Appendix: Elementary Theory of Nucleation

Phase fluctuations occur as random events due to the thermal vibration of atoms. An individual fluctuation may or may not be associated with a reduction in free energy, but it can only survive and grow if there is a reduction. There is a cost associated with the creation of a new phase, the interface energy, a penalty which becomes smaller as the particle surface to volume ratio decreases. In a metastable system this leads to a critical size of fluctuation beyond which growth is favoured.

Consider the homogeneous nucleation of α from γ. For a spherical particle of radius r with an isotropic interfacial energy $\sigma_{\alpha\gamma}$, the change in free energy as a function of radius is:

$$\Delta G = \frac{4}{3}\pi r^3 \Delta G_{CHEM} + \frac{4}{3}\pi r^3 \Delta G_{STRAIN} + 4\pi r^2 \sigma_{\alpha\gamma} \qquad (1)$$

where $\Delta G_{CHEM} = G_V^{\alpha} - G_V^{\gamma}$, G_V is the Gibbs free energy per unit volume of α and G_{STRAIN} is the strain energy per unit volume of α. The variation in ΔG with size is illustrated in Fig. 1; the maximum in the curve is found by differentiating equation 1 with respect to r:

$$\frac{\partial(\Delta G)}{\partial r} = 4\pi r^2 [\Delta G_{CHEM} + \Delta G_{STRAIN}] + 8\pi r \sigma_{\alpha\gamma}$$

r^* is obtained by setting this result to zero:

$$r^* = -\frac{2\sigma_{\alpha\gamma}}{\Delta G_{CHEM} + \Delta G_{STRAIN}}$$

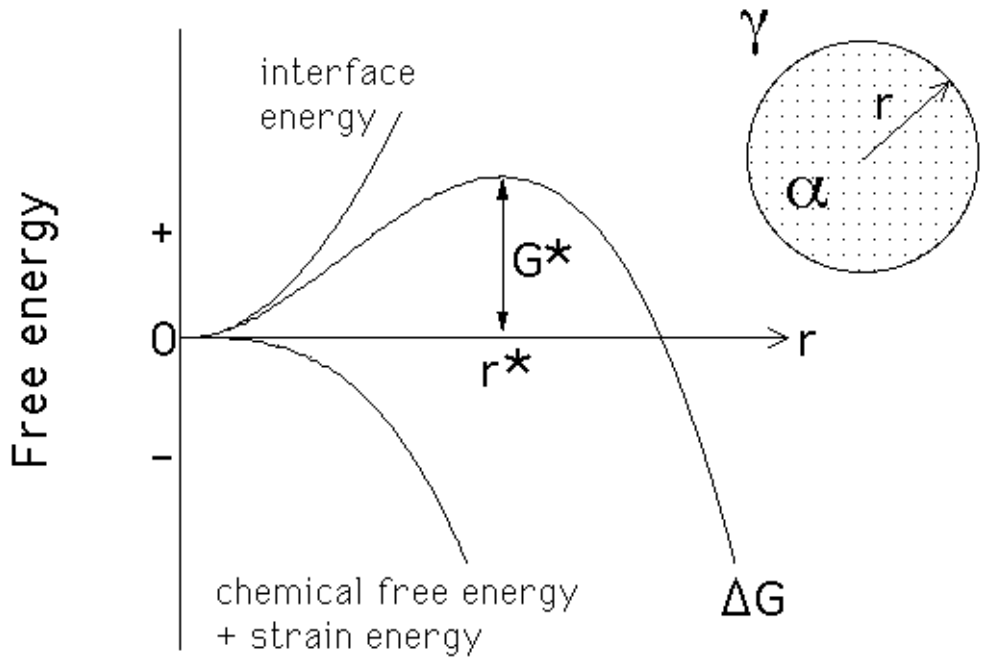

Fig. 1: The activation energy barrier G^* and the critical nucleus size r^* according to classical nucleation theory based on heterophase fluctuations.

When the value of r^* is substituted into equation 1, the activation energy is obtained as:

$$G^* = \frac{16\pi\sigma_{\alpha\gamma}^3}{3(\Delta G_{CHEM} + \Delta G_{STRAIN})^2}$$

The important outcome is that in classical nucleation the activation energy varies inversely with the square of the driving force. And the mechanism involves random phase fluctuations. The nucleation rate per unit volume, I_V will depend on the attempt frequency ν, the number density of nucleation sites N_V and the probability of successful attempts. There is also a barrier Q to the transfer of atoms across the interface:

$$I_V = N_V \nu \exp\left\{-\frac{G^*}{kT}\right\} \exp\left\{-\frac{Q}{kT}\right\}$$