Particle Size and Nucleation

M. Ceriotti - MX304

EPFL

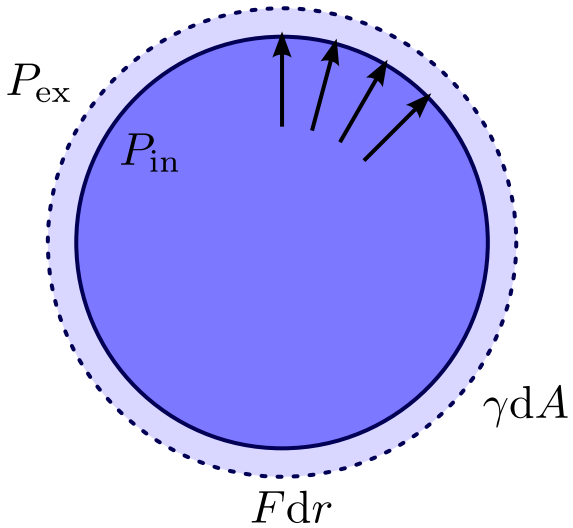
Outline

- Chapter 4.6 of your book (9 & 10 could also deserve reading)
- Laplace pressure, Ostwald ripening
- Nucleation from the melt, thermal stability of (nano)particles

Laplace Pressure

- The surface energy term for a spherical droplet leads to a force acting perpendicular to the surface
- This force must be balanced by a pressure difference between the inside and the outside of the droplet
- Pressure for a water droplet: 1mm$\rightarrow$0.001atm; 1nm$\rightarrow$1000atm!

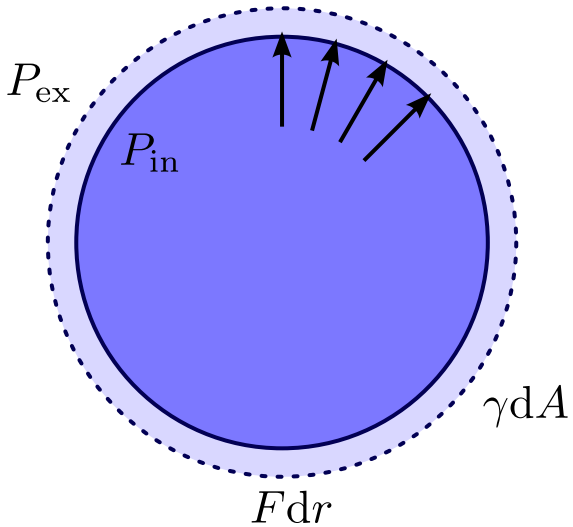
$$F\mathrm{d}r = \gamma \mathrm{dA} \qquad A = 4\pi r^2 \qquad \mathrm{d}A = 8\pi r \mathrm{dr}$$



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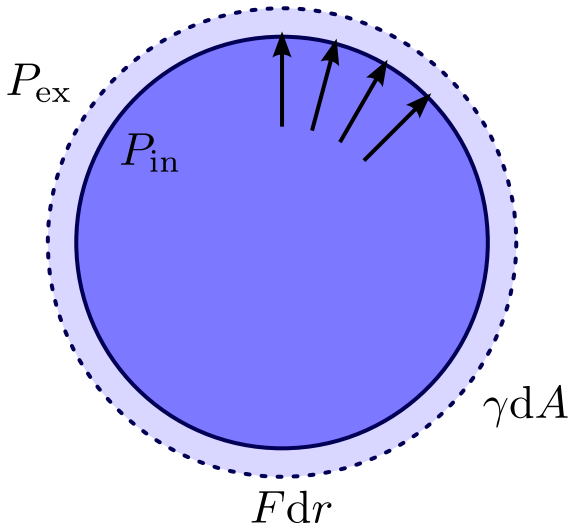
$$P_{\text{in}} - P_{\text{ex}} = \Delta P = F/A = 8\pi\gamma_{\text{LV}} r/A = \frac{2\gamma_{\text{LV}}}{r}$$



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Kelvin Equation

- We start in an equilibrium condition, and change the pressure. In order to maintain the equilibrium between the droplet and the vapor one must have

$$\mathrm{d}G_{\mathrm{in}} = \mathrm{d}G_{\mathrm{ex}} \longrightarrow V_{\mathrm{in}}\mathrm{d}P_{\mathrm{in}} = V_{\mathrm{ex}}\mathrm{d}P_{\mathrm{ex}} \longrightarrow \mathrm{d}P_{\mathrm{in}} = \frac{V_{\mathrm{ex}}}{V_{\mathrm{in}}}\mathrm{d}P_{\mathrm{ex}}$$

- ... but the change in Laplace pressure is related to the change in size

$$\mathrm{d}P_{\mathrm{in}} - \mathrm{d}P_{\mathrm{ex}} = 2\gamma_{LV}\mathrm{d}\left(\frac{1}{r}\right) \longrightarrow (V_{\mathrm{ex}} - V_{\mathrm{in}})\,\mathrm{d}P_{\mathrm{ex}} = 2\gamma_{\mathrm{LV}}V_{\mathrm{in}}\mathrm{d}\left(\frac{1}{r}\right)$$

- Now, assume $V_{\mathrm{ex}} \gg V_{\mathrm{in}}$, and that the vapor follows the ideal gas equation so $V_{\mathrm{ex}} = RT/P_{\mathrm{ex}}$

