EPFL
École polytechnique fédérale de Lausanne

Institute of Materials - Institute of Bioengineering
sunmil.epfl.ch

SuNMiL
Supramolecular NanoMaterials and Interfaces Laboratory

Interfacial Phenomena
Lesson 5

MSE 304

Francesco Stellacci

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Key Topics in the Previous Class

$\tilde{\gamma}$ excess surface free energy $\rightarrow$ f_{ij} surface stress

$\tilde{\gamma}(hkl)$

$$\rightarrow \tilde{\gamma}_{12} = \tilde{\gamma}_1 + \tilde{\gamma}_2 - W_{12}$$

$$\tilde{\gamma}_{SL} - \tilde{\gamma}_{SV} + \tilde{\gamma}_{LV}\cos\theta = 0 \quad \text{Young's theorem}$$

$$\gamma_{LV}(1 + \cos\theta) = W_{SV/L} \quad \text{Young-Dupré equation}$$

Phase Equilibrium: a Key Summary

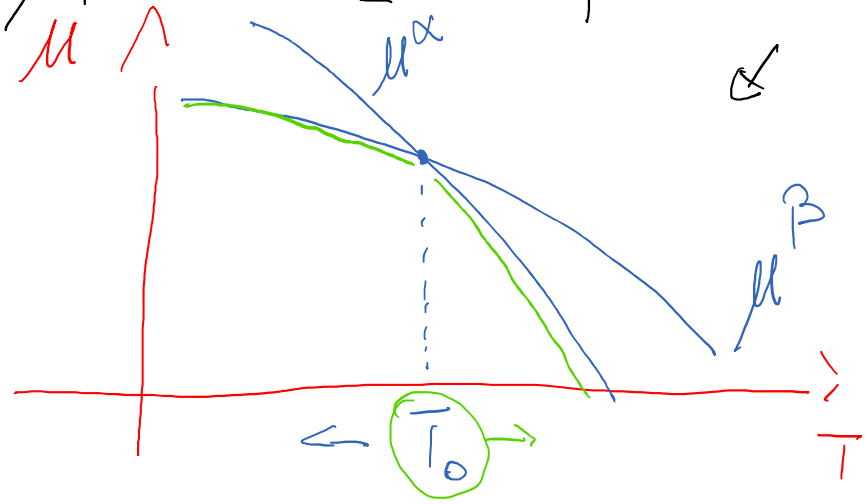
multi phase system $\alpha, \beta, \ldots$ $dG = 0$ @ a minimum

$d(G^\alpha - G^\beta) = 0$ $\quad G^\alpha = G^\beta$

$\left(\frac{\delta G}{\delta n_i}\right)_{T,P,n_{j\neq i}} = \mu_i$ chemical potential

$\mu_i^\alpha = \mu_i^\beta \quad \forall i \quad \forall \alpha, \beta$

One component system



α, β

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The Chemical Potential of a Phase of Finite Size

$$dG = V dp - S dT + \sum_{\alpha} \sum_{i} \mu_i^{\alpha} dn_i^{\alpha} + \sum_{\alpha} \gamma_{\alpha} dA_{\alpha} + \sum_{\alpha\beta} \gamma_{\alpha\beta} dA_{\alpha}$$

$dA_{\alpha} = -dA_{\beta}$

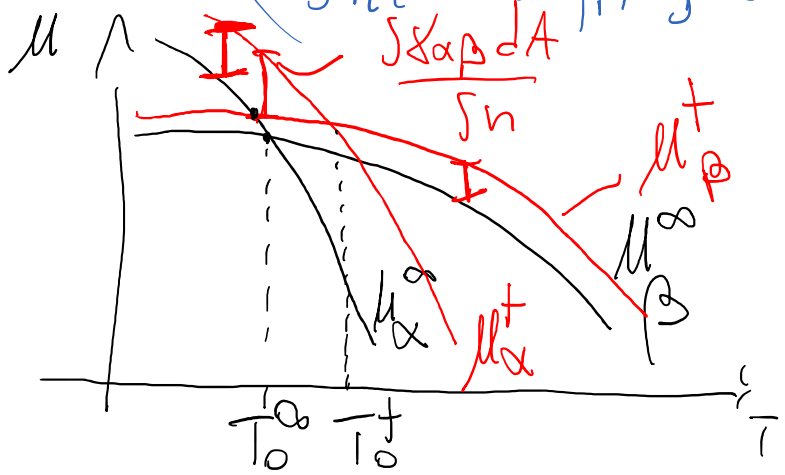
$\gamma_{\alpha} dA_{\alpha} + \gamma_{\beta} dA_{\beta}$

$(\gamma_{\alpha} - \gamma_{\beta}) dA_{\alpha} \Rightarrow \gamma_{\alpha\beta} dA_{\alpha}$

$$\mu_i^{\alpha} = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{j\neq i}}$$

one component

$$\mu_i^{\alpha} = \mu_i^{\infty} + \left(\frac{\partial \int \gamma_{\alpha\beta} dA_{\alpha}}{\partial n_i}\right)_{T,P,n_{j\neq i}}$$



$\frac{S}{V}$ ratio

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Size Dependence of a Generic Phase Transition

$dG = 0$

$0 = V^{\alpha} dp - S^{\alpha} dT + \mu^{\alpha} dn^{\alpha} + \gamma_{\alpha} dA_{\alpha} - [V^{\beta} dp - S^{\beta} dT - \mu^{\beta} dn^{\beta} - \gamma^{\beta} dA_{\beta}]$

1 component

2 phase

$\mu^{\alpha} = \mu^{\beta}$

$dn^{\alpha} = -dn^{\beta}$

$S^{\alpha} dT = -S^{\beta} dT$

$$(V^{\alpha} - V^{\beta}) dp = \gamma_{\alpha\beta} dA_{\alpha}$$

$$dV\, dp = \gamma_{\alpha\beta} dA_{\alpha} \Rightarrow dp = \gamma_{\alpha\beta} \left(\frac{dA}{dV}\right) = *$$

$$* = \gamma_{\alpha\beta} \frac{d(4\pi r^2)}{d\left(\frac{4}{3}\pi r^3\right)} = \gamma_{\alpha\beta} \frac{2}{r} \Rightarrow \boxed{dp = \frac{2\gamma_{\alpha\beta}}{r}}$$

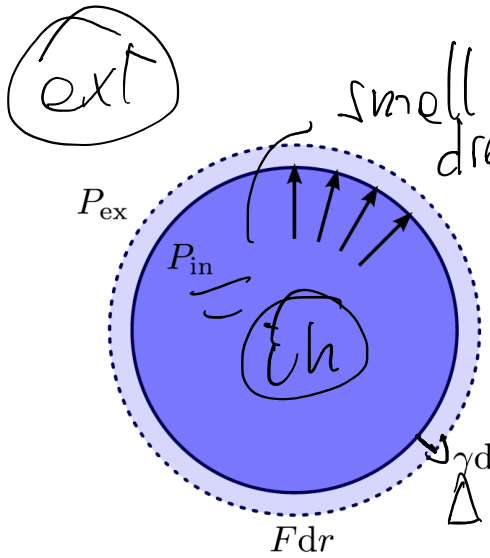
α, β

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→0.001atm; 1nm→1000atm!

