[pex21] Catalytic freezing of spherical cap

Container walls provide sites of nucleation for the freezing process with lower activation barriers compared to nucleation from pure liquid (homogeneous nucleation). Consider a solid spherical cap heterogeneously nucleated against a flat catalyst surface. The radius of the completed sphere is r. The angle θ remains constant during the nucleation process. Its value is dictated by the balance of interfacial tensions between liquid (l), solid (s), and catalyst (c):

$$\gamma_{sl} \cos\theta = \gamma_{cl} - \gamma_{cs} \qquad \text{(Young's equation)}.$$

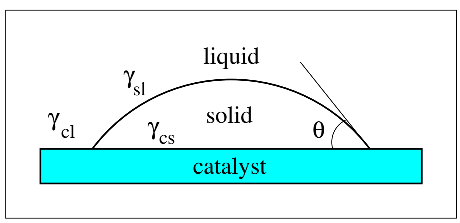
If the melting temperature is T_m and the latent heat is L_m then the change in Gibbs free energy when the liquid is undercooled by $\Delta T \doteq T_m - T$ has three terms that depend on r as follows:

$$\Delta G(r) = -\frac{L_m \Delta T}{T_m} V_s(r) + \gamma_{sl} A_{sl}(r) + (\gamma_{cs} - \gamma_{cl}) A_{cs}(r),$$

where $V_s(r)$, $A_{sl}(r)$, and $A_{cs}(r)$ are the volume, the curved surface, and the flat surface of the cap, respectively.
(a) Show that $\Delta G(r)$ has a maximum at $r_c = 2\gamma_{sl} T_m / L_m \Delta T$, which means that caps with $r > r_c$ grow spontaneously.
(b) Show that the energy barrier for this kind of heterogeneous nucleation is

$$\Delta G(r_c) = \frac{1}{4}(1-\cos\theta)^2(2+\cos\theta)\Delta G_0, \quad \Delta G_0 = \frac{16\pi}{3}\gamma_{sl}^3 \left(\frac{T_m}{L_m \Delta T}\right)^2.$$

The quantity ΔG_0 is the energy barrier for homogeneous nucleation, represented by the case $\theta = \pi$.



[adapted from Jones 2002]

Solution: