1. The classical nucleation theory explains why homogeneous crystal nucleation is difficult: crystals need to exceed a critical size in order to grow, and the ones that are smaller than that will dissolve. In the absence of a seed, a rare, spontaneous fluctuation is needed to form a critical nucleus. The Gibbs free energy of a spherical isotropic nucleus in the liquid is often expressed as

$$\Delta G = -\frac{4}{3}\pi r^3 \overline{\Delta G_{SL}} + 4\pi r^2 \gamma_{SL}$$

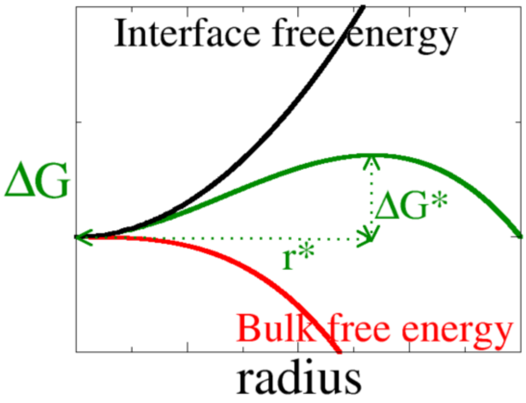
Where $\Delta G_{SL} > 0$ and $\gamma_{SL} > 0$

a) Plot the change of ΔG as a function of r. Determine the size of the critical nucleus γ_c, and the corresponding free energy barrier.

b) What will happen if we add seed crystals to the undercooled liquid phase, given that the seed crystals have the same composition as the nuclei in liquid? Discuss for the cases 1) when the seed crystals are smaller than the critical nucleus, and 2) when they are larger than the critical nucleus.

Solution:

a) In the plot below, the variation of the volume free energy, interfacial energy and the overall free energy change as a function of r is shown. Since the interfacial contribution goes as r^2 and that of bulk free energy as r^3, at smaller r, interfacial energy always dominates, and being a positive energy, it actually suppresses the formation of solid. Unless the size of the solid is above some size wherein the (negative) bulk free energy change can more than compensate for the (positive) interfacial energy, the solid will not be stable (even if it forms). Thus, one can identify the critical radius of the solid that is stable when formed in the undercooled liquid by minimizing ΔG with respect to r:



$$\left[\frac{d\Delta G}{dr}\right] r = r_c = 0$$

$$-4\,\pi {r_c}^2 \Delta G_{SL} + 8\pi r_c \gamma_{SL} = 0$$

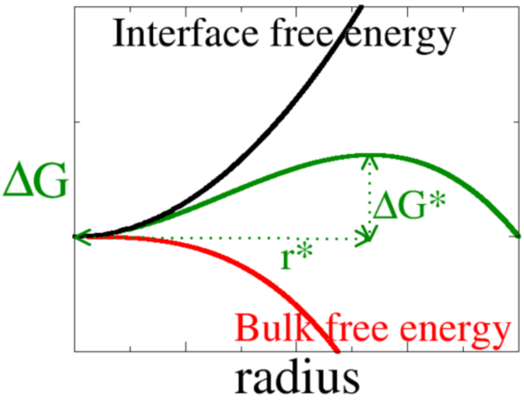
$$r_c = 2\gamma_{SL}/\Delta G_{SL}$$

And the corresponding activation energy will be known by calculating ΔG at critical r (insert $r_c = 2\gamma_{SL}/\Delta G_{SL}$ into $\Delta G = -\frac{4}{3}\pi {r_c}^3 \Delta G_{SL} + 4\pi {r_c}^2 \gamma_{SL}$)

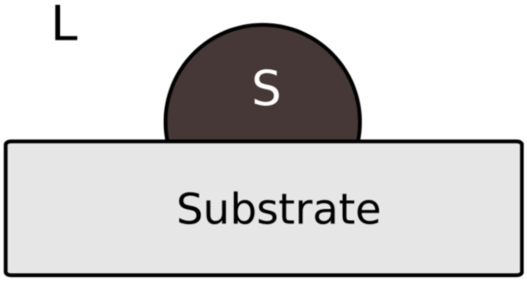
Which will eventually yield ΔG^*as:

$$\Delta G^* = \frac{16\pi\gamma_{SL}^3}{3\Delta G_{SL}^2}$$

b) When the seed crystals are smaller than the critical nucleus, they will have a very little effect.
On the other hand, when the seed crystals are larger than the critical nucleus, free energy will decrease, so these nuclei are more probable. Therefore, adding seed crystals whose size is bigger than that of r_c would promote crystallization.



