MATE 664 Lecture 15

Heterogeneous Nucleation

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Learning outcomes

After this lecture, you will be able to:

- **Compare** heterogeneous nucleation with homogeneous nucleation
- **Analyze** the driving-force terms in both cases
- **Derive** the ratio between heterogeneous and homogeneous nucleation barriers and rates
- **Recall** methods for determining the equilibrium nucleation shape

Recall: key results from homogeneous nucleation

Homogeneous (spherical) nucleus gives the following results:

- Critical nucleus size

$$n_c = -\frac{8}{27}\left[\frac{\eta\gamma_{\alpha\beta}}{\mu_\beta - \mu_\alpha}\right]^3$$

- Nucleation free energy barrier

$$\Delta G_c = \frac{4}{27}\frac{(\eta\gamma)^3}{(\mu_\beta - \mu_\alpha)^2}$$

- Nucleation rate

$$J = Z\beta_c n_t \exp(-\frac{\Delta G_c}{k_B T}) \tag{1}$$

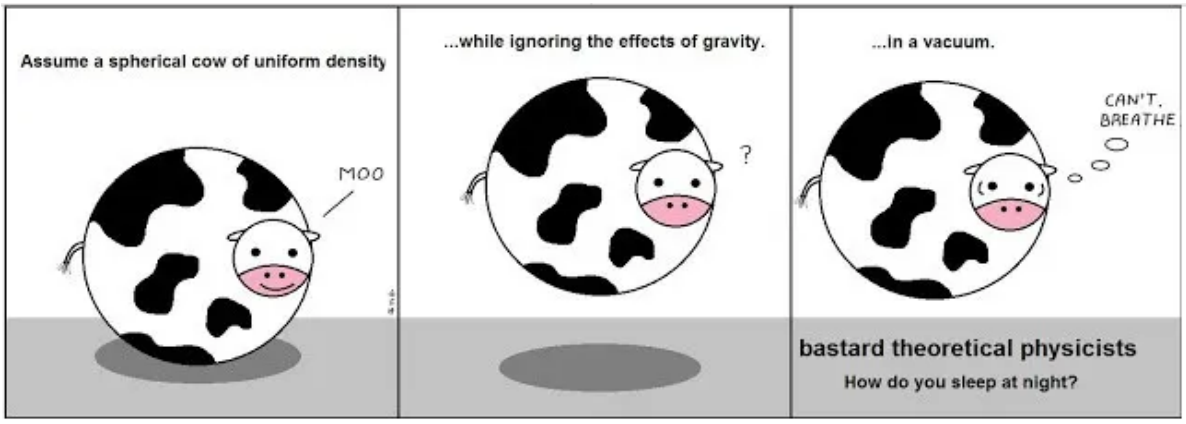
$$Z = \sqrt{\frac{\Delta G_c}{3\pi n_c^3 k_B T}} \tag{2}$$

Recall: homogeneous nucleation implications

- $\Delta G_c \propto \gamma^3$: very sensitive to the interfacial free energy
- Zeldovich factor Z is around 0.1
- Particles can shrink when they are not reaching n_c!
- Rule of thumb: $\Delta G_c \leq 76 k_B T$, otherwise no detectable nucleation
- At $T = 298$ K, $\Delta G_c \leq 1.95$ eV

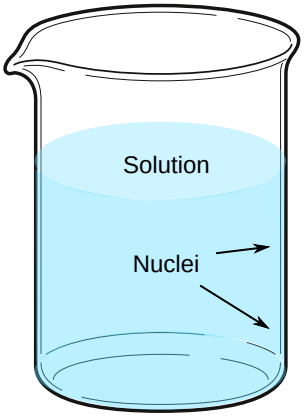
What's the missing picture?