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

$A = 4\pi r^2$



$F dr = p \cdot dA = \gamma dA$

$$\frac{F}{A} = \frac{p \cdot \frac{dA}{dr}}{A} = \frac{p}{4\pi r^2} \cdot \frac{8\pi r\, dr}{dr} =$$

$$\Delta p = \frac{F}{A} = \frac{2p}{r} = \frac{2\gamma_{LV}}{r} = \frac{2\gamma_{\alpha\beta}}{r}$$

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Kelvin's Equation

$$dp = d\left(\frac{2\gamma_{LV}}{r}\right)$$

$$dG_{int} = dG_{ex}$$

$$V_{int}\, dp_{in} = V_{ex}\, dp_{ex}$$

$$\rightarrow dp_{in} = -\frac{V_{ex}}{V_{int}}\, dp_{ext}$$

$$d\left(p_{ex} - p_{int}\right) = d\left(\frac{2\gamma_{LV}}{r}\right)$$

$V_{ext} \gg V_{int}$ ext $\Rightarrow$ Vapor, int $\Rightarrow$ Liquid

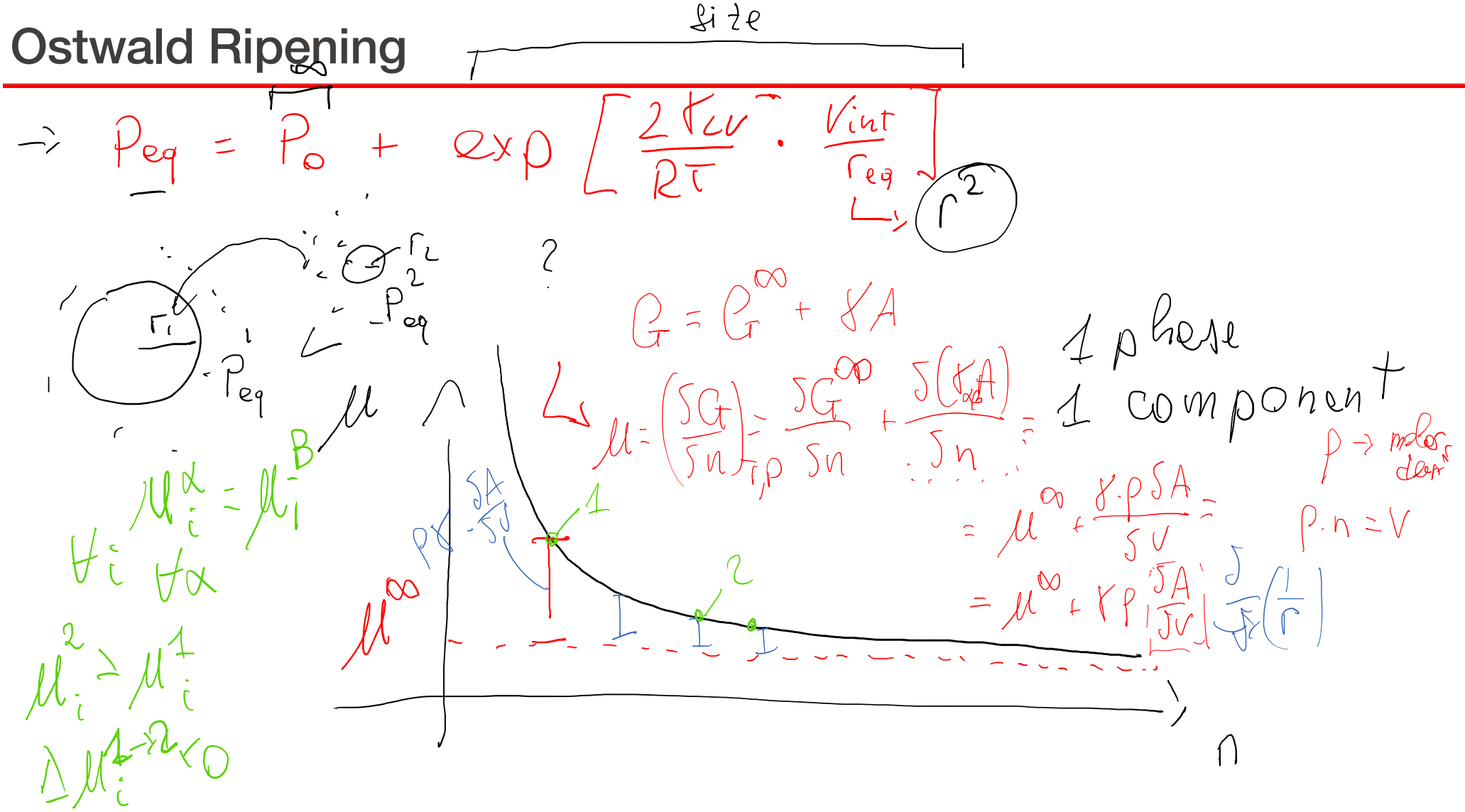
$$dp_{ex}\left(1 + \frac{V_{ext}}{V_{int}}\right) = d\left(\frac{2\gamma_{LV}}{r}\right)$$

$$V_{ext} = \frac{RT}{p_{ext}}$$

$$\left(V_{int} + V_{ext}\right) dp_{ex} = 2\gamma_{LV} V_{int}\, d\left(\frac{1}{r}\right) \Rightarrow \int_{p_0}^{p_{eq}} \frac{dp_{ex}}{p_{ex}} = \frac{2\gamma_{LV} \cdot V_{int}}{RT} \int_{\infty}^{r_{eq}} d\left(\frac{1}{r}\right)$$

$$\ln\frac{p_{eq}}{p_0} = \frac{2\gamma_{LV} V_{int}}{RT}\left(\frac{1}{r_{eq}}\right)$$