2. Crystallization can also be facilitated by introducing foreign substances. In fact, heterogeneous nucleation, nucleation starting at a surface, is faster and more common than homogeneous nucleation.
   a) Take γ_{SL}, $\gamma_{SS'}$, $\gamma_{S'L}$ to be the interfacial free energy between solid-liquid, solid-substrate, and substrate-liquid, respectively. Can you predict the equilibrium shape of a nucleus formed on the substrate? Assume $\gamma_{SL}+\gamma_{SS'}-\gamma_{S'L}>0$. Hint: you may want to revisit Young's equation introduced in the previous lectures.



   b) For simplification, imagine the shape of the solid particle as a truncated sphere. For the nucleus formed on the substrate as in (a), can you write out the expression for the free energy ΔG as a function of its volume?
   c) Make a plot to illustrate the relationship between ΔG and the volume of the nucleus both in heterogeneous nucleation and in homogeneous nucleation. How do the free energy barriers of the two compare to each other?
   d) Suppose for this system γ_{SL} is constant across all temperatures, and the chemical potential ΔG_{SL} can be expressed as

$$\overline{\Delta G_{SL} S} = H_f \frac{T_m - T}{T_m}$$

Where $H_f > 0$ is the constant of latent heat per unit volume, and T_m is the melting point of the system. Based on these assumptions, can you write down the nucleation free energy barrier as a function of temperature T?

e) According to (d), will the system solidify at $T = T_m$? Write down the condition between $\gamma_{SL}, \gamma_{SS'}$ and $\gamma_{S'L}$, under which the system will solidify at $T = T_m$?

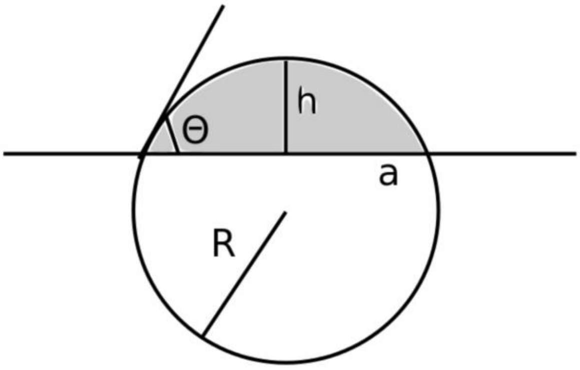
Solution:

a) The energetic relation $\gamma_{SL}+\gamma_{SS'}-\gamma_{S'L}>0 \quad \rightarrow \quad \gamma_{SL}+\gamma_{SS'} > \gamma_{S'L}$ indicates that the particle is non-wettable on the substrate, so there will be a non-zero contact angle θ.

The shape of a nucleus formed on the substrate is a truncated sphere with contact angle θ following the Young's equation:

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

$$\theta = arccos\left(\frac{\gamma_{S'L} - \gamma_{SS'}}{\gamma_{SL}}\right)$$



b) The free energy of the nucleus is composed of two parts, the bulk energy of the nucleus and its interfacial energies. To

Take the height of the cap as $h = R(1 - cos\theta)$

then the volume of the truncated sphere is

$$V = \frac{\pi h^2}{3}(3R - h)$$

Write V in terms of R:

$$V = \frac{\pi}{3} R^3 (1 - cos\theta)^2 (2 + cos\theta)$$

$$R = (\frac{3}{\pi})^{\frac{1}{3}} (1 - cos\theta)^{-\frac{2}{3}} (2 + cos\theta)^{-\frac{1}{3}} V^{\frac{1}{3}}$$

And the curved surface area A_{SL} of the sphere cap is

$$A_{SL} = 2\pi Rh = 2\pi R^2 (1 - cos\theta) = (8\pi^3)^{\frac{1}{3}} (\frac{9}{\pi^2})^{\frac{1}{3}} (1 - cos\theta)^{-\frac{4}{3}} (2 + cos\theta)^{-\frac{2}{3}} V^{\frac{2}{3}} (1 - cos\theta)$$

$$= (72\pi)^{\frac{1}{3}} (1 - cos\theta)^{-\frac{1}{3}} (2 + cos\theta)^{-\frac{2}{3}} V^{\frac{2}{3}}$$