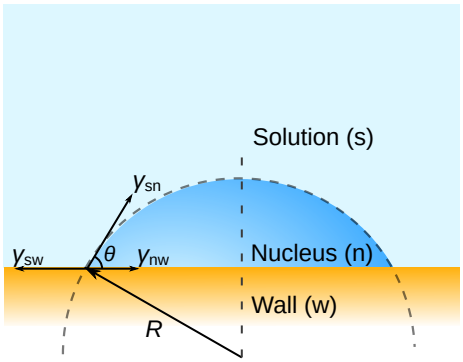
Can we really treat the nuclei as spheres?



Practical considerations: heterogeneous nucleation

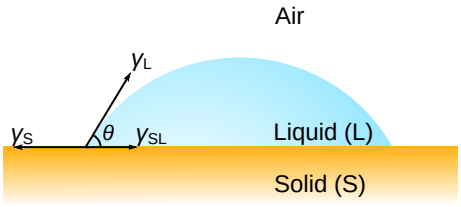
- General idea: can we have smaller ΔG_c if other competing energies exist in the system?
- Analog: nucleation of crystals on a beaker wall
- Need to consider the free energy change before and after wall surface is covered by the nucleus





Triple interface balance: the Young's equation

Analogous to the classical wetting theory, the "contact angle" on a droplet can be described by the Young's equation



$$\gamma_{\mathrm{S}} = \gamma_{\mathrm{L}} \cos\theta + \gamma_{\mathrm{SL}}$$

Heterogeneous nucleation on a wall: volume vs surface

The geometry of the droplet gives:

- Volume of nucleus: $V_{\mathrm{n}} = \frac{\pi R^3}{3}(2 - 3\cos\theta + \cos^3\theta)$
- Interfacial area of nucleus with solution: $A_{\mathrm{s}} = 2\pi R^2(1 - \cos\theta)$
- Interfacial area of nucleus with wall: $A_{\mathrm{c}} = \pi R^2 \sin^2\theta$

Final solution to heterogeneous nucleation barrier:

$$\Delta G_c^{\mathrm{het}} = V_{\mathrm{n}}\Delta G_{\mathrm{V}} + \gamma_{\mathrm{sn}} A_{\mathrm{s}} + (\gamma_{\mathrm{nw}} - \gamma_{\mathrm{sw}})A_{\mathrm{c}}$$

Heterogeneous nucleation on a wall: results

We can compare the hetero- and homogeneous barriers:

$$\frac{\Delta G_{\text{het}}}{\Delta G_{\text{homo}}} = \frac{2 - 3\cos\theta + \cos^3\theta}{4} = f$$