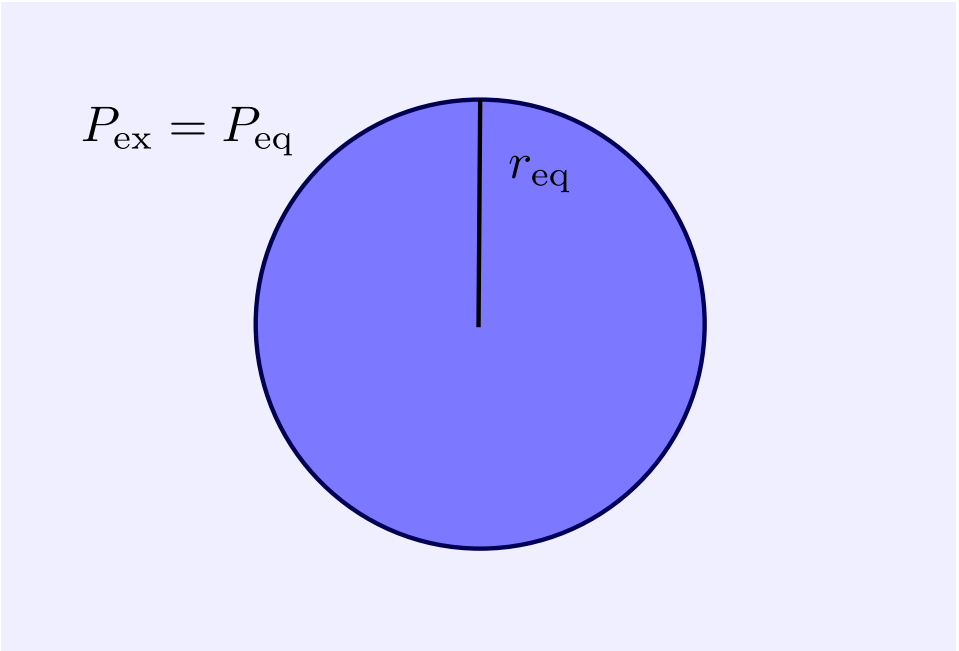
$$\frac{\mathrm{d}P_{\mathrm{ex}}}{P_{\mathrm{ex}}} = \frac{2\gamma_{\mathrm{LV}}V_{\mathrm{in}}}{RT}\mathrm{d}\left(\frac{1}{r}\right) \longrightarrow \boxed{\ln\frac{P_{\mathrm{eq}}}{P_0} = \frac{2\gamma_{\mathrm{LV}}V_{\mathrm{in}}}{RT}\frac{1}{r_{\mathrm{eq}}}}$$ Kelvin Equation

Consequences of Kelvin Equation

$$\ln \frac{P_{eq}}{P_0} = \frac{2\gamma_{LV} V_{in}}{RT} \frac{1}{r_{eq}}$$ Kelvin Equation

- Every droplet in equilibrium with a constant-pressure vapor reservoir is in unstable equilibrium
- Given two droplets of different size, the larger will grow at the expense of the smaller (coarsening/Ostwald ripening)

$$dV = 4\pi r_1^2 dr_1 = -4\pi r_2^2 dr_2 \qquad dG = 8\pi\gamma_{LV}\left(1 - \frac{r_1}{r_2}\right) r_1 dr_1$$