The contact area between the nucleus and the substrate is:

$$A_{SS'} = \pi a^2 = \pi R^2 sin^2\theta = \pi R^2 (1 - cos^2\theta) = \pi R^2 (1 - cos\theta)(1 + cos\theta) = (\pi^3)^{\frac{1}{3}} (\frac{9}{\pi^2})^{\frac{1}{3}} (1 - cos\theta)^{-\frac{4}{3}} (2 + cos\theta)^{-\frac{2}{3}} V^{\frac{2}{3}} (1 - cos\theta)(1 + cos\theta) = (9\pi)^{\frac{1}{3}} (1 + cos\theta)(1 - cos\theta)^{-\frac{1}{3}} (2 + cos\theta)^{-\frac{2}{3}} V^{\frac{2}{3}}$$

So we have

$$A_{SL} = (72\pi)^{\frac{1}{3}} (1 - cos\theta)^{-\frac{1}{3}} (2 + cos\theta)^{-\frac{2}{3}} V^{\frac{2}{3}}$$

and

$$A_{SS'} = (9\pi)^{\frac{1}{3}}(1 + cos\theta)(1 - cos\theta)^{-\frac{1}{3}}(2 + cos\theta)^{-\frac{2}{3}}V^{\frac{2}{3}}$$

Plug these values into the expression for

$$\Delta G(V) = -V\Delta G_{SL} + A_{SL}\gamma_{SL} + A_{SS'}(\gamma_{SS'} - \gamma_{S'L})$$

And obtain:

$$\begin{aligned}\Delta G(V) &= -V\Delta G_{SL} + A_{SL}\gamma_{SL} + A_{SS'}(\gamma_{SS'} - \gamma_{S'L}) \\ &= -V\Delta G_{SL} + (72\pi)^{\frac{1}{3}}(1 - cos\theta)^{-\frac{1}{3}}(2 + cos\theta)^{-\frac{2}{3}}V^{\frac{2}{3}}\gamma_{SL} \\ &+ (9\pi)^{\frac{1}{3}}(1 + cos\theta)(1 - cos\theta)^{-\frac{1}{3}}(2 + cos\theta)^{-\frac{2}{3}}V^{\frac{2}{3}}(\gamma_{SS'} - \gamma_{S'L}) \\ &= -V\Delta G_{SL} + (9\pi)^{\frac{1}{3}}(1 - cos\theta)^{-\frac{1}{3}}(2 + cos\theta)^{-\frac{2}{3}}V^{\frac{2}{3}}(2\gamma_{SL} + (1 \\ &+ cos\theta)(\gamma_{SS'} - \gamma_{S'L})) = -V\Delta G_{SL} + (9\pi)^{\frac{1}{3}}(1 - cos\theta)^{\frac{2}{3}}(2 + cos\theta)^{\frac{1}{3}}V^{\frac{2}{3}}\gamma_{SL}\end{aligned}$$

c) For homogeneous nucleation,

$$\Delta G(V) = -V\Delta G_{SL} + (36\pi)^{\frac{1}{3}}V^{\frac{2}{3}}\gamma_{SL}$$

(just a rewrite of spherical homogeneous nucleation as a function of sphere volume of the nucleus, as you've seen in question 1 and in the lecture)

Notice that the geometrical constant $(9\pi)^{\frac{1}{3}}(1 - cos\theta)^{\frac{2}{3}}(2 + cos\theta)^{\frac{1}{3}}$ for heterogeneous nucleation is smaller than the geometrical constant $(36\pi)^{\frac{1}{3}}$ for homogeneous nucleation. This means that the free energy barrier for heterogeneous nucleation is lower.

d) $\Delta G(V) = -VH_f\frac{T_m - T}{T_m} + (9\pi)^{\frac{1}{3}}(1 - cos\theta)^{\frac{2}{3}}(2 + cos\theta)^{\frac{1}{3}}V^{\frac{2}{3}}\gamma_{SL}$

e) From what you derived from d), $\Delta G(V)$ is composed of the negative part from the bulk energy as well as positive energy change from the interfacial energies. As $T = T_m$, the bulk energy part is now zero. In order for nucleation to happen, $\Delta G(V) \leq 0$

So only if the contact angle $\theta = 0$, i.e. complete wetting, the opposite of non-wetting as in a), which means the interfacial energies satisfy the following relation:

$$\gamma_{S'L} \geq \gamma_{SL} + \gamma_{SS'}$$