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Module 8: Boiling

Lecture 30: Fundamentals of Nucleate Boiling

Nucleation and Bubble Growth

The nucleation is a process in which finite size clusters of molecules encompassing properties of the second phase appear in the host liquid. This could be the initiation of bubble formation during boiling or cavitation and crystal formation during solidifications.

The nucleation process is generally subdivided into two categories: homogeneous nucleation and heterogeneous nucleation. The homogeneous nucleation refers to the first appearance of a bubble in the liquid pool and far away from the bounding walls. The heterogeneous nucleation is a process in which bubbles form at pits, scratches and grooves on a heated surface submerged in a pool of liquid. Before going for the detailed description and analysis of these processes, let us look at the conditions for mechanical and thermal equilibrium of a bubble with the host liquid.

The condition for mechanical equilibrium which was developed earlier simply states that the pressure in a perfectly spherical bubble must exceed the ambient by $2\sigma/R$

$$p_v - p_l = \frac{2\sigma}{R} \quad (8.1)$$

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In a gravitational field, the bubble being lighter than the surrounding liquid will buoy away, however here we are considering a static equilibrium such that the bubble is relatively small in size and is held in place. Now if the bubble is in thermal equilibrium with the liquid, the temperature of the bubble and the liquid should be the same, i.e.

$$T_b = T_l \quad (8.2)$$

Since from thermodynamic equilibrium consideration, the vapor must be at the saturation temperature corresponding to pressure in the bubble and we know from the equation of state that saturation temperature increases with pressure, the bubble or the liquid temperature should be higher than the saturation temperature corresponding to the pressure in the liquid. In other words, the liquid must be superheated. The degree of superheat can be determined if we combine the mechanical equilibrium condition with the **Clausius-Clapeyron equation; which relates the differential change in saturation temperature with pressure as**

$$\frac{\Delta P}{\Delta T} = \frac{h_{fg}}{v_{fg} \left(T_{sat} + \frac{\Delta T}{2} \right)} \quad (8.3)$$

In equation (8.3), T_{sat} is the absolute saturation temperature corresponding to the system pressure and v_{fg} is the difference in specific volumes of vapor and liquid at the system pressure. For $\Delta T \ll T_{sat}$, **equation (8.3)** can be approximately written as

$$\frac{\Delta P}{\Delta T} = \frac{h_{fg}}{v_{fg} T_{sat}} \quad (8.4)$$

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Substituting for ΔP in equation (8.4), the liquid superheat is obtained as

$$(T_l - T_{sat}) \equiv (T_b - T_{sat}) = \frac{2\sigma v_{fg} T_{sat}}{R h_{fg}} \quad (8.5)$$

At low pressures the specific volume of vapor is much larger than that of the liquid such that v_{fg} in Equation 8.5, can be replaced by $1/\rho_v$ without making any appreciable error.

With this change, equation (8.5) becomes.

$$(T_l - T_{sat}) = \frac{2\sigma T_{sat}}{R \rho_v h_{fg}} \quad (8.6)$$

Example 1: Calculate water superheat if a steam bubble of radius 10^{-3} cm is to coexist with the liquid at a system pressure of one atmosphere.

$$T_l - T_{sat} = \frac{2 \times 58.9 \times 10^{-3} \times 373}{10^{-5} \times 0.5977 \times 2.257 \times 10^6} = 3.26K$$

Thus we see that for a relatively small bubble, the required liquid superheat is not very large. The superheat will tend to decrease as the system pressure is increased.

Another observation that can be made about the requirement of thermal equilibrium is that a bubble in the absence of any mass transfer will have to shrink upon introduction into a pool of liquid if the liquid superheat is more than the temperature corresponding to the initial bubble radius. Similarly if the superheat is smaller than that corresponding to the temperature in the bubble, the bubble will have to expand.

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Homogeneous Nucleation

The classical theory of homogeneous bubble nucleation is a mixture of macroscopic and molecular concepts. The process of creation of a bubble in a superheated liquid is initiated by a cluster of activated molecules. These molecules have energies that are considerably in excess of the average.

Generally a cluster is constantly growing or diminishing in size as additional activated molecules join or break away from it. When a cluster attains a size such that its excess availability is maximum it takes on the form of a bubble. If the activated cluster has a density which is different than the surrounding liquid, surface tension can be presumed to exist at the interface between the two. For a certain volume of liquid containing an activated cluster of radius r , the availability can be written as

$$A = (n_t - n_a) g_l + n_a g_a + 4\pi r^2 \sigma \quad (8.7)$$

Here n_t is the total number of molecules, n_a is the number of activated molecules in the **cluster** and g_l and g_a are the specific Gibbs functions of the nonactivated and activated moluculous respectively

Note : *Availability is an intrinsic property of a system and represents its potential to do work.*

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if ρ_a is the fluid density in the activated cluster, M is the molecular weight and N_A is the Avogadro's number, an expression for the number of activated molecules can be written as

$$n_a = \frac{4}{3}\pi r^3 \rho_a \frac{N_A}{M} \quad (8.8)$$

substitution of (8.8) in (8.7) yields

$$A = n_t g_l + \frac{4}{3}\pi r^3 \rho_a \frac{N_A}{M} (g_a - g_l) + 4\pi r^2 \sigma \quad (8.9)$$

Since in the absence of a cluster of activated molecules, the availability of the system will be $n_t g_l$ the excess availability in the presence of an activated cluster can be written from equation (8.9) as

$$\Delta A = \frac{4}{3}\pi r^3 \rho_a \frac{N_A}{M} (g_a - g_l) + 4\pi r^2 \sigma \quad (8.10)$$

At the metastable equilibrium, the excess availability of the system with respect to the cluster radius will be maximum. This equilibrium or critical cluster radius can be obtained by differentiating (8.10) with respect of r and setting it equal to zero. We obtain

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$$\frac{d(\Delta A)}{dr} = \frac{4\pi r_c^2 \rho_a N_a}{M} (g_a - g_l) + 8\pi r_c \sigma = 0 \quad (8.10)$$

or

$$r_c = \frac{2\sigma M}{\rho_a N_a (g_l - g_a)} \quad (8.11)$$

Substituting for $(g_a - g_l)$ from **equation (8.11) into equation (8.10)**, the excess availability is obtained as

$$\Delta A = 4\pi r^2 \sigma \left(1 - \frac{2r}{3r_c} \right) \quad (8.12)$$

Figure 8.3 shows the dimensionless excess availability as a function of dimensionless cluster radius r/r_c . The maximum value of the excess availability is

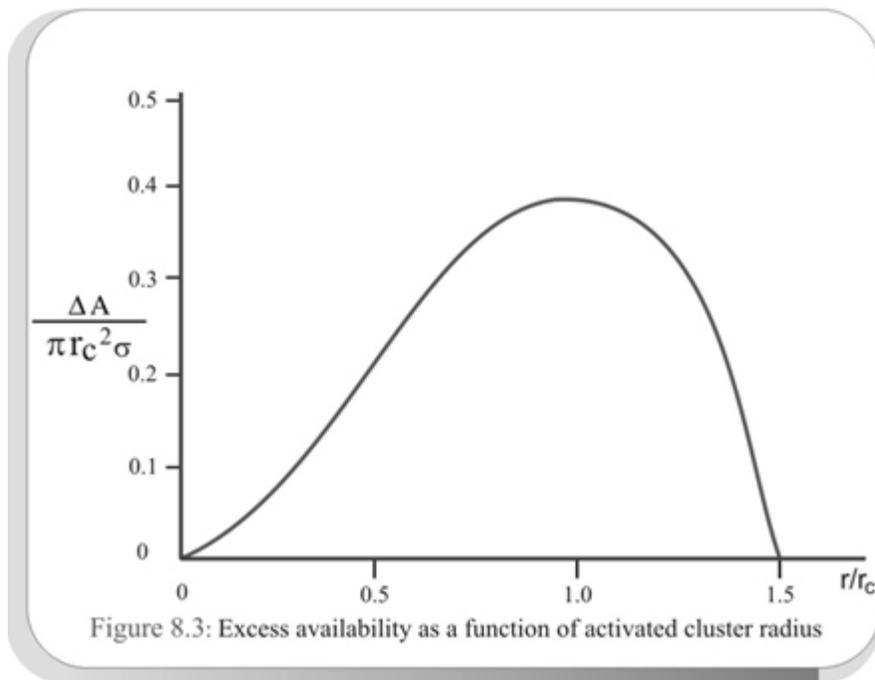
$$\Delta A_{max} = \frac{4\pi r_c^2 \sigma}{3} \quad (8.13)$$

The rate at which activated clusters appear per unit volume of the liquid per unit time

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can be written as

$$J = f e^{-(\Delta A_{max}/kT_l)}$$

Where **f** is the frequency of **molecular collisions per unit volume** and **k** is **Boltzmann** constant.

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In writing **equation (8.14)** it is assumed that nucleation will occur when the excess availability of the cluster is several times that of the kinetic energy of a molecule which is characterized by kT_l . As such the ratio $\Delta A_{max}/kT_l$ represents a dimensionless number rather than number of molecules. From kinetic theory, the frequency of molecular collisions per unit volume per unit time is written as

$$f = \frac{NkT_l}{h} \quad (8.15)$$

In **equation(8.15)** N is the number of molecules per m^3 and h is Planck's constant. Substituting equation **(8.15)** in **(8.14)** , dividing by J and taking logarithm of both sides gives.

$$\frac{\Delta A_{max}}{kT_l} = \ln \left(\frac{NkT_l}{Jh} \right) \quad (8.16)$$

With ΔA_{max} given by **equation (8.13)**, the critical cluster radius is obtained from **equation (8.16)** as

$$r_c = \left[\frac{3kT_l}{4\pi\sigma} \ln \left(\frac{NkT_l}{Jh} \right) \right]^{1/2} \quad (8.17)$$

The critical radius as given by **equation(8.17)** is not very sensitive to the value of J. Any variation in J from J from $10^{-6} - 10^6$ will yield critical radii which will differ only by a few percent from each other. In the above expression the surface tension σ and the number density N are evaluated at the liquid temperature T_l . Using the critical radius in the condition for the mechanical equilibrium, the pressure in the cluster which now appears as a bubble can be written as

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$$P_b - P_l = \frac{2\sigma}{\left[\frac{3kT_l}{4\pi\sigma} \ln\left(\frac{NkT_l}{Jh}\right)\right]^{1/2}} \quad (8.18)$$

Equation(8.18) has two unknowns P_b and T_l . However thermal equilibrium requires T_l to be the saturation temperature corresponding to pressure P_b . Thus employing the equation of state, both P_b and T_l can be determined.

Example 2:

Calculate the superheat necessary for homogeneous nucleation in water at one atmosphere pressure.

$$N_A = 6.022 \times 10^{26} \text{ molecules/kg-mol}, \quad h = 0.626 \times 10^{-34} \text{ Js}, \quad k = 1.3806 \times 10^{-23} \text{ J/molK}.$$

Let us carry out the calculations by assuming $J = 1$.

We make a table by choosing different values of T_l and calculating P_b from **equation(8.18)** finally compare it with what obtained from the Steam Tables.

Table 8.1

<i>Temperature</i> K	<i>P_b (N/m²)</i> <i>Eqn (8.18)</i>	<i>P_b (N/m²)</i> Steam Table
520	27.3 X 10 ⁶	3.78 X 10 ⁶
560	12.77 X 10 ⁶	7.13 X 10 ⁶
572	8.46 X 10 ⁶	8.46 X 10 ⁶

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