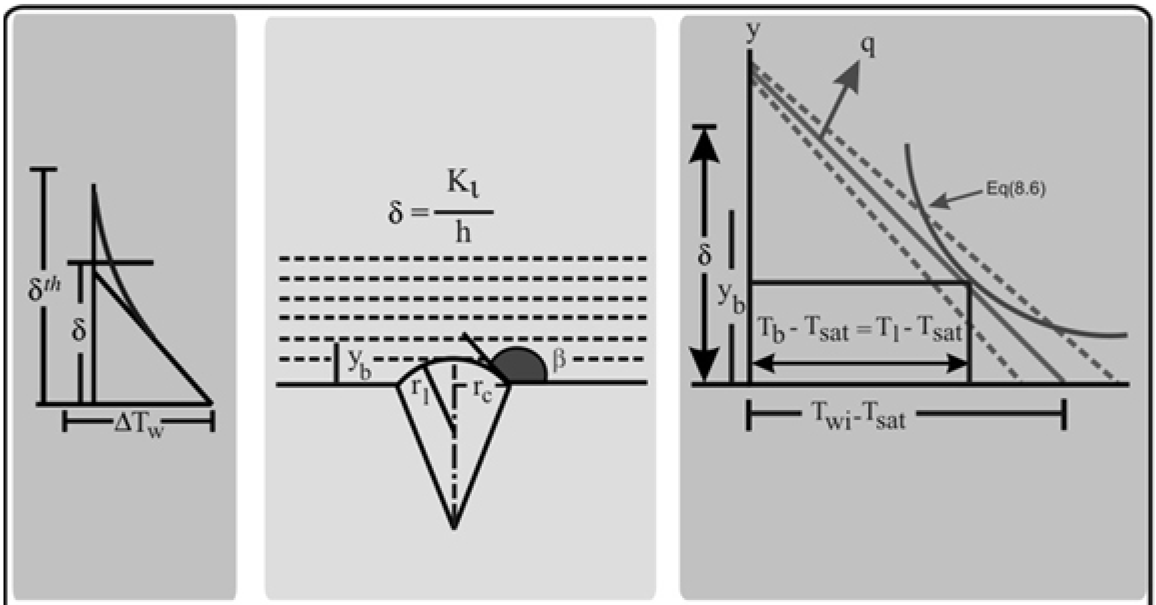

Figure 8.7: Inception of nucleation in a Non-uniform temperature field

For a contact angle of $\pi/2$, the height of the bubble and the radius of the bubble embryo will be equal to the radius of the mouth of the cavity. For contact angles different than $\pi/2$, the **radius and height of a spherical embryo is related to the cavity radius as**

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$$r_b = \frac{r_c}{C_1} \quad \text{where} \quad C_1 = sin\beta \qquad \textbf{(8.22)}$$

$$y_b = \frac{r_c C_2}{C_1} \quad \text{where} \quad C_2 = 1 + cos\beta \qquad \textbf{(8.23)}$$

Differentiating the liquid temperature in **Equation (8.21) and (8.6)** with respect to distance and equating the two derivatives we obtain

$$\frac{2C_2\sigma T_{sat}}{y^2\rho_v h_{fg}} = \frac{(T_w - T_{sat})}{\delta} \qquad \textbf{(8.24)}$$

In terms of the radius of the nucleating cavity is **equation (8.24)** can be written as

$$r_c = \left[\frac{2C_1^2\sigma T_{sat}\delta}{C_2\rho_v h_{fg}(T_w - T_{sat})}\right]^{1/2} \qquad \textbf{(8.25)}$$

If we replace the wall superheat with wall heat flux, the expression for r_c becomes

$$r_c = \left[\frac{2C_1^2\sigma T_{sat}k_l}{C_2\rho_v h_{fg}q}\right]^{1/2} \qquad \textbf{(8.26)}$$

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Substituting for r_c from **equation (8.26)** into **equation (8.6),** the required liquid superheat at the tip of the bubble is

$$(T_l - T_{sat}) = \left[\frac{2C_2\sigma T_{sat}q}{\rho_v h_{fg} k_l}\right]^{1/2} \qquad \textbf{(8.27)}$$

The wall superheat at nucleation is obtained from **equation (8.21)** after substituting for $(T_l - T_{sat})$ from **equation (8.27)** and y_b from **equation (8.23)** as.

$$(T_w - T_{sat}) = \left[\frac{8C_2\sigma T_{sat}q}{\rho_v h_{fg} k_l}\right]^{1/2} \qquad \textbf{(8.28)}$$

For a contact angle of $\pi/2$, both C_1 and C_2 are unity so that wall superheat atnucleation is twice the liquid superheat at the top of the bubble embryo or the cavity radius is half of the film thickness.