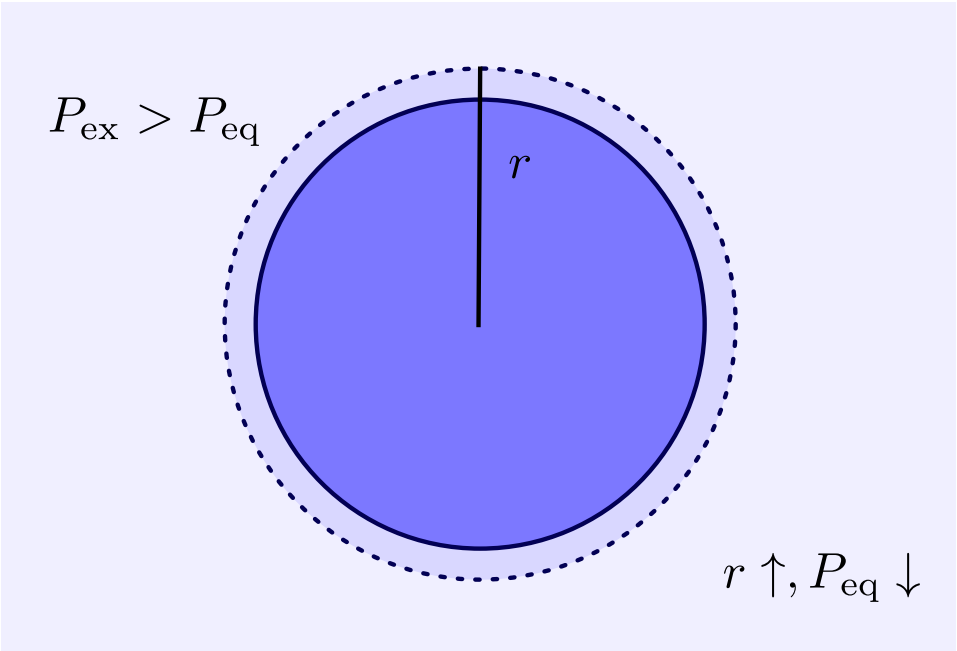


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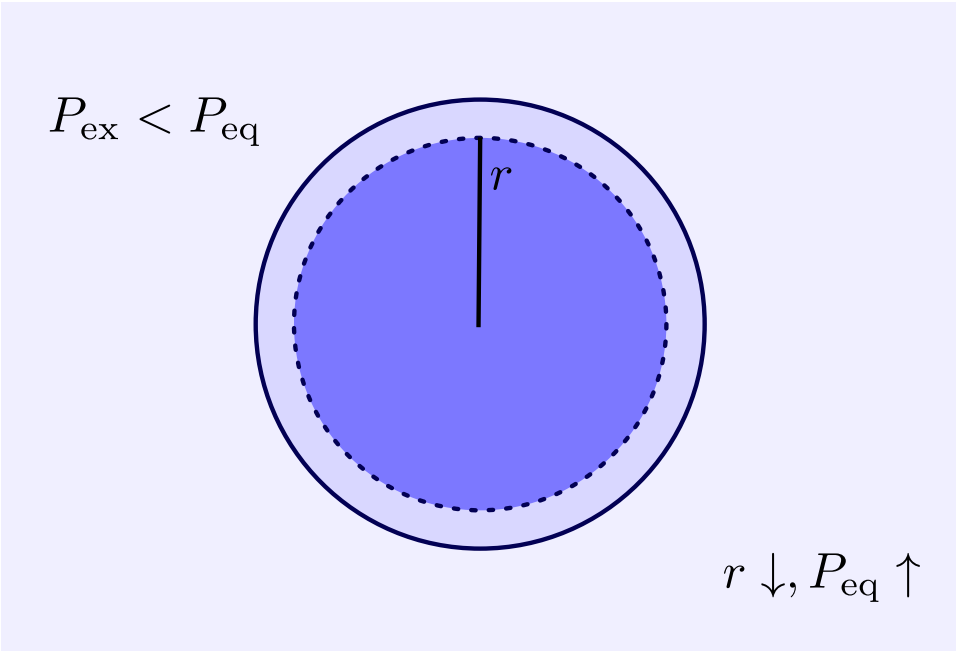


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