

Module 3: "Nucleation and Growth"

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Heterogeneous Nucleation

In practice heterogeneous nucleation occurs more readily than homogeneous nucleation. It requires less energy than homogeneous nucleation. In case of heterogeneous nucleation, vapors condense on phase boundaries (solid surfaces). These solid surfaces are generally found as impurity within the vapors. Due to lower surface energy, the free energy barrier reduces and facilitates nucleation at these preferential sites. Surfaces having contact angles (θ) between phases greater than zero encourage particles to nucleate.

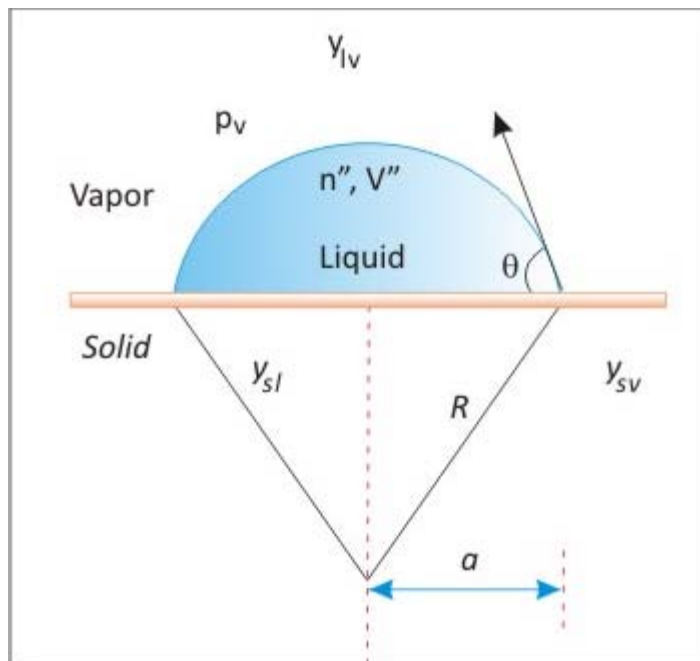


Fig. 5.5: Schematic diagram of heterogeneous nucleation on a solid surface

The physics of the problem remains same as that of homogeneous nucleation except that we have to account for surface tension of solid phase for calculation of free energy change (ΔF).

Assumptions:

- Size of impurities present is larger than the critical radius of the nucleus. So we can assume solid surfaces as flat.
- The nucleus is part of a sphere. This assumption is valid since the effect of gravity is negligible for small nuclei (diameter around 10 to 100 nm). Along with this we also neglect the effect of van der Waals interactions which in reality will be significant for such small dimensions.

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Volume of the spherical drop (V^n) making a contact angle (θ) with the solid surface is given as

$$V^n = \frac{\pi R^3}{3} (1 - \cos \theta)^2 (2 + \cos \theta) \quad (5.11)$$

where R is the radius of the spherical drop. The area of the curved surface of the liquid drop i.e. liquid-vapor interface (A_{lv}) is given by

$$A_{lv} = 2\pi R^2 (1 - \cos \theta); \quad (5.12)$$

Change in free energy per unit volume of the condensed phase of the system is given as

$$\Delta F = -n^n R^* T \ln \left(\frac{p_v}{p_0} \right) + \sum A_i \gamma_i - \sum A_{i0} \gamma_{i0} \quad (5.13a)$$

Where, R^* is the ideal gas constant, T is absolute temperature, $\sum A_{i0} \gamma_{i0}$ and $\sum A_i \gamma_i$ are the surface energies before and after the formation of the nucleus respectively. The ratio (p_v/p_0) is known as super-saturation ratio.

$$\begin{aligned} \sum A_i \gamma_i &= 2\pi R^2 (1 - \cos \theta) + \pi a^2 \gamma_{sl}; \\ \sum A_{i0} \gamma_{i0} &= \pi a^2 \gamma_{sv} \end{aligned} \quad (5.13b)$$

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Substituting the values in equation (5.13b), the free energy change takes the form

$$\Delta F = F - F_0 = -n'' R^* T \ln \left(\frac{p_v}{p_0} \right) + \gamma_{lv} 2\pi R^2 (1 - \cos \theta) + \pi a^2 (\gamma_{sl} - \gamma_{sv}); \quad (5.14)$$

Thus, this process is also favorable only when $p_v/p_0 > 1$ as in homogeneous nucleation.

From Fig. 57, we can write

$$a = R \sin \theta \quad (5.15)$$

So from equation (98), we get

$$\Delta F = F - F_0 = -n'' R^* T \ln \left(\frac{p_v}{p_0} \right) + \gamma_{lv} 2\pi R^2 (1 - \cos \theta) + \pi R^2 (\gamma_{sl} - \gamma_{sv}) \sin \theta \quad (5.16a)$$

From Young's equation, we know

$$\gamma_{lv} \cos \theta + \gamma_{sl} = \gamma_{sv} \quad (5.16b)$$

The above equation is valid for the values of θ such that $-1 < \cos \theta < 1$. If \bar{V}'' is the molar volume of liquid and V is volume of liquid condensed on surface then, $n\bar{V} = V$.