Ostwald Ripening



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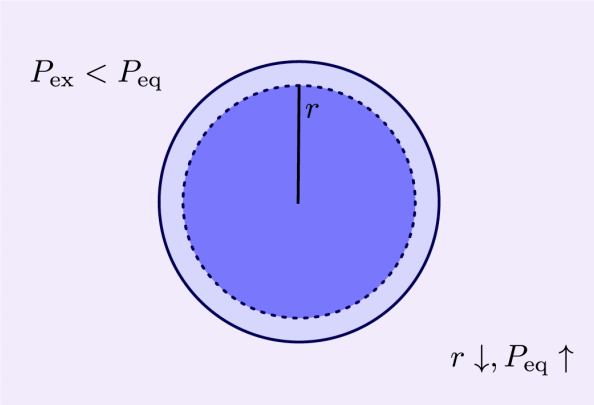
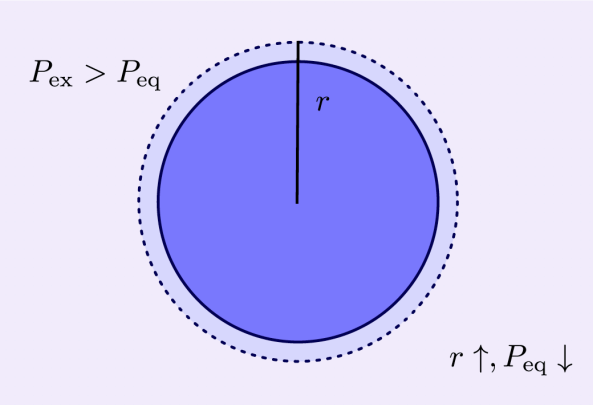
Stability of a Droplet

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

- Every droplet in equilibrium with a constant-pressure vapor reservoir is in unstable equilibrium

?





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Nucleation and Growth: Outline

1) Simple TD

2) equilibrium approach

3) liquid solution approach

Nucleation and Growth: First Approach

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{j\neq i}}$$

$$G_\alpha = \left(\frac{\partial G}{\partial V^\alpha}\right)_{T,P,V^{\beta\neq\alpha}}$$

$$\Delta G(r) = \frac{4}{3}\pi r^3 \Delta \bar{G}_{SL} + 4\pi r^2 \gamma_{SL}$$

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

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

ΔG_{SL}

$\rho = \frac{n}{V}$

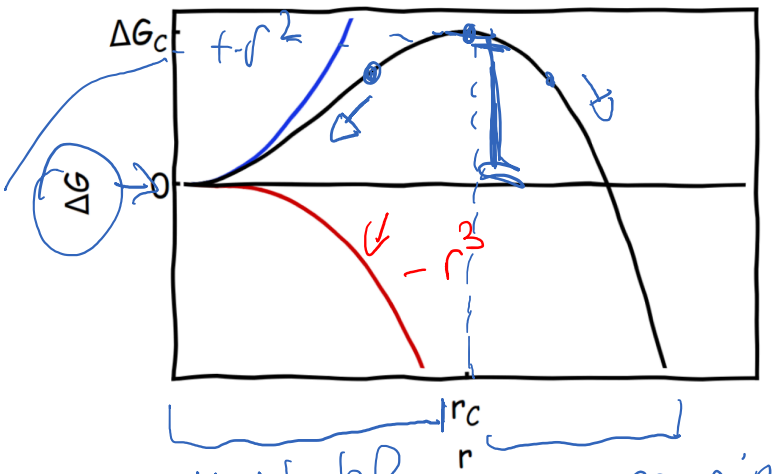
$\alpha = 1$, $\beta = 3$

$\mu^\alpha = \mu^\beta$

1 component

$N\mu = N\mu^\infty + N^{surface}\mu$

$\Delta \bar{G}_{\alpha\beta} = \mu_\alpha^\infty - \mu_\beta^\infty$



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Nucleation and Growth: Second Approach

$$\Delta G_f^0 = (\mu_l - \mu_v)n$$

Where

μ_l *is the liquid chemical potential and* μ_v *is the solid chemical potential*

Assuming an ideal vapor we can write

$$(\mu_l - \mu_v)n = -nk_BT \ln S$$

Where k_B is the Boltzmann constant and S, the supersaturation parameter, is the ratio between the vapor pressure P and the saturation equilibrium vapor pressure P_e

$$S = P/P_e$$

Nucleation and Growth: Second Approach

This contribution will always be favorable to cluster formation for the materials we are interested in.
At the same time when generating a drop we always are generating a new surface. The surface free energy will always be a destabilizing factor.
It can be shown that this energy is:

$$\gamma_s^0 = \gamma_{LV} * Area = \gamma_{LV} * 4\pi\left(\frac{3v}{4\pi}\right)^{\frac{2}{3}} n^{\frac{2}{3}}$$

$\gamma_{LV} \cdot A_{LV}$

$\gamma_{LV} = \text{interfacial energy per unit area}$

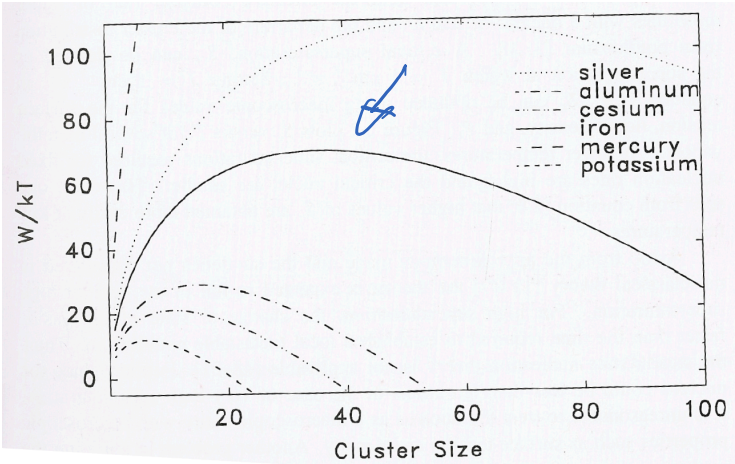
$v = \text{volume of an atom}$

$n = \text{number of atoms}$

It should be obvious by looking at the equation just written that the total free energy of formation of for this droplet of material depends on the number of atoms that compose the droplet. In fact:

$$\Delta G = W(n) = -nk_B T \ln S + \gamma_{LV} 4\pi\left(\frac{3v}{4\pi}\right)^{\frac{2}{3}} n^{\frac{2}{3}}$$

The free energy can be seen as the reversible work made to form a cluster of n atoms.