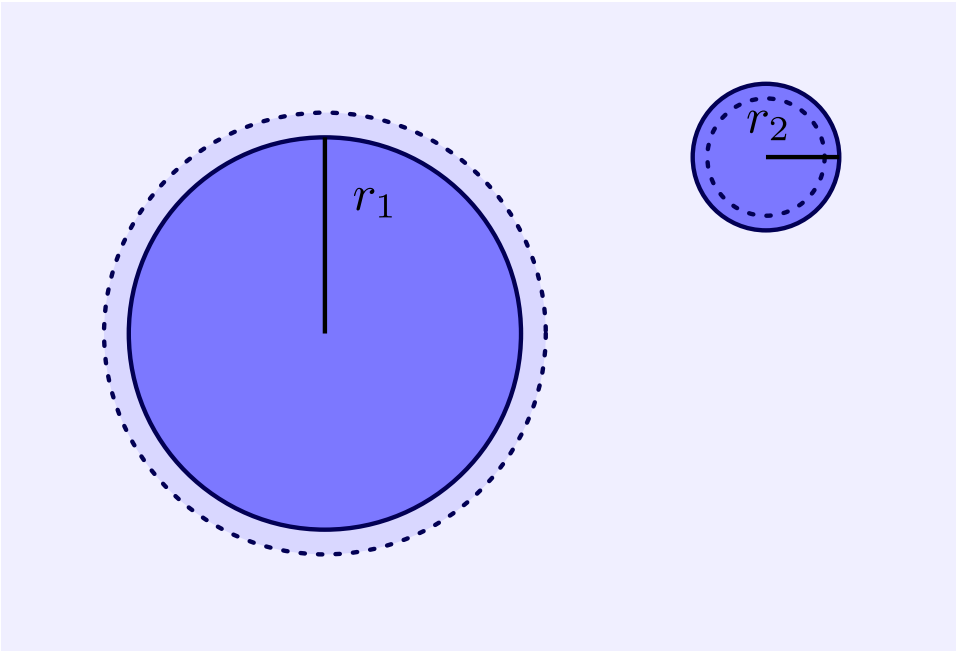


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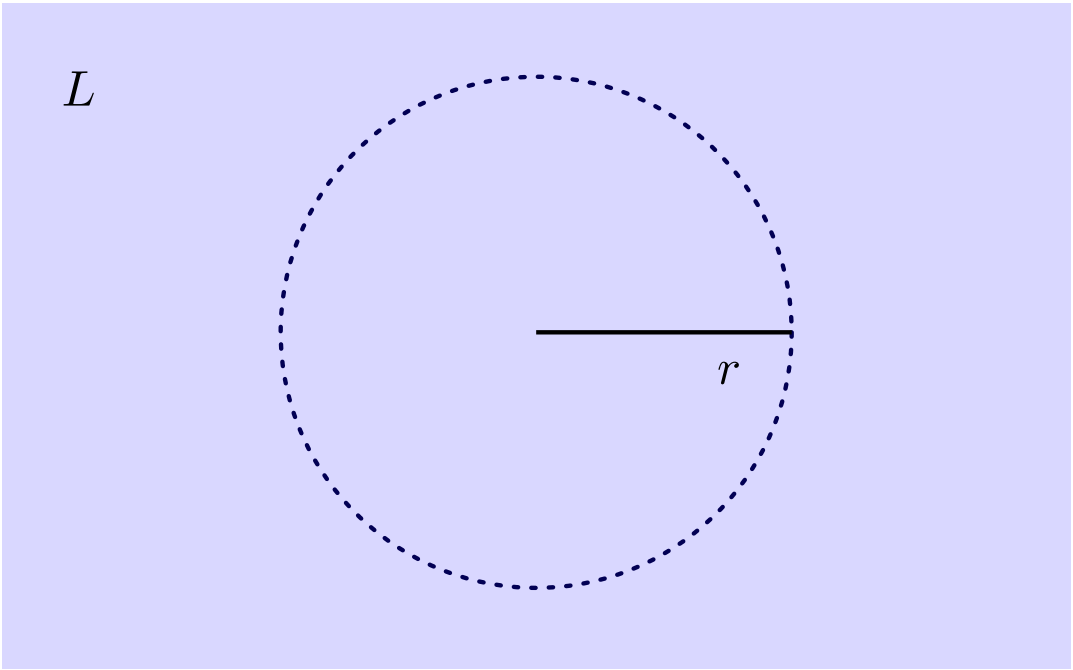
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Nucleation From the Melt

