

Crystal Growth

Lec18: Heterogeneous Nucleation

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1 Classical Nucleation Theory

1.1 Heterogeneous Nucleation

Nucleation on a foreign surface, i.e an interface got created between two phases. Since if we break a phase into two we have to create dangling bonds between atoms. The energy associated with the breaking of these bonds is called interfacial energy (represented in per mol).

So, which will nucleate first, obviously the one which require less energy to form, or one whose ΔG^* will be less. The critical radius of nucleation and energy barrier for heterogeneous nucleation is given by:

$$r^* = \frac{2\gamma_{lv}V_l}{\Delta\mu}$$

$$\Delta G_{hetero} = \Delta G_{homo}f(\theta) \tag{1}$$

$$V_{hetero}^* = V_{homo}^*f(\theta)$$

Where,

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

Plot of equation 2 is shown in figure 2

It can be seen that if $\theta = 180$ the energy barrier for heterogeneous and homogeneous nucleation is same and if $\theta = 0$, then it predicts that $\Delta G = 0$ and

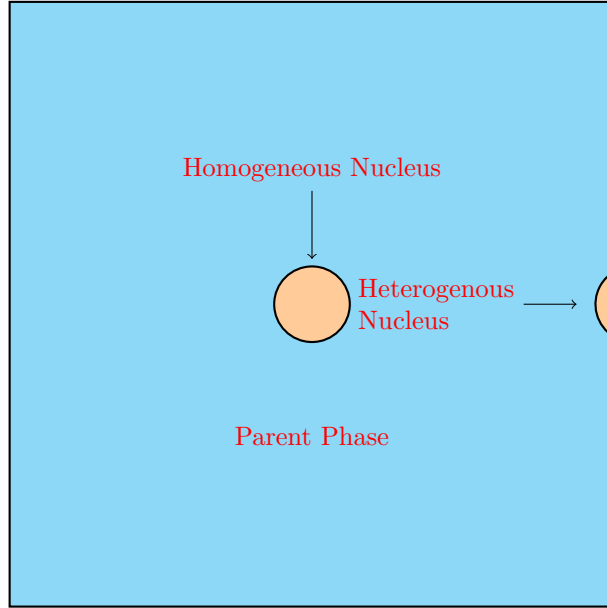


Figure 1: Homogeneous and heterogenous nucleation from infinite parent phase

$r^* = 0$, which is not totally right. Since we considering 3D nucleation theory where we have neglected the edge energy associated with the periphery of the nucleated droplet, if we consider it then ΔG^* and r^* will comes out to be finite. In 2d nucleation theory this energy plays a major role and it can't be neglected.

Figure above shows diagramatic condstruction of youngs equation.

$$\gamma_{sv} = \gamma_{ls} + \gamma_{lv}\cos(\theta) \quad (3)$$

In equation 3 γ 's are surface energy which are scalar, then how come it is written such that its a force balance equation. It is because if we consider all surface energies and subject it to the constraint that to find a shape which minimises energy we will get the Young's equation. In Young's construction γ 's are surface tension which is vector (sine it is a kind of force). Heterogenous nucleation is easy than homogeneous nucleation for same radius of r , because heterogenous nuclei has smaller volume (so less energy required to form it) as given by equation 1. From figure for $\theta = 0$, complete wetting, means film spreads over substrate i.e bond formation energy of substrate and film has less energy associated than film-film and $\theta = 180$ means film-substrate bonds are costlier than film-film, so its case of non-wetting.

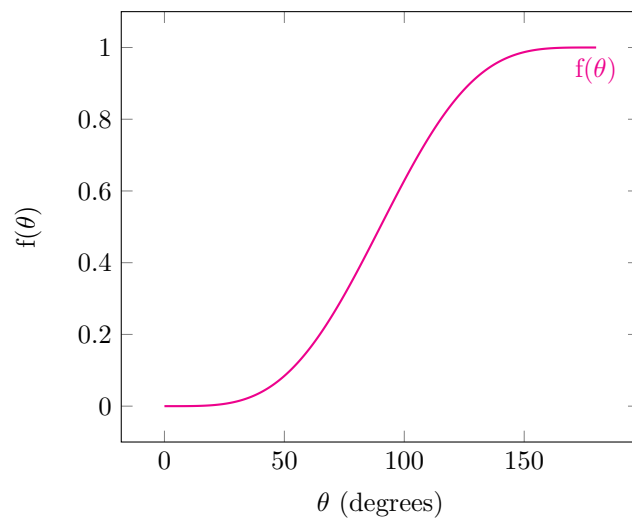


Figure 2: Plot of $f(\theta)$

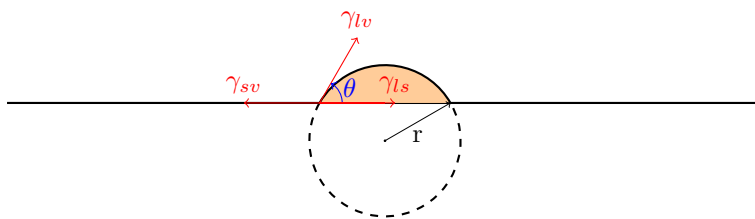


Figure 3: Heterogeneous Nucleation from vapor phase

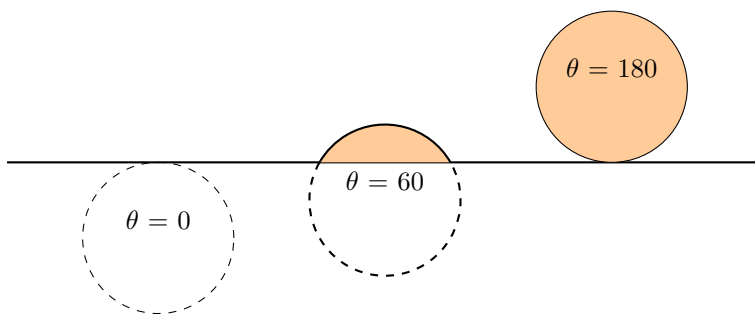


Figure 4: Nucleus size with θ