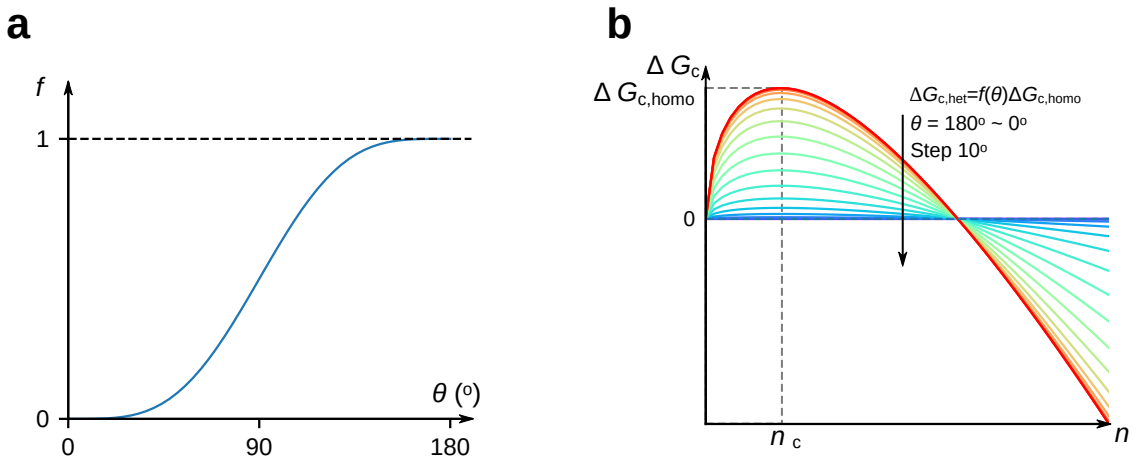


Figure 1: Plot of f as function of contact angle θ

Heterogeneous in binary alloys: geometry

- At triple-interface, we have the balance

$$\gamma_{\alpha\alpha} = 2\gamma_{\alpha\beta} cos\psi$$

- Grain boundary $\gamma_{\alpha\alpha} \neq 0$
- What does $\gamma_{\alpha\alpha} = 0$ mean? Homogeneous nucleation!

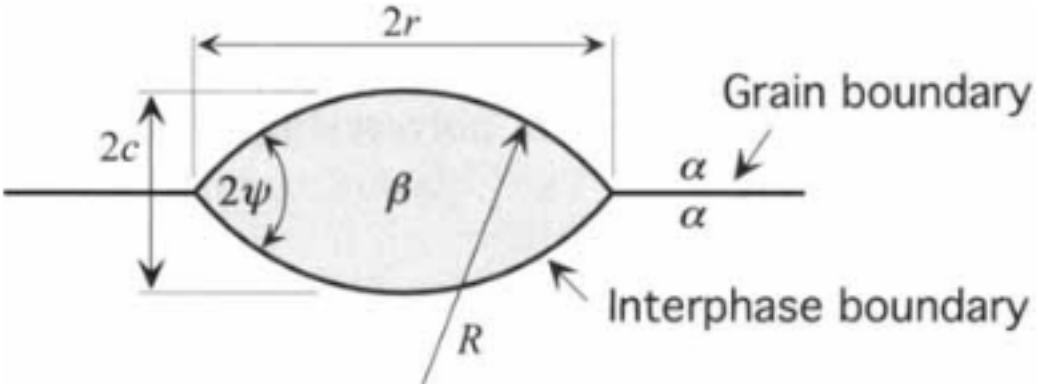


Figure 2: Nucleation At Grain Boundary

Heterogeneous in binary alloys: ΔG_c^{het} results

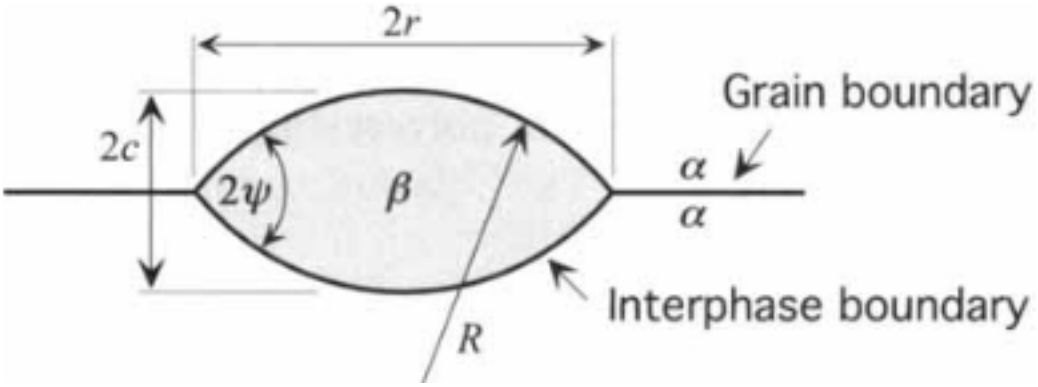


Figure 3: Nucleation At Grain Boundary

- Volume $V = \frac{2\pi R^3}{3}(2 - 3\cos\psi + \cos^3\psi)$
- Area of cap $A_c = 4\pi R^2(1 - \cos\psi)$
- Area below the cap: $A_b = \pi r^2 = \pi R^2(1 - \cos^2\psi)$

Overall heterogeneous nucleation barrier:

$$\Delta G_c^B = (\frac{2\pi R^3}{3}\Delta G_m + 2\pi R^2\gamma_{\alpha\beta})(2 - 3\cos\psi + \cos^3\psi)$$