- Let's write the energetics of a sphere of solid of radius r embedded in a liquid
- Find the maximum to determine the critical radius and energy

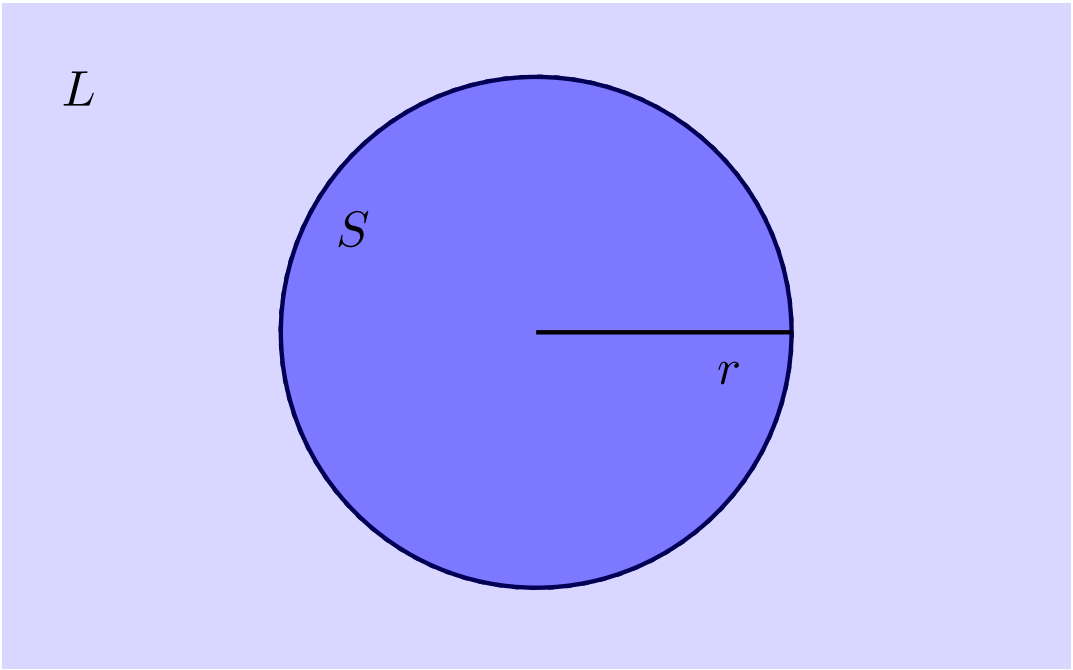
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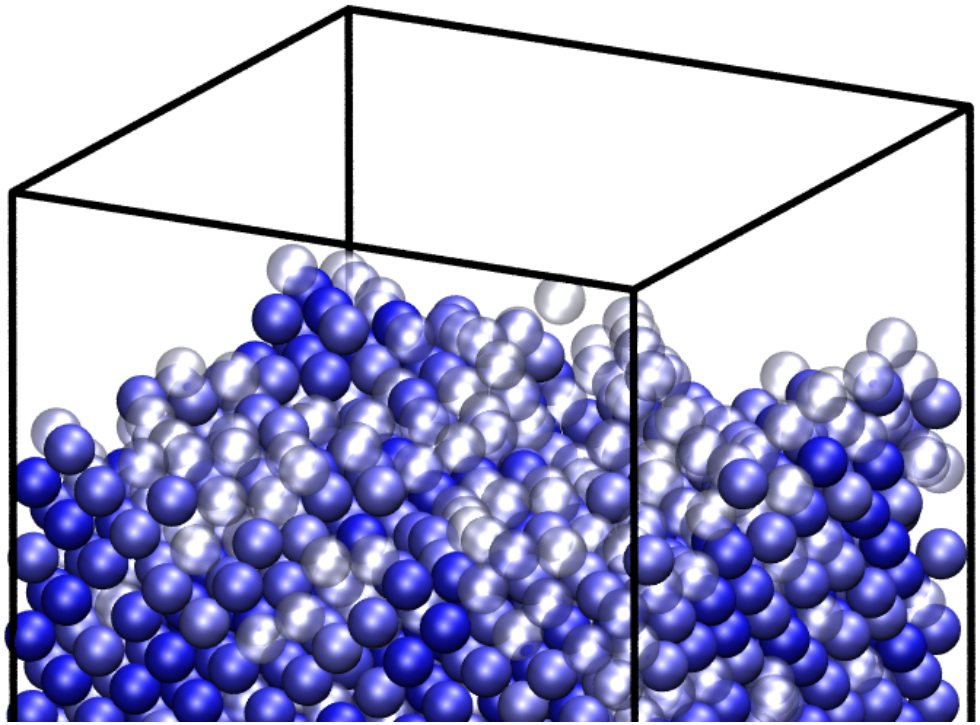
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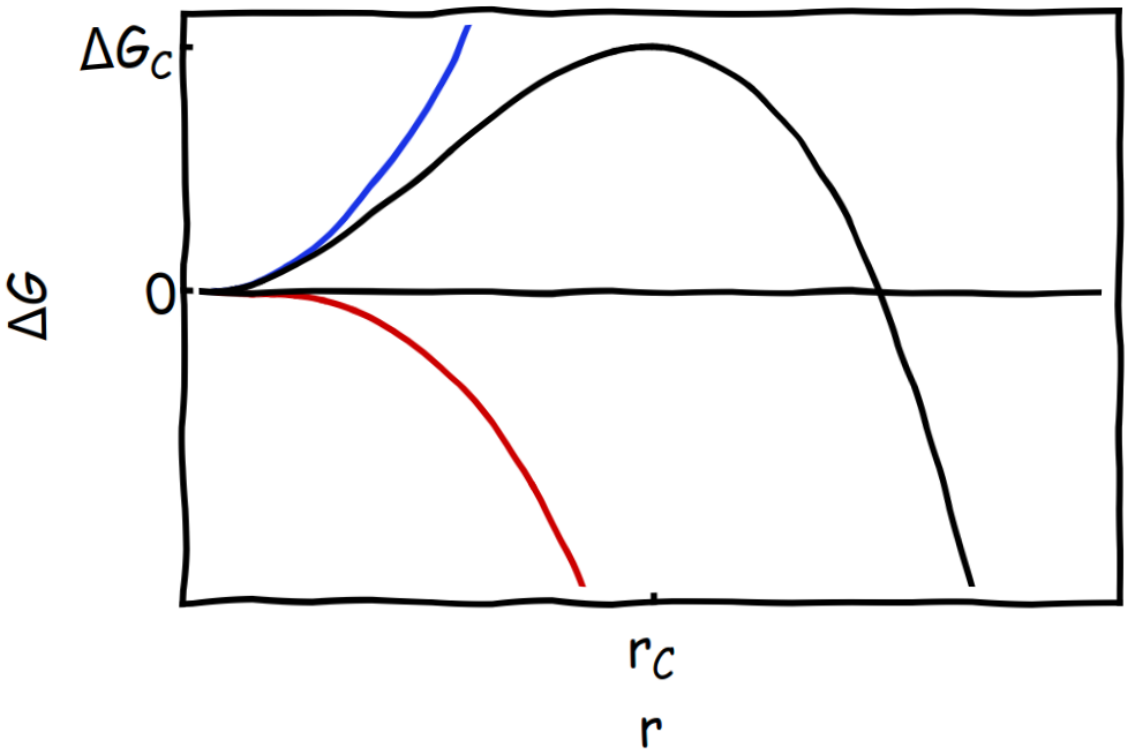