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Nucleation and Growth: Second Approach

The smallest cluster size (n^*) at which this happens is given by solving the equation

$$\frac{\partial W}{\partial n} = 0$$

It can be shown that:

$$n^* = \frac{32\pi\sigma^3 v^2}{3\left(k_B T \ln S\right)^3}$$

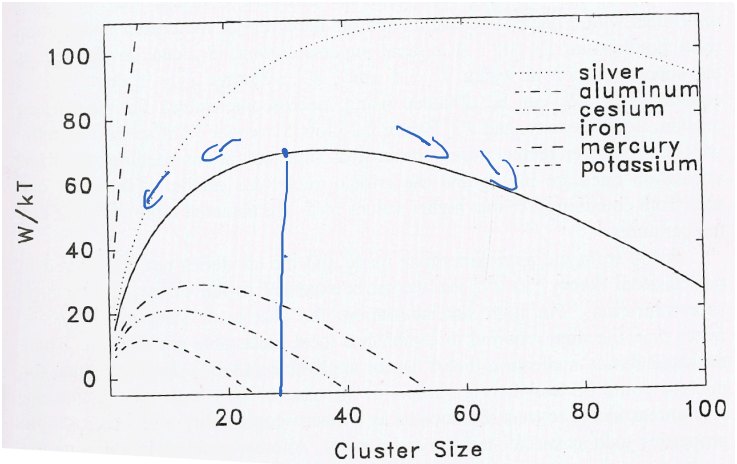
$$r^* = \frac{2\sigma v}{kT \ln S}$$

The value $W(n^*)$ is often referred as the barrier height for nucleation or nucleation energy.

Its value is:

$$W(n^*) = \frac{16\pi\sigma^3 v^2}{3\left(k_B T \ln S\right)^2}$$

find similarities with 1 treatment



Nucleation and Growth: Third Approach, Self-Assembly

Let's consider a solution containing molecules that form aggregates of various sizes. We will identify each aggregate with a number N that indicated the number of molecule that are in that aggregate. 1= single molecule, 2= dimer, 3= trimer, etc.

We can then define X_N as the dimensionless molar fraction of molecules that are in solution as the N^{th} aggregate. (Molar fraction = moles of X in 1L/ total moles in 1L, for aqueous solution take molar concentration and divide by 55.5)

NOTE that $X_N \leq 1$ by definition

$$0 \leq X_N = \frac{N}{T_{mole}} \leq 1$$

$$0 \leq \frac{N}{T_{mole}} \leq 1$$

molecules in solution

X_1 aggregate of size 1

X_2 " " " 2

If we call C as the total molar fraction at any time the following equation has to be verified:

$$C = X_1 + X_2 + X_3 + \quad + X_N = \sum_{N=1}^{\infty} X_N = \sum_{N=1}^{\infty} X_N$$

$$X_N + X_S = 1$$

The molar fraction (i.e. the concentration) of the N^{th} aggregate will be X_N/N

For this solution to be in equilibrium the condition to be met is that the chemical potential of each species present in solution has to be identical.

$$\mu_i = \mu_i^0 + kT \ln X_i$$

This equilibrium condition will determine the concentration of the various species

$$\mu = \mu_N^0 + \frac{kT}{N}\ln\left(\frac{X_N}{N}\right) = \cos\tan t = \mu_1^0 + kT\ln(X_1)$$

μ_i^N μ_i^1

$$\mu_i^\alpha = \mu_i^\beta \quad \forall\alpha \; \forall i$$

Nucleation and Growth: Third Approach, Self-Assembly

Our main equation is:

$$\mu_N^0 + \frac{kT}{N}\ln\left(\frac{X_N}{N}\right) = \mu_1^0 + kT\ln(X_1)$$

If we rewrite it in more general terms

$$\mu_N^0 + \frac{kT}{N}\ln\left(\frac{X_N}{N}\right) = \mu_M^0 + \frac{kT}{M}\ln\left(\frac{X_M}{M}\right)$$

and solve for X_N

We find

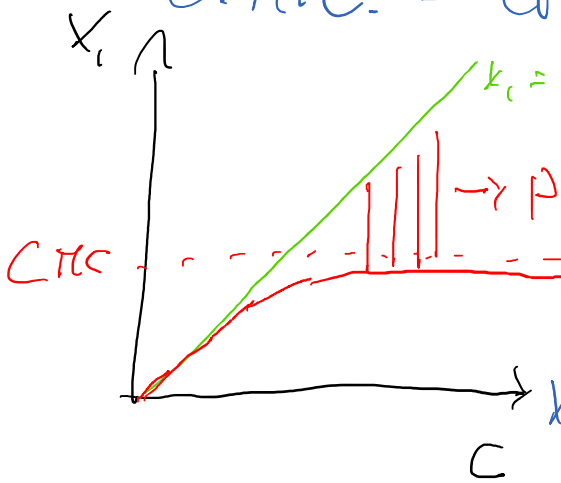
$$X_N = N\left\{\frac{X_M}{M}\exp\left[\frac{M\left(\mu_M^0 - \mu_N^0\right)}{kT}\right]\right\}^{\frac{N}{M}}$$

That gives the concentration of molecules in the N^{th} aggregate as a function of the concentration of molecule in the M^{th} aggregate.

In particular we can rewrite this for M=1

$$X_N = N\left\{X_1\exp\left[\frac{\left(\mu_1^0 - \mu_N^0\right)}{kT}\right]\right\}^N$$

C.M.C. = critical micelle concentration



$$X_i \exp\frac{(\mu_i^0 - \mu_N^0)}{KT} \leq 1$$

$$X_N = f(X_1)$$

$$X_1 \leq \exp\left(-\frac{\mu_1^0 - \mu_N^0}{KT}\right) \equiv C.M.C.$$

Nucleation and Growth: Third Approach, Self-Assembly

$$X_N = N\left\{X_1 \exp\left[\frac{\left(\mu_1^0 - \mu_N^0\right)}{kT}\right]\right\}^N$$

There is one necessary condition for the formation of aggregates: μ_N^0 has to change as a function of N. If that doesn't happen

$$X_N = NX_1^N$$

Since $X_1<1$, $X_N<<1$

Let's look now at a chain of N molecules in which the bond energy is αkT the total free energy of such a molecule will be $N\mu_N^0$

Thus

$$N\mu_N^0 = -(N-1)\alpha kT$$

$$\mu_N^0 = -\left(1-\frac{1}{N}\right)\alpha kT = \mu_\infty^0 + \frac{\alpha kT}{N}$$

In this case μ_N^0 decreases with N and converges asymptotically to the bulk value.

