Crystal Growth
Lec17: Homogeneous Nucleation

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November 24, 2021

Contents

1 Classical Nucleation Theory

1.1 Homogeneous Neculeation

$\Delta G = RTln(\frac{P}{P_{eq}})$ If P = P_{eq} i.e equillibrium vapor pressure, system is in equillibrium. Note this is for two infinite phases.
Let phase 1 is Φ_1 and phase 2 is Φ_2 , these two are infinite phases. These are in equillibrium when chemical potential (μ_1) of the atom in bulk of Φ_1 is equal to the chemical potential (μ_2) of the atom in the bulk of Φ_2.
Equillibrium:

$$\mu_1 = \mu_2 \tag{1}$$

Above 1 is condition for Equillibrium

If suppose we want to make an Infinite child phase out of Infinite parent phase we can set $\Delta\mu$ slightly greater than 0. But lets say we have an infinite vapor phase of H_2O (parent phase) and we want to nucleate a child phase, a droplet of water say of 100 μm diameter from it. Then we have to spend extra energy to make surface of it, and this is costlier than making an infinite phase in terms of Energy per mol of substance.

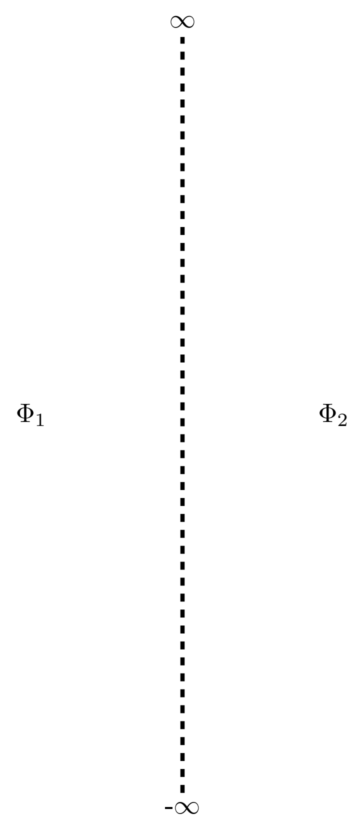

Figure 1: Two infinite phases Φ_1 and Φ_2 in equillibrium

From figure 2 a finite child phase(μ^c_{finite}) has been created from an infinite parent phase ($\mu^p_{infinite}$). Earlier both the infinite parent phase and infinite child phase were in equillibrium since $\mu^c_{infinite} = \mu^p_{infinite}$, now the chemical potential of atom in the bulk of child phase has been increased. For Infinite parent phase to remain in equillibrium with the child phase, it has to increase it s energy or equivalently free energy per mol of substance i.e it has to increase its chemical potential equal to the child phase.

$$\mu^{p'}_{infinite} = \mu^c_{finite} \tag{2}$$

The difference between $\mu^{p'}_{infinite}$ and $\mu^p_{infinite}$ is called **supersaturation**, and now the infinite parent can make child phase from a droplet of size r to an infinite child phase.