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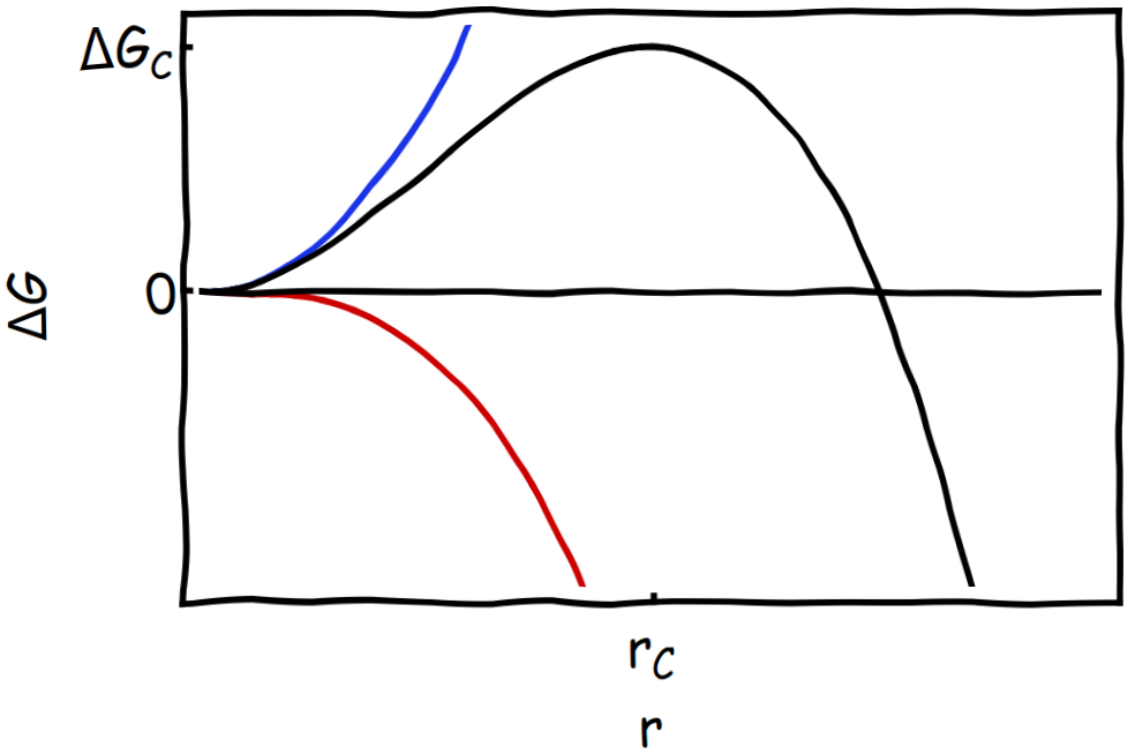
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$$\frac{\partial}{\partial r}\Delta G(r) = 0 \rightarrow r_c = \frac{2\gamma_{SL}}{\Delta G_{SL}},\ \Delta G(r_c) = \frac{16\pi}{3}\frac{\gamma_{SL}^3}{\Delta G_{SL}^2}$$