Ratio between hetero- and homogeneous nucleation energy barriers

Compare the two barriers, they are quite similar

$$\Delta G_c^H = (\frac{4\pi R^3}{3}\Delta G_m + 4\pi R^2 \gamma_{\alpha\beta}) \tag{3}$$

$$\Delta G_c^B = (\frac{2\pi R^3}{3}\Delta G_m + 2\pi R^2 \gamma_{\alpha\beta})(2 - 3\cos\psi + \cos^3\psi) \tag{4}$$

Ratio:

$$\frac{\Delta G_c^B}{\Delta G_c^H} = \frac{1}{2}(2 - 3\cos\psi + \cos^3\psi) \tag{5}$$

This is similar to our case of heterogeneous nucleation on a wall, but with different coefficient (why?)!

Heterogeneous nucleation barrier

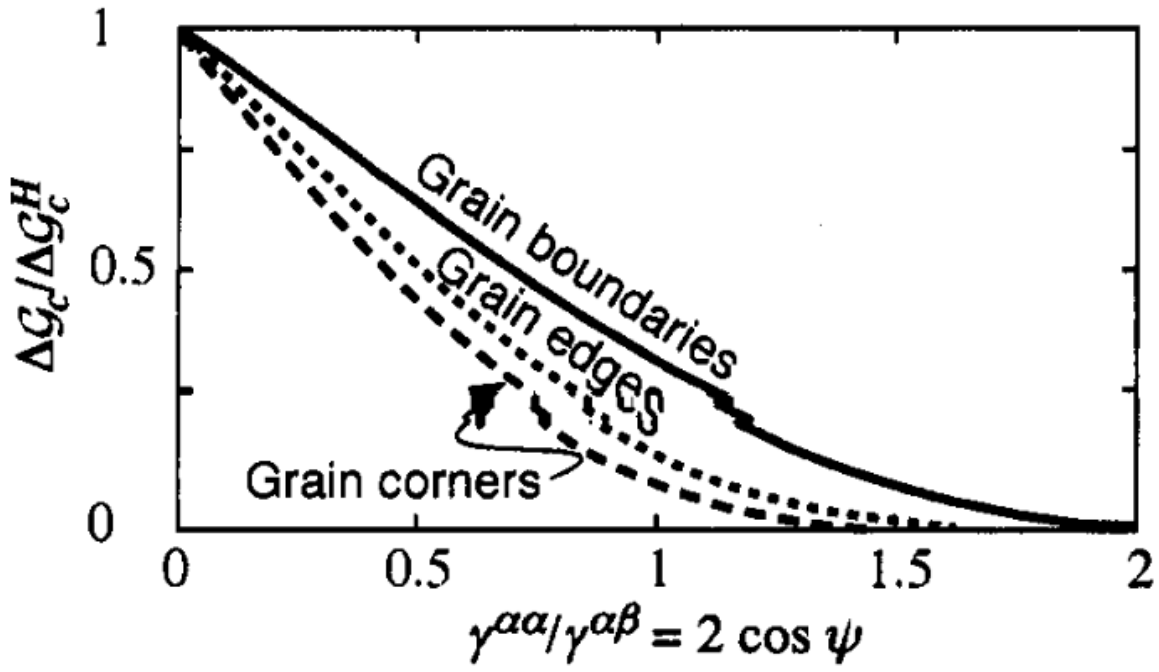


Figure 4: Comparison between nucleations along defects

Heterogeneous nucleation in alloys: other nucleus dimensionalities

- From previous figure we see that ΔG_c on defect becomes smaller for lower-dimensionality defects
- But do low dimensional defects always win? Not essentially.
- Number of sites available also decreases.