Example 3: Calculate the cavity size and the minimum wall superheat for nucleation from a surface submerged in a pool of saturated water at one atmosphere pressure, The wall heat flux is $10^5 W/m^2$. Assume the contact angle to be $\pi/2$.

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Solution :-

From **equation (8.25)**, the cavity radius is calculated as.

$$r_c = \left[\frac{2(58.7)\ 10^{-3}\ (373.15)\ (0.681)}{(0.597)\ (2.257)\ 10^6\ (10^5)}\right]^{1/2} = 14.88 \times 10^{-6} m$$

The wall superheat for inception of boiling is found from **equation (8.28)** as

$$(T_w - T_{sat}) = \left[\frac{8(58.7)\ 10^{-3}\ (373.15)(10^5)}{(0.597)\ (2.257)\ 10^6\ (0.681)}\right]^{1/2} = 4.36^o C$$

The cavity size obtained here is fairly large. It is possible that such a cavity will be filled with liquid and will not serve as a nucleation site. For the same heat flux if smaller cavities have to nucleate, the observed superheat at inception will be higher. It is interesting to note that the size of the nucleating cavity is about 3 orders of magnitude larger than the equilibrium cluster size for homogeneous nucleation.

Next, let us determine the range of cavities that can nucleate if the wall superheat exceeds the minimum wall superheat for nucleation.Eliminating the liquid temperature from **equation (8.6)** and **(8.21)** and substituting for bubble height and bubble radius from **equations (8.22)** and **(8.23)**, we obtain

$$(T_w - T_{sat})\left(1 - \frac{C_2 r_c}{C_1 \delta}\right) = \frac{2C_1 \sigma T_{sat}}{\rho_v h_{fg} r_c} \qquad \textbf{(8.29)}$$

$$r_c^2 - \frac{C_1}{C_2}\delta r_c + \frac{2C_1^2 \sigma T_{sat} \delta}{C_2 \rho_v h_{fg}(T_w - T_{sat})} = 0 \qquad \textbf{(8.30)}$$

This is a quadratic equation in $r_{c_1}\ and\ r_{c_2}$ the two roots of the equation are found to be

$$r_{c_{1,2}} = \frac{C_1 \delta}{2C_2}\left[1 \pm \sqrt{1 - \frac{8C_2 \sigma T_{sat}}{\rho_v h_{fg}(T_w - T_{sat})\delta}}\right] \qquad \textbf{(8.31)}$$

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In **Figure 8.7,** the intercepts of the dotted line representing temperature distribution in the film with the liquid superheat predicted from **equation (8.6)** represent the cavity radii $r_{c1}\ and\ r_{c2}$. For a given wall heat flux and superheat any cavity lying in the size range $r_{c1}\ and\ r_{c2}$ can nucleate.If the heated surface is subjected to forced flow conditions, the thermal layer becomes thin. This in turn will reduce the film thickness δ . As can be seen from **equation (8.31)**, the radius of the nucleating cavities will shrink as δ is reduced.We know from the earlier discussions that small cavities require higher superheat to nucleate.Thus the flow over the surface will tend to increase the inception superheat or suppress the nucleation process. Another point that should be made here is that in developing flows, the thermal layer thickness is a function of distance from inlet or the leading edge.

For example, for laminar flow over a at plate, the thermal layer thickness increases as square root of distance from the leading edge. Therefore, the farther the location, the larger will be the size of the nucleating cavities and smaller the required wall superheat. Theoretically, the effect of flow velocity and distance from the leading edge or inlet could be included in the film thickness of **Figure 8.7**. However, as mentioned earlier, the predictions will be sensitive to the size and shape of the available cavities and the contact angle.

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