It can be shown that for a disc the equation becomes:

$$\mu_N^0 = \mu_\infty^0 + \frac{\alpha kT}{N^{\frac{1}{2}}}$$

2D

For a sphere:

$$\mu_N^0 = \mu_\infty^0 + \frac{\alpha kT}{N^{\frac{1}{3}}}$$

3D

Nucleation and Growth: Third Approach, Self-Assembly

More in general we can write:

$$\mu_N^0 = \mu_\infty^0 + \frac{\alpha kT}{N^p}$$

If we now substitute this equation in

$$X_N = N\left\{X_1 \exp\left[\frac{\left(\mu_1^0 - \mu_N^0\right)}{kT}\right]\right\}^N$$

we get

$$X_N = N\left\{X_1 \exp\left[\frac{\left(\mu_1^0 - \mu_N^0\right)}{kT}\right]\right\}^N = N\left\{X_1 \exp\left[\alpha\left(1 - \frac{1}{N^p}\right)\right]\right\}^N = N\left\{X_1 \exp[\alpha]\right\}^N \exp-\left[\alpha N^{1-p}\right]$$

But X_N cannot exceed 1 thus there is a concentration of X_1 called *critical micelle concentration* (CMC) at which X_1 cannot grow more and larger aggregates have to form. Such concentration is

$$\left(X_1\right)_{crit} = CMC \approx \exp-\left[\frac{\left(\mu_1^0 - \mu_N^0\right)}{kT}\right]$$

At the critical concentration:

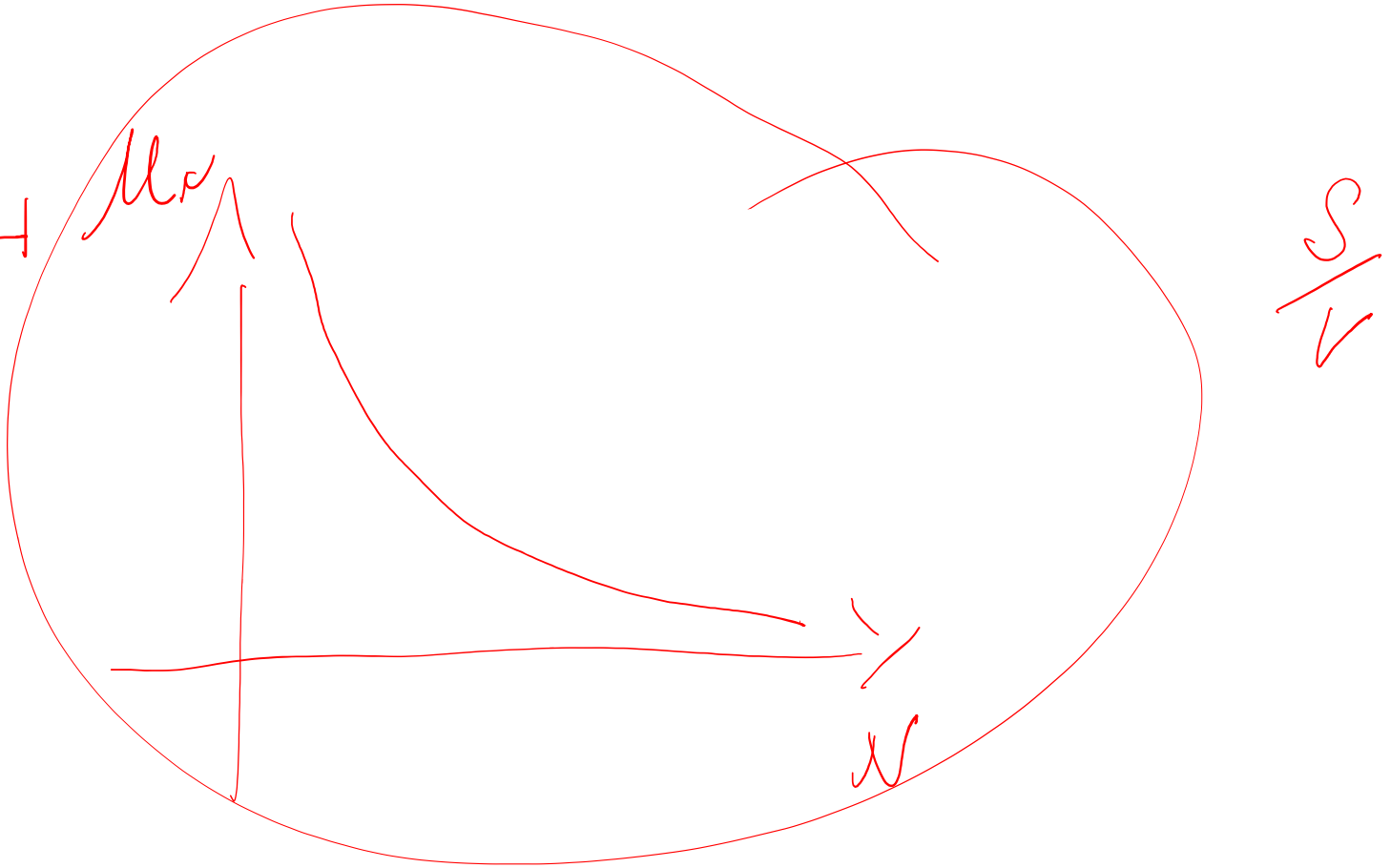
$$X_N = N\left\{X_1^{\,crit} \exp[\alpha]\right\}^N \exp-\left[\alpha N^{1-p}\right]$$

Nucleation and Growth: Third Approach, Self-Assembly

$$(X_1)_{crit} = CMC \approx \exp - \left[\frac{(\mu_1^0 - \mu_N^0)}{kT} \right]$$