Assume the average grain size is L, with grain boundary thickness δ, available sites follows

$$n^{\text{defect}} \propto n_t (\frac{\delta}{L})^{3-d}$$

Competition between hetero- and homogeneous nucleation rates

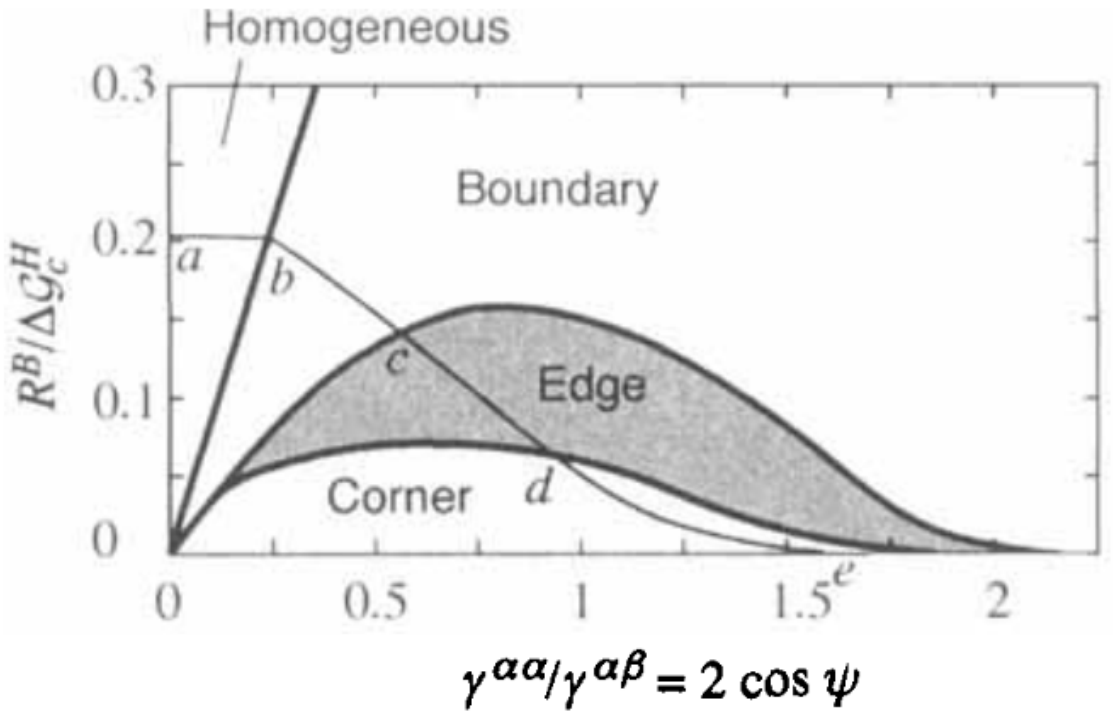
When considering the rates, **two** factors matter in the overall J equation:

- Free energy barrier $\exp(-\Delta G_c / k_B T)$ (hetero > homo)
- Total available sites n_t (hetero < homo)

$$\ln(\frac{J^B}{J_H}) = \ln(\frac{\delta}{L}) + \frac{\Delta G_c^H - \Delta G_c^B}{k_B T}$$

Overall nucleation regimes

- $R_B = k_B T \ln(\frac{L}{\delta})$
- Homogeneous nucleation favours when $R_B > \Delta G_c^H - \Delta G_c^B$



What else may be missing?

- The nucleation geometry may be very different from spherical or curved!
- Different facets have distinct surface free energy
- Overall goal: when the volume V is fixed, can we know the equilibrium shape of a crystal, so that surface energy is minimized?
- Wulff construction: optimizing the geometry of equilibrium shape
- Higher energy facet would have longer distance to the center!