Undercooling and Nucleation Rate

- Temperature dependence of $\Delta G_{SL}(T) = \Delta H_{SL} - T\Delta S_{SL}$

$$\Delta G_{SL}(T_{SL}) = 0 \longrightarrow \Delta S_{SL} = \frac{\Delta H_{SL}}{T_{SL}}$$

- Nucleation rate is Arrhenius-like - an example for ice nucleation

$$k = k_0 \exp -\frac{\Delta G(r_c)}{k_B T} = k_0 \exp\left(-\frac{16\pi}{3k_B T}\gamma_{SL}^3 \Big/ \left(1 - \frac{T}{T_{SL}}\right)^2 \Delta H_{SL}^2\right)$$

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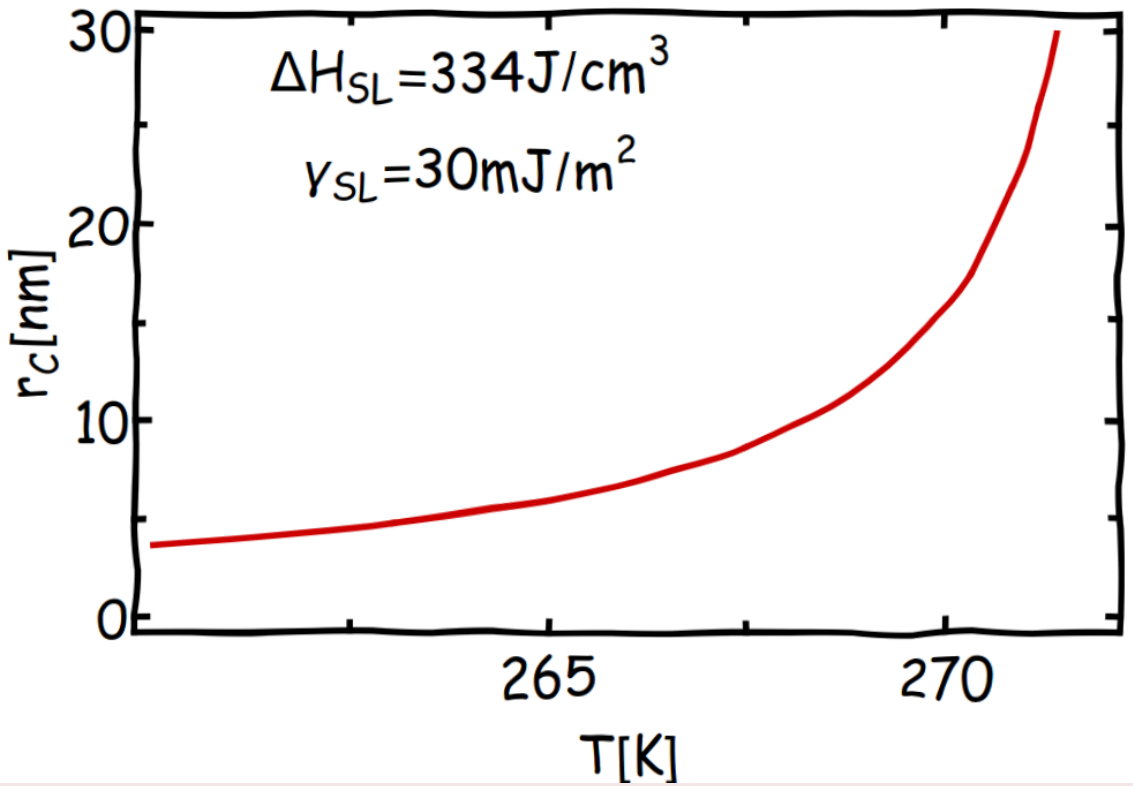
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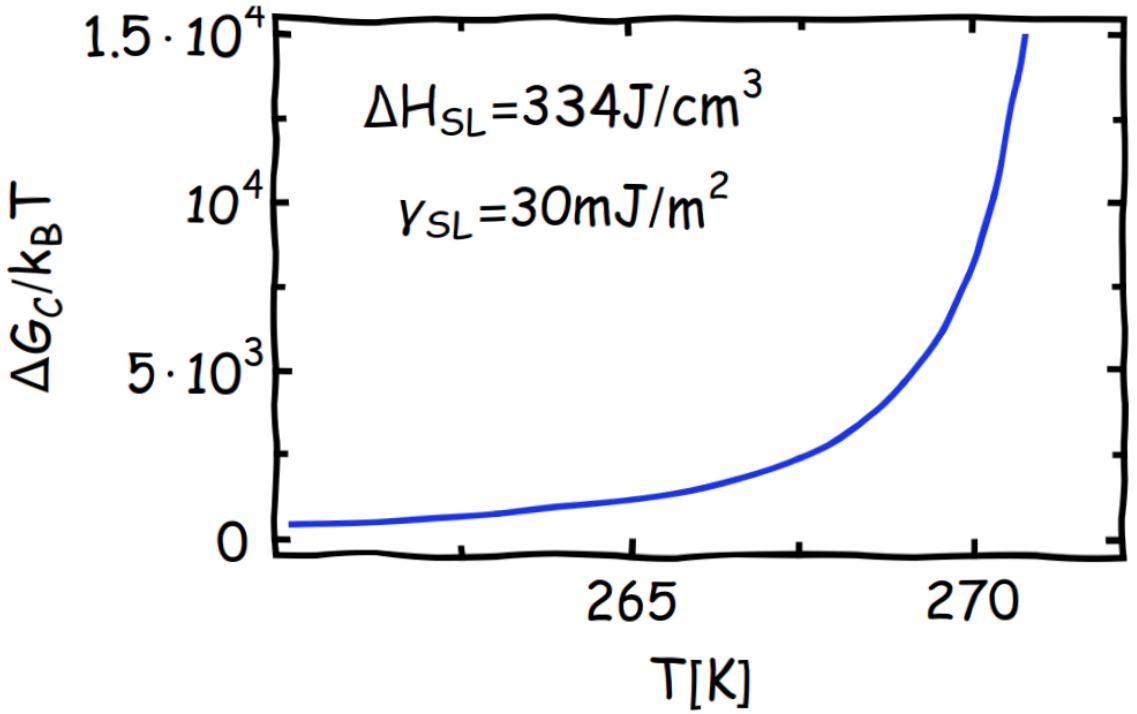
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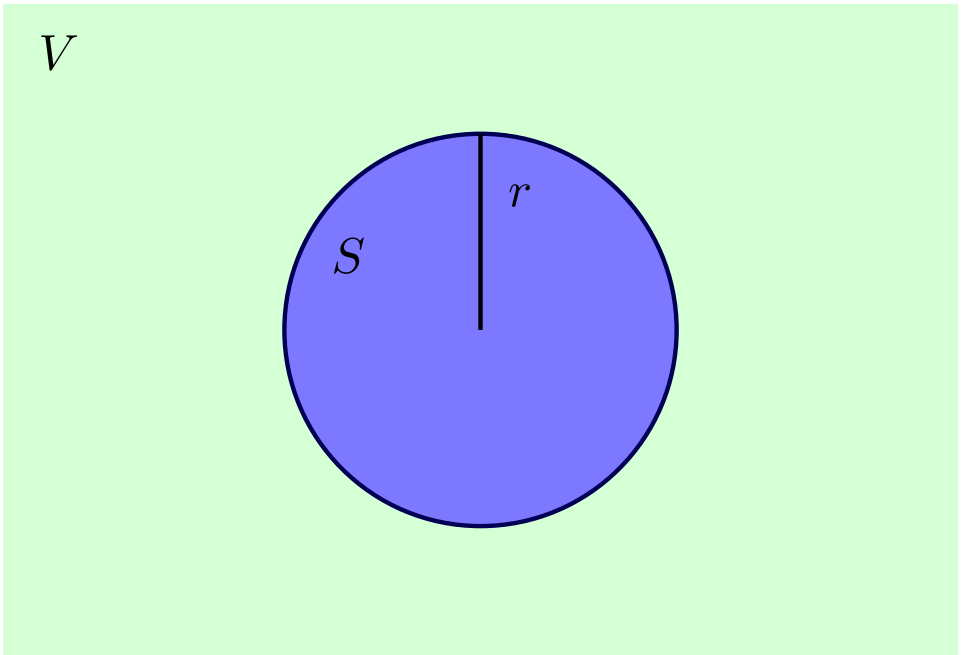