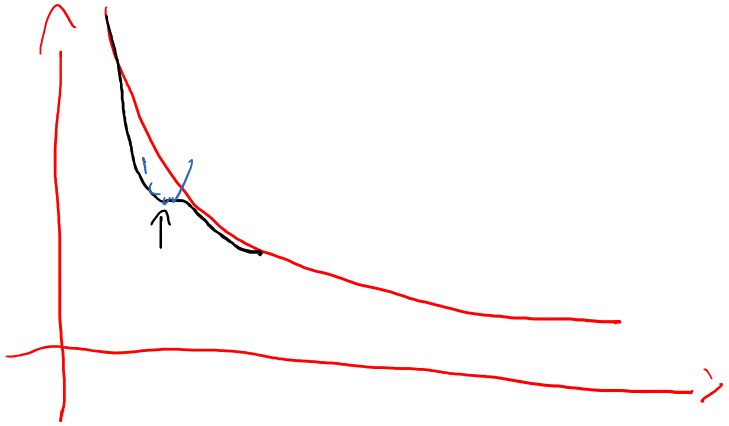
At the critical concentration:

$$X_N = N \{ X_1^{crit} \exp[\alpha] \}^N \exp - [\alpha N^{1-p}]$$



Nucleation and Growth: Third Approach, Self-Assembly

$$X_N = N\left\{X_1 \exp\left[\frac{\left(\mu_1^0 - \mu_N^0\right)}{kT}\right]\right\}^N$$



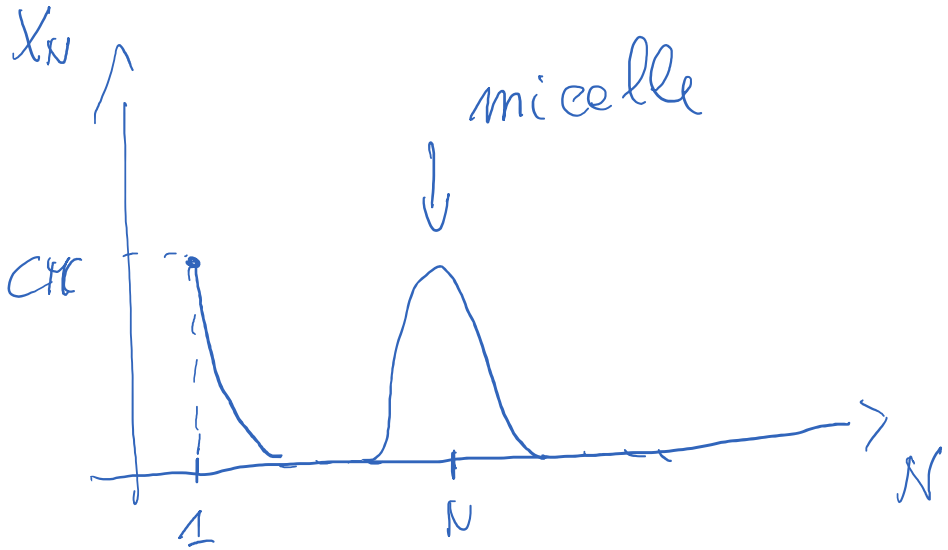
In that can we can expand around that minimum:

$$\mu_N^0 - \mu_M^0 = \Lambda(\Delta N)^2$$

Then:

$$X_N = N\left\{\frac{X_M}{M}\exp\left[\frac{M\left(\mu_M^0 - \mu_N^0\right)}{kT}\right]\right\}^{\frac{N}{M}} = N\left\{\frac{X_M}{M}\exp\left[\frac{M\Lambda(\Delta N)^2}{kT}\right]\right\}^{\frac{N}{M}}$$

Nearly a Gauss



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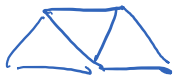
Nucleation and Growth: A Special Case

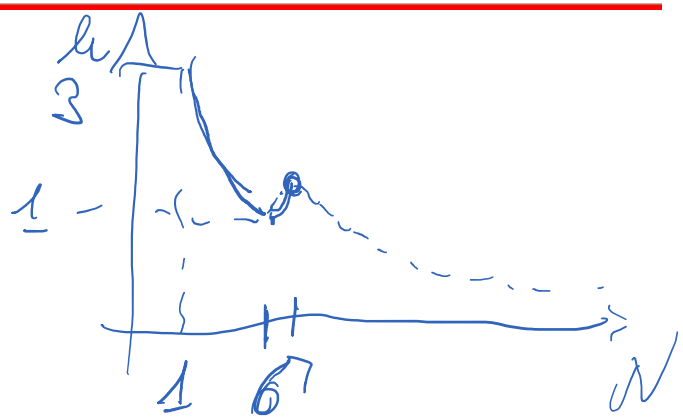
$Y = \Gamma_{12} \cdot l \cdot 3$

$\triangle \quad 2 \cdot Y = 6 \cdot \Gamma_{12} l$

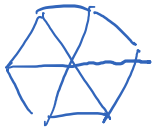
$4\Gamma_{12} l$



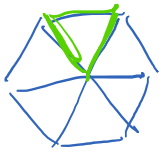
$5\Gamma_{12} l$



MAGIC NUMBER CLUSTER

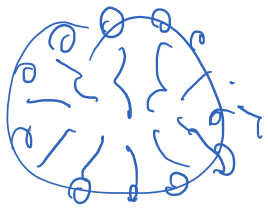


$6\Gamma_{12} l \rightarrow$ pos ▽ $1 \cdot \Gamma_{12} l$



$9\Gamma_{12} l$

$\frac{9}{7} = 1.\ldots$

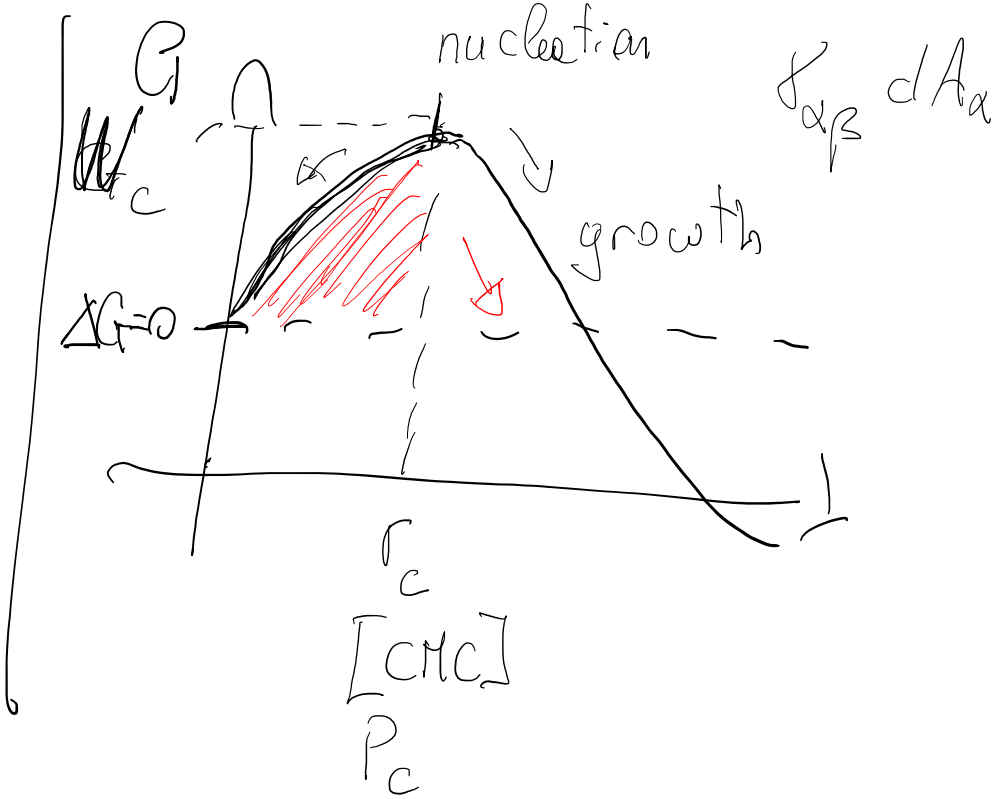


Summary - Nucleation and Growth

1) Simple TD

2) variable p

3) variable c



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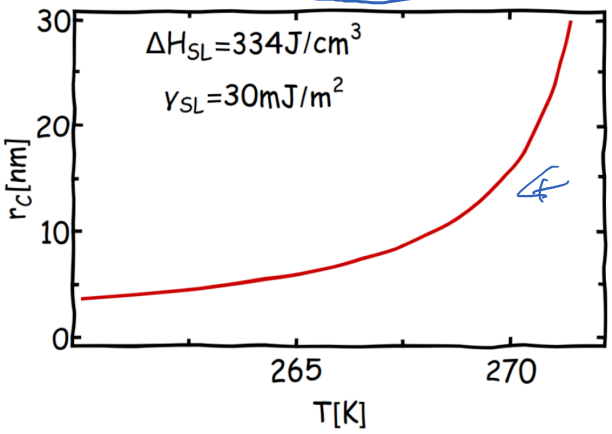
Nucleation Rate

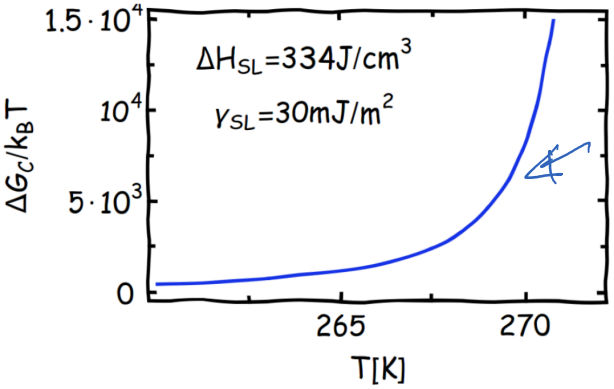
- Temperature dependence of $\Delta G_{SL}(T) = \Delta H_{SL} - T\Delta S_{SL}$

$$\Delta G_{SL}(T_{SL}) = 0 \longrightarrow \Delta S_{SL} = \frac{\Delta H_{SL}}{T_{SL}} \qquad \Delta G_{SL}(T) = \Delta H_{SL}(1 - T/T_{SL})$$

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

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





$$\Delta G_{SL}(T_{SL}^{\infty}) = 0$$

$$\Delta \bar{H}_{SL} = T\Delta \bar{S}_{SL} \simeq 0$$

$$\Delta \bar{S}_{SL} = \frac{\Delta \bar{H}_{SL}}{T}$$

$$\Delta G_{SL}(T) = \Delta \bar{H}_{SL}\left(1 - \frac{T}{T_{SL}^{\infty}}\right)$$

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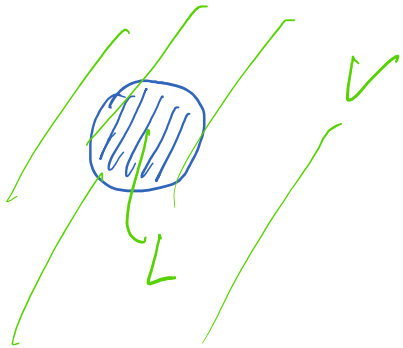
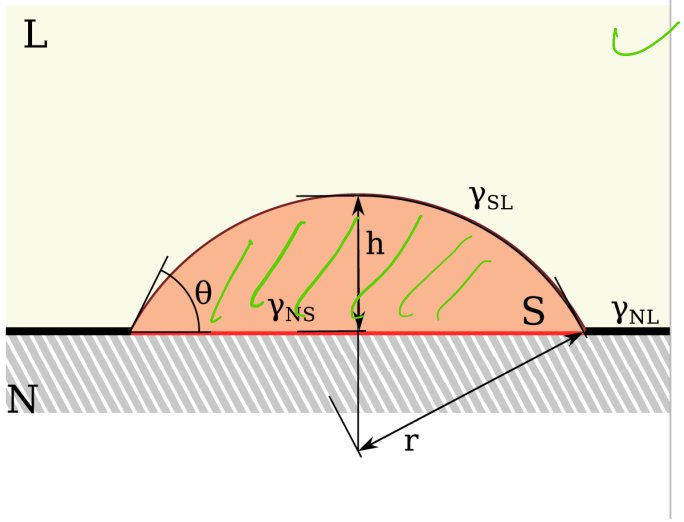
Heterogeneous Nucleation



- 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

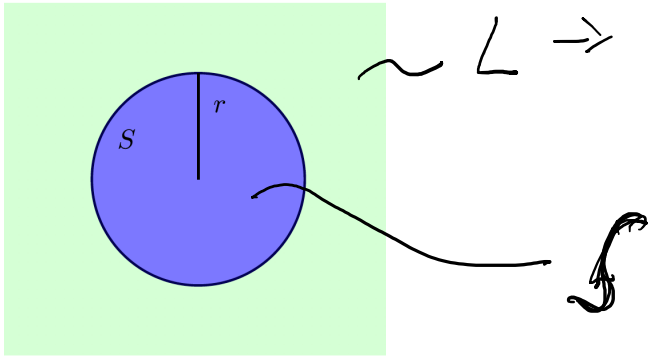


Melting Point Depression

$$\Delta G_{SL} = -\frac{4}{3}\pi r^3 \Delta G^{\infty}_{SL} + 4\pi r^2 \gamma_{SL} = -\frac{4}{3}\pi r^3 \left(1 - \frac{T}{T^{\infty}_{SL}}\right)\Delta H^{\infty}_{SL} + 4\pi r^2 \gamma_{SL} = 0$$

$$-\frac{r}{3}\Delta H^{\infty}_{SL}\left(1 - \frac{T}{T^{\infty}_{SL}}\right) = -\gamma_{SL} \Rightarrow 1 - \frac{T}{T^{\infty}_{SL}} = \frac{3\gamma_{SL}}{r\,\Delta H^{\infty}_{SL}}$$

$$\frac{T}{T^{\infty}_{SL}} = 1 - \frac{3\gamma_{SL}}{\Delta H^{\infty}_{SL} \cdot r}$$

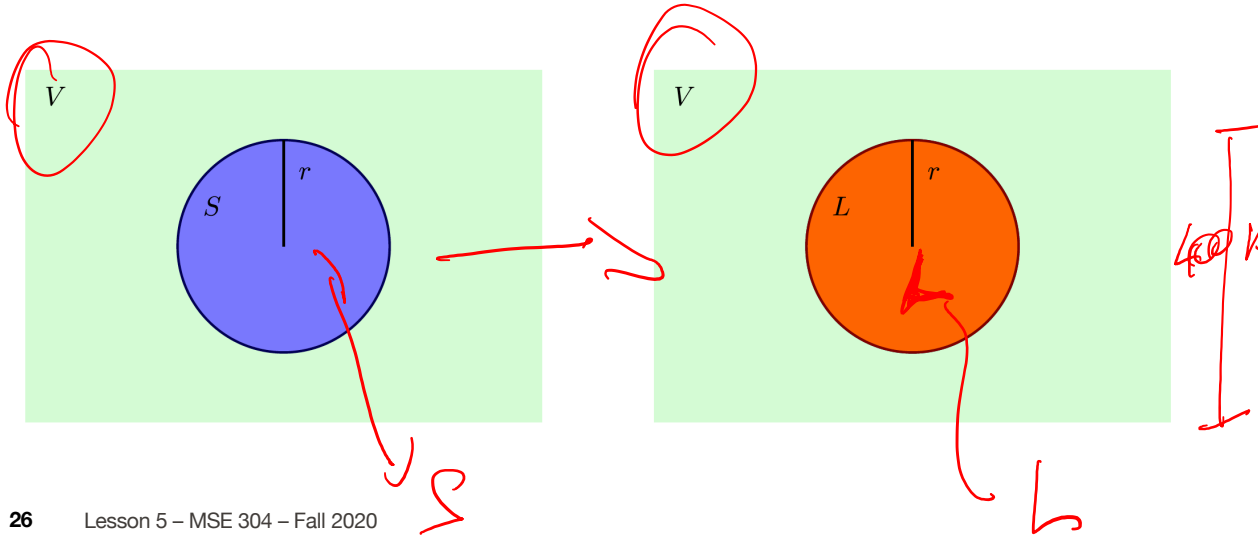


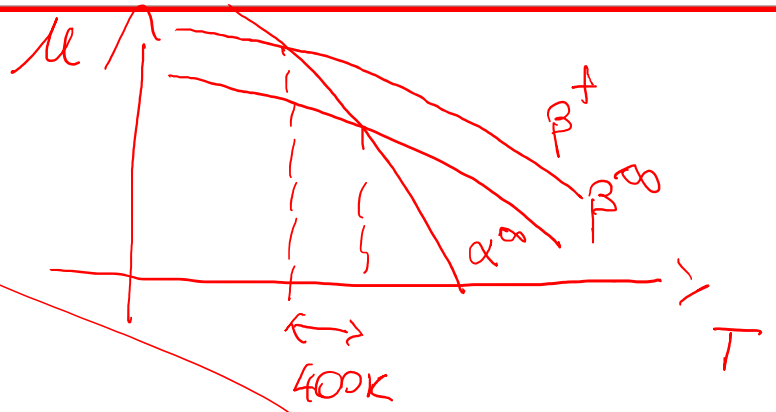
$\sim L \to \infty$

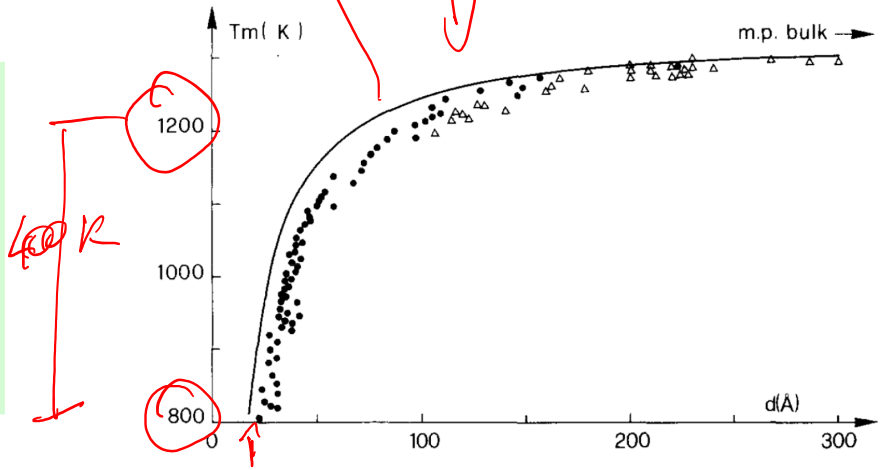
finite size

Melting Point Depression

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







Conclusions

Key materials science concept are a direct derivation of interfacial energy

→ nucleation and growth
→ melting point depression
→ micelles