Wulff construction for equilibrium crystal shape

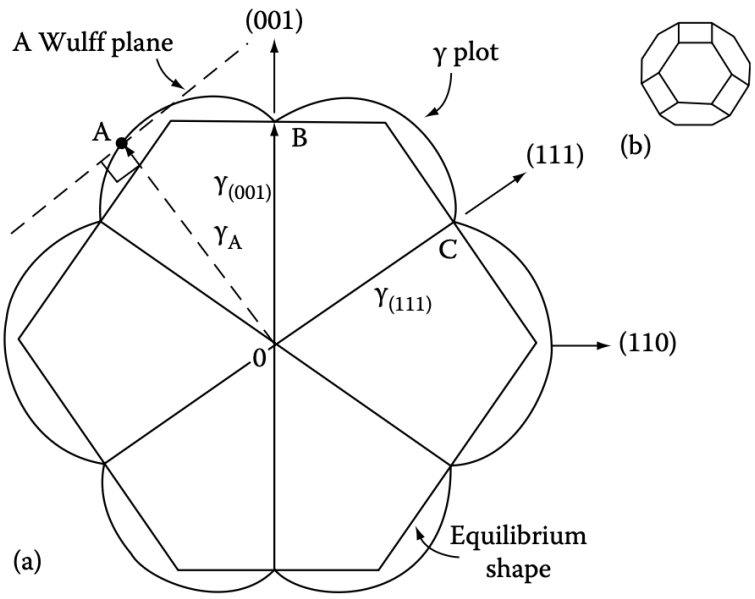


FIGURE 3.5
(a) A possible $[\bar{1}10]$ section through the γ-plot of an fcc crystal. The length OA represents the free energy of a surface plane whose normal lies in the direction OA. Thus $OB = \gamma_{(001)}$, $OC = \gamma_{(111)}$ etc. Wulff planes are those such as that which lies normal to the vector OA. In this case the Wulff planes at the cusps (B, C, etc.) give the inner envelope of all Wulff planes and thus the equilibrium shape, (b) The equilibrium shape in three dimensions showing {100} (square faces) and {111} (hexagonal faces).

Theoretical Wulff construction for elements

Crystalium demo

Tran et al. Scientific Data, 2016, 3:160080

Nucleation: example demo

19.1 An equilibrium temperature–composition diagram for an A–B alloy is shown in Fig. 19.18*a*. A nucleation study is carried out at 800 K using an alloy of 30 at. % B. The alloy is initially homogenized at 1200 K, then quenched to 800 K where the steady-state homogeneous nucleation rate is determined to be 10^6 m^{-3} s^{-1}. Since this rate is so small as to be barely detectable, it is desired to change the alloy composition (i.e., increase the supersaturation) so that with the same heat treatment the nucleation rate is increased to 10^{21} m^{-3} s^{-1}. Estimate the new alloy composition required to achieve this at 800 K. Use the free energy vs. composition curves in Fig. 19.18*b*, and assume that the interphase boundary energy per unit area, γ, is 75 mJ m^{-2}. List important assumptions in your analysis.

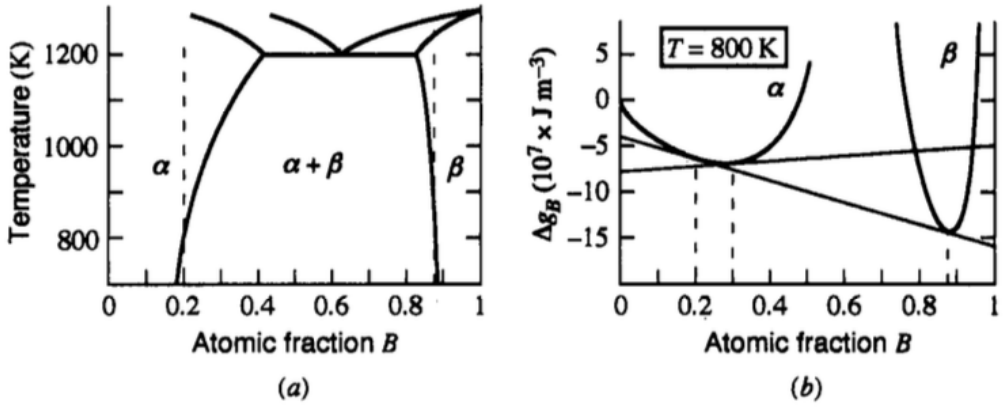


Figure 19.18: **(a)** Equilibrium diagram for A–B alloy. **(b)** Plot of free-energy density, Δg_B, vs. atomic fraction of component B at $T = 800$ K.