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Applying Young's equation in the energy change relation (equation 5.16), we have

$$\Delta F = -\frac{\pi R^3}{3\bar{V}^n} R^*T(1 - \cos \theta)^2(2 + \cos \theta) \ln \left(\frac{p_v}{p_o} \right) + \gamma_{lv} \pi R^2 (1 - \cos \theta)^2(2 + \cos \theta)$$

$$\Delta F = \left[-\frac{\pi R^3}{3\bar{V}^n} R^*T \ln \left(\frac{p_v}{p_o} \right) + \gamma_{lv} \pi R^2 \right] (1 - \cos \theta)^2(2 + \cos \theta) \quad (5.17)$$

Below critical radius (R_c) the nuclei will shrink whereas above R_c , it will be stable and will increase to minimize free energy barrier, ΔF . For critical radius, $\frac{\partial \Delta F}{\partial R} = 0$. Applying the above result to equation (100) we get,

$$\frac{R^*T}{\bar{V}^n} \ln \left(\frac{p_v}{p_o} \right) = \frac{2\gamma_c}{R_c}; \quad (5.18a)$$

The equation resembles the Kelvin equation. This resemblance in homogeneous and heterogeneous nucleation case is due to a common assumption of nucleus being a part of a sphere.

So the critical potential barrier for heterogeneous nucleation (ΔF_c) is given by

$$\Delta F_c = \left[\frac{4\pi R_c^2 \gamma_{lv}}{3} \right] f \theta \quad (5.18b)$$

$$\text{Where, } f(\theta) = \frac{(1 - \cos \theta)^2(2 + \cos \theta)}{4}$$

Note: The term in the square braces is same as that in the homogeneous nucleation case. So we can write that the free energy barrier for heterogeneous nucleation is equal to that of homogeneous nucleation multiplied by $f(\theta)$

$$\Delta F_{\text{het}} = \Delta F_{\text{hom}} f \theta; \quad (5.18c)$$

Values of $f(\theta)$ corresponding to different values of θ are listed in Table 5.2.

Table 5.2: Variation of $f(\theta)$ with contact angle θ

Contact Angle (θ°)	$f(\theta)$
0	0.0
90	0.5
180	1.0

From equation (5.18c) it is clear that for $\theta = 180^\circ$ the energy barrier will be the same as homogenous nucleation and for $\theta = 0^\circ$ there is no energy barrier. Thus ΔF_c will decrease for heterogeneous nucleation (Fig. 5.6a). Hence more wettable the surface, (i.e. larger the value of θ) smaller is the energy barrier for the vapors to condense.

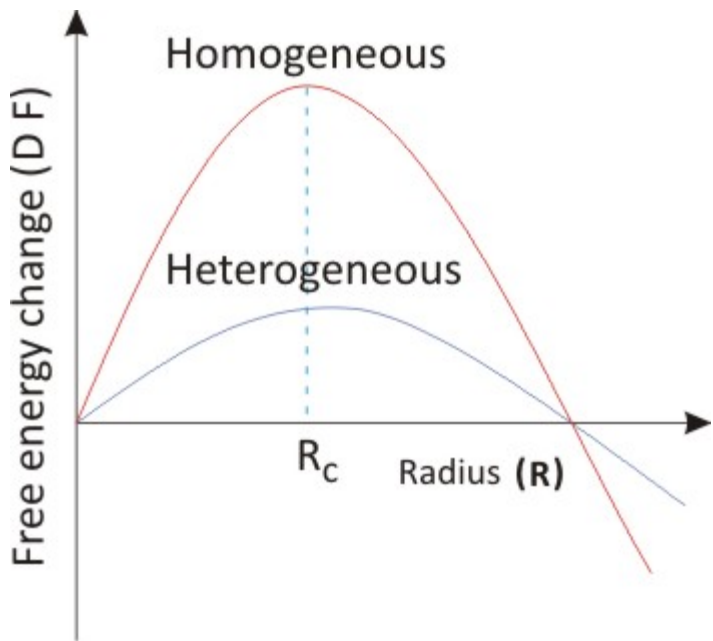


Fig. 5.6a: Comparison of free energy barrier between homogeneous and heterogeneous nucleation.

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Rate of nucleation

Rate of nucleation (I) for single nuclei is given by

$$I \propto \exp(-\Delta F_c/kT) \quad (5.18d)$$

Where, k is the Boltzmann constant and T is absolute temperature. As ΔF_c is smaller for heterogeneous nucleation, the corresponding rate of nucleation (I) will be higher but the critical radius remains same in both cases.

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