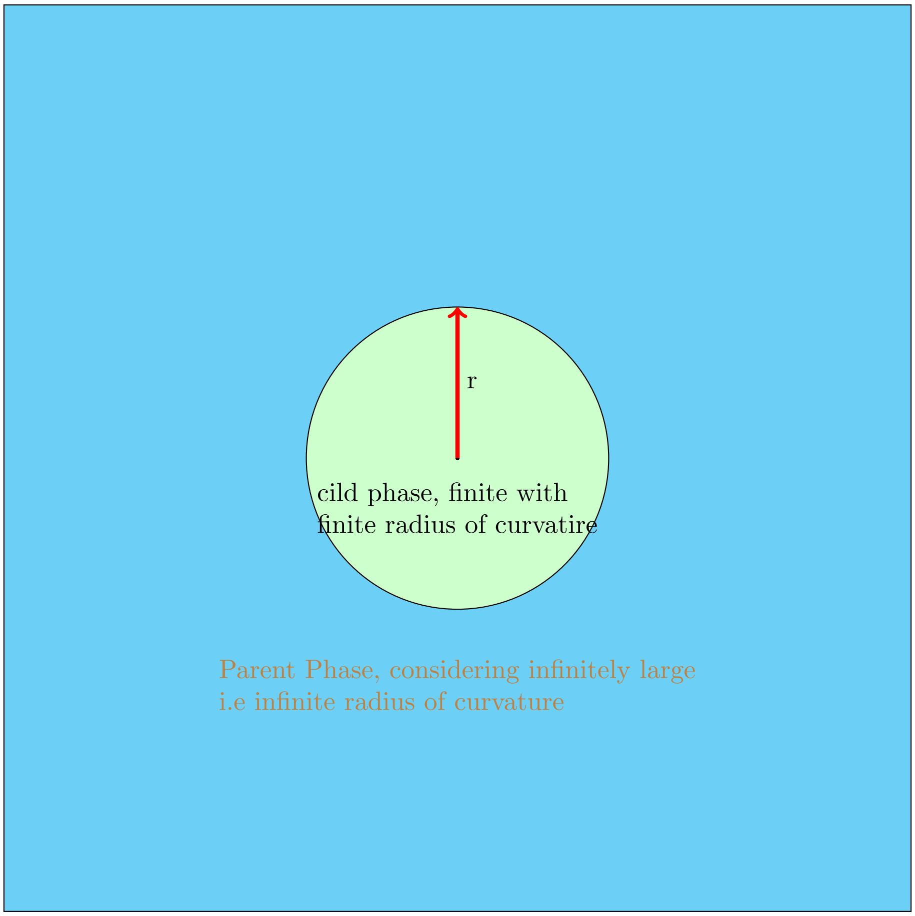

Figure 2: Homogeneous Nucleation

1.1.1 Critical radius and ΔG^*or homogeneous nucleation

From figure 3 we have conceptualize the supersaturation. Now consider figure 2 where a small spherical nucleus of radius r have been formed from infinite parent phase.

$$\begin{aligned} \Delta G &= -\Delta G_v + \Delta G_{sur} \\ &= -\frac{4\pi}{3}\frac{r^3}{V_l}\Delta\mu + 4\pi r^2\gamma \end{aligned} \tag{3}$$

So when plotting above equation posses a maxima at critical radius.

From figure 4 it can be seen that the value of critical radius (r^*) and ΔG^* can be found by applying principle of maxima-minima.

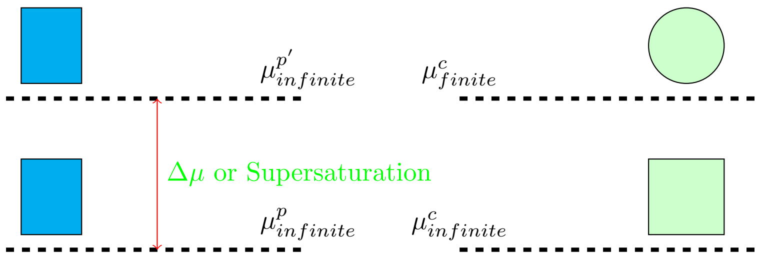

Figure 3: Supersaturation to Nucleate a finite phase from an infinite parent phase

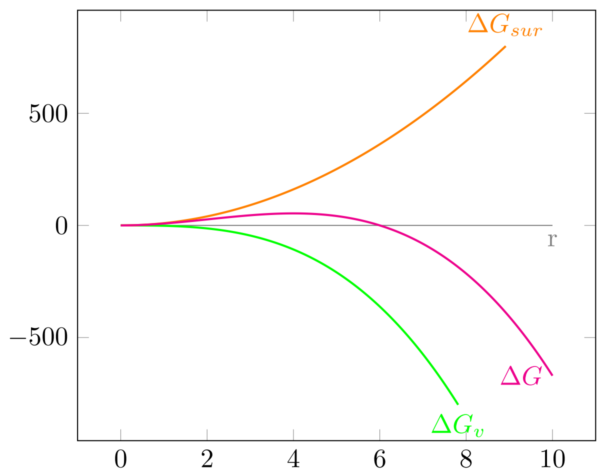

Figure 4: Free energy vs radius of homogenous nuclei

$$\frac{\partial \Delta G}{\partial r} = 0$$

$$r^* = \frac{2\gamma V_l}{\Delta\mu} \tag{4}$$

$$\Delta G^* = \frac{16\pi}{3}\frac{\gamma^3 V_l^2}{\Delta\mu^2}$$

So, Classical nucleation theory predicts nucleation is easier when r^* is low , i.e it is easier to form nuclii of 10 atoms than 100 atoms $\implies$ when $\Delta\mu$ is high nucleation is easy and form smaller sized nucleii. Also note ΔG^* is the barrier to nucleation, this will also come in nucleation rate exression and sits on exponential, so very cruicial parameter and is controlled by $\Delta\mu$ which is

controlled by P, T, n etc.
Further reading: Compare equation 4 with Gibbs-Thompson equation and also with Laplace equation (see. markov).