Nucleation demo: how do we get the values?

Solution. Important assumptions include that the interfacial free energy is isotropic, that elastic strain energy is unimportant, and that the nucleation rates mentioned are for steady-state nucleation. The critical barrier to nucleation, $\Delta\mathcal{G}_c$, can be calculated for the 0.3 atomic fraction B alloy using the *tangent-to-curve* construction on the curves in Fig. 19.18*b* to provide the value $\Delta g_B = -9 \times 10^7$ J m^{-3} for the chemical driving force for this supersaturation at 800 K. $\Delta\mathcal{G}_c$ is given for a spherical critical nucleus by

$$\Delta\mathcal{G}_c = \frac{16\pi\gamma^3}{3(\Delta g_B)^2} = \frac{16\pi(75 \times 10^{-3})^3}{3(-9 \times 10^7)^2} = 8.73 \times 10^{-19}\text{J} \qquad (19.60)$$

Nucleation demo: supersaturation limit

Note that at this temperature, $kT = 1.38 \times 10^{-23} \times 800 = 1.10 \times 10^{-20}$, so that at 800 K and $X_B = 0.3$, $\Delta\mathcal{G}_c \approx 79kT$. Based on the criterion that for significant nucleation $\Delta\mathcal{G}_c \leq 76kT$ (Section 19.1.7), it is reasonable that the nucleation rate is "barely detectable" in the alloy with $X_B = 0.3$.

The steady-state nucleation rate will be proportional to $\exp[-\Delta\mathcal{G}_c/(kT)]$ so we know that at 800 K and $X_B = 0.3$,

$$10^6 = C' \exp(-79) \tag{19.61}$$

where the constant C' is equal to $N\beta Z$ in the classical theory for steady-state nucleation. We need to find the critical nucleation barrier necessary to achieve the nucleation rate of 10^{21}, and this will be

$$\frac{10^6}{10^{21}} = \frac{\exp(-79)}{\exp[-\Delta\mathcal{G}_c/(kT)]} \tag{19.62}$$

or

$$\ln 10^{-15} = -79 + \frac{\Delta\mathcal{G}_c}{kT} \quad \text{or} \quad -34.54 + 79 = \frac{\Delta\mathcal{G}_c}{kT} \tag{19.63}$$

and thus for the higher nucleation rate we must have $\Delta\mathcal{G}_c \approx 44.5kT = 4.91 \times 10^{-19}\text{J}$. Next, solve for the chemical driving force required to get $\Delta\mathcal{G}_c$ down to this value, as follows:

$$\Delta g_B = \sqrt{\frac{16\pi\gamma^3}{3\Delta\mathcal{G}_c}} = \sqrt{\frac{16\pi \times (75 \times 10^{-3})^3}{3 \times 4.91 \times 10^{-19}}} = -12 \times 10^7 \,\text{J}\,\text{m}^{-3} \tag{19.64}$$

Finally, use the free-energy density vs. composition curves and work the tangent-to-curve construction in reverse. Using the result that $\Delta g_B = -12 \times 10^7 \,\text{J}\,\text{m}^{-3}$, the corresponding tangent to the α-phase curve will be at about 33 at. % B.

This calculation serves as a good example of the high sensitivity of nucleation rate to the degree of supersaturation.

Summary

- Nucleation is a type of discontinuous phase transformation that is triggered by the difference in free energy at supercooling / supersaturation
- At unsteady-state conditions, nucleation free energy barrier is caused by the positive interfacial energy
- Nucleation free energy barrier is characterized by ΔG_c, giving critical nucleus size n_c
- The evolution of particle number at each size N_n can be described by a "diffusion-like" analog