Melting Point Depression

- Small particles also have reduced melting point!

$$\Delta G_{SL}(T)\frac{4}{3}\pi r^3 = (\gamma_{SV} - \gamma_{LV})\,4\pi r^2$$

- In practice these phenomenological theories show deviations at the extreme nanoscale

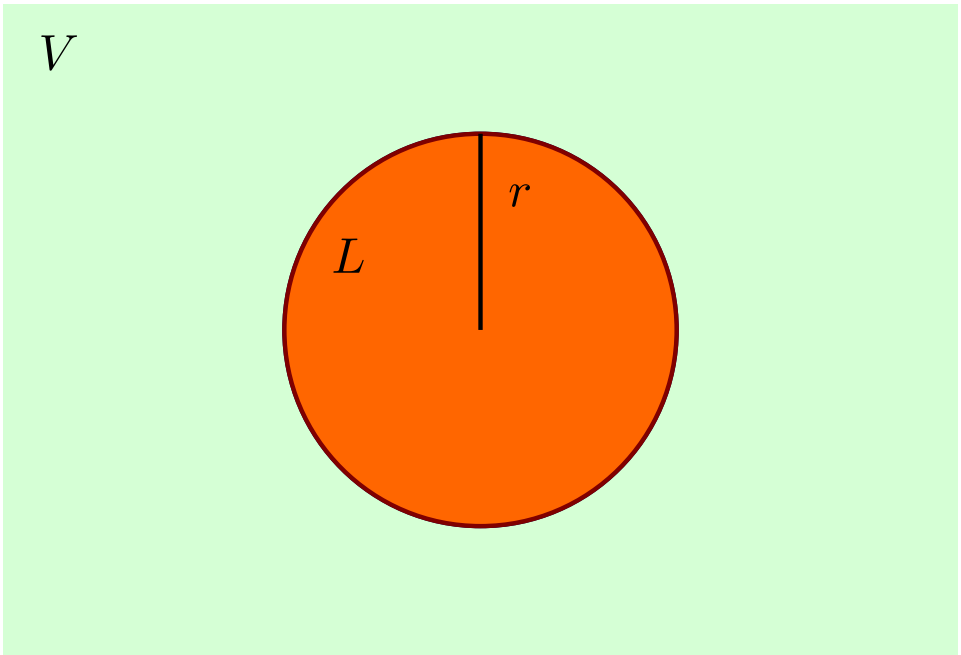


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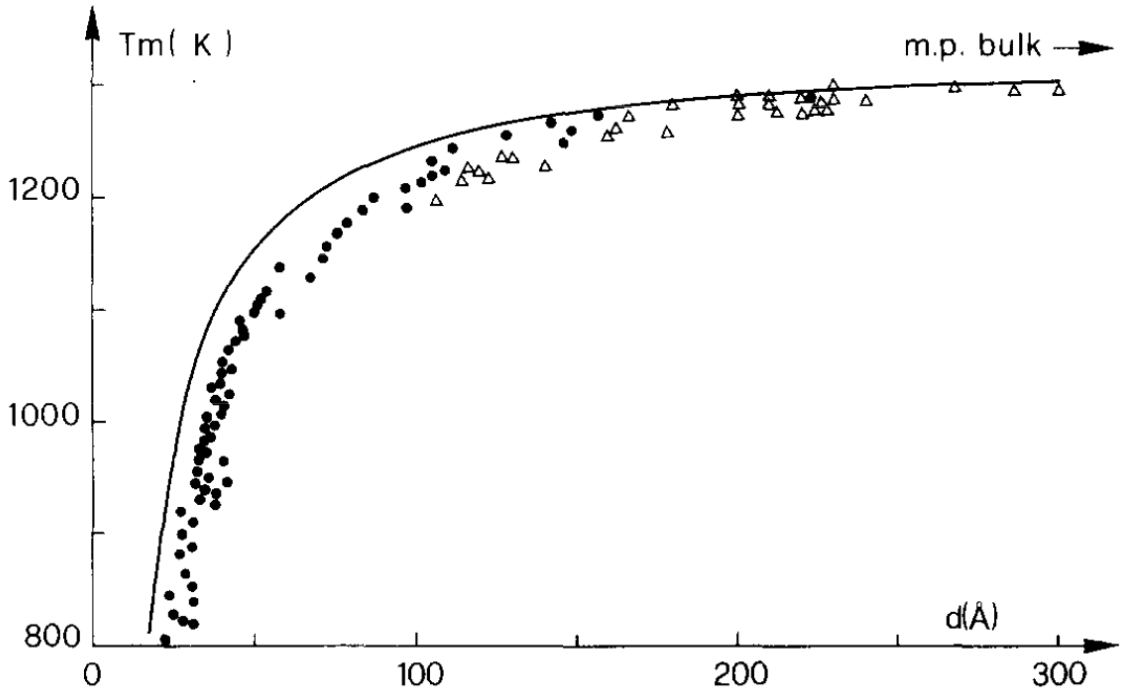


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$$\frac{T}{T_{SL}} = 1 - \frac{3\left(\gamma_{SV} - \gamma_{LV}\right)}{\Delta H_{SL} r}$$

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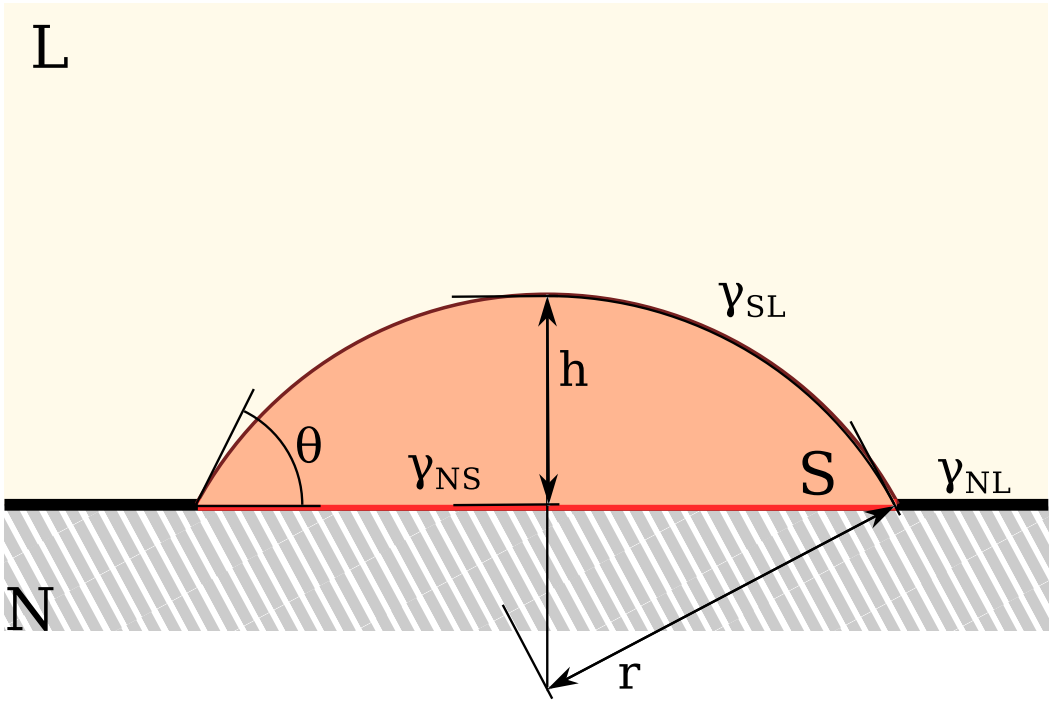
Heterogeneous Nucleation

- Nucleation can also (and most often does!) happen at interfaces
- The shape of the critical nucleus is determined by a combination of Young equation, and the balance between solid-liquid surface energy and bulk free energy of phase transition.
- It is easy to see that if the solid has some affinity for the nucleus, the free-energy barrier for this process will be lower than homogeneous nucleation



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