19.2: Classical Nucleation Theory

Let's summarize the thermodynamic theory for the nucleation of a liquid droplet by the association of molecules from the vapor. The free energy for forming a droplet out of n molecules (which we refer to as monomers) has two contributions: a surface energy term that describes the energy needed to make droplet interface and a volume term that describes the cohesive energy of the monomers.

$$\Delta G_n = \gamma a - \Delta\epsilon V \tag{19.2.1}$$

Note the similarity to our discussion of the hydrophobic effect, where γ was just the surface tension of water. $\Delta\varepsilon$ is the bulk cohesive energy—a positive number. Since this is a homogeneous cluster, we expect the cluster volume V to be proportional to n and, for a spherical droplet, the surface area a to be proportional to $V^{2/3}$ and thus $n^{2/3}$ (remember our discussion of hydrophobic collapse). To write this in terms of monomer units, we can express the total area in terms of the average surface area per molecule in the droplet:

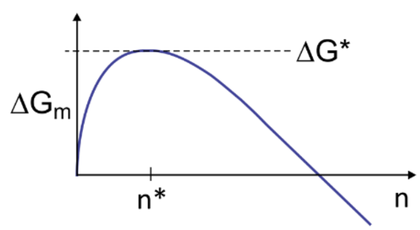
$$\alpha = a/n \tag{19.2.2}$$

and as the monomer volume V_0. Then the free energy is

$$\Delta G_n = \gamma\alpha n^{2/3} - \Delta\epsilon V_0 n \tag{19.2.3}$$

and the chemical potential of the droplet as

$$\begin{aligned} \Delta\mu_n &= \frac{\partial \Delta G_m}{\partial n} \\ &= \frac{2}{3}\gamma_0 \alpha n^{-1/3} + \Delta\epsilon V_0 \end{aligned}$$



These competing effects result in a maximum in ΔG versus n, which is known as the **critical nucleation cluster size** n^*. The free energy at n^* is positive and called the nucleation barrier ΔG^*. We find n^* by setting Equation ??? equal to zero:

$$n^* = \left(\frac{2\gamma_0\alpha}{3\Delta\epsilon V_0}\right)^3 \tag{19.2.4}$$

and substituting into Equation 19.2.3

$$G^* = \frac{4}{27}\frac{(\gamma_0\alpha)^3}{(\Delta\epsilon V_0)^2} \tag{19.2.5}$$

For nucleation of a liquid droplet from vapor, if fewer than n* monomers associate, there is not enough cohesive energy to allow the growth of a droplet and the nucleus will dissociate. If more than n^* monomers associate, the droplet is still unstable, but the direction of spontaneous change will increase the size of the droplet and a liquid phase will grow from the nucleus. The process of micelle formation requires a balance of attractive and repulsive forces that stabilize an aggregate, which can depend on surface and volume terms. Thus the $\Delta G_{micelle}$ has a similar form, but the signs of different factors may be positive or negative.

P. S. Richard, Nucleation: theory and applications to protein solutions and colloidal suspensions, J. Phys.: Condens. Matter 19 (3), 033101 (2007).