MATE 664 Lecture 14

Introduction To Nucleation Theory

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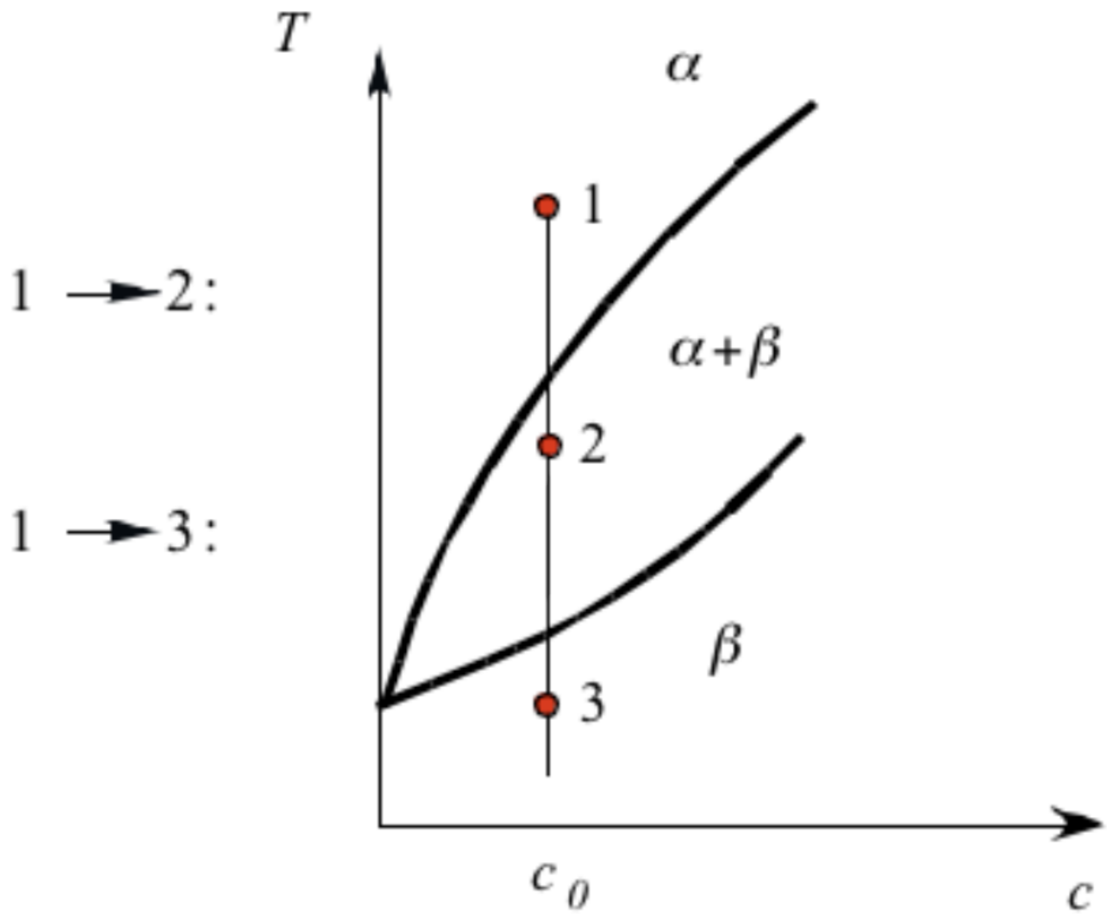
Learning outcomes

After this lecture, you will be able to:

- **Identify** the driving force when a system becomes supercooled or supersaturated
- **Describe** the difference between discontinuous and continuous phase transformations
- **Analyze** the nucleation free energy barrier ΔG_c
- **Describe** the role of surface and interfacial energy in nucleation
- **Describe** the pseudo-steady-state kinetic model for nucleation

Phase-diagram in non-equilibrium region

- How to induce phase transformation from a phase diagram?
- Going low in temperature –> (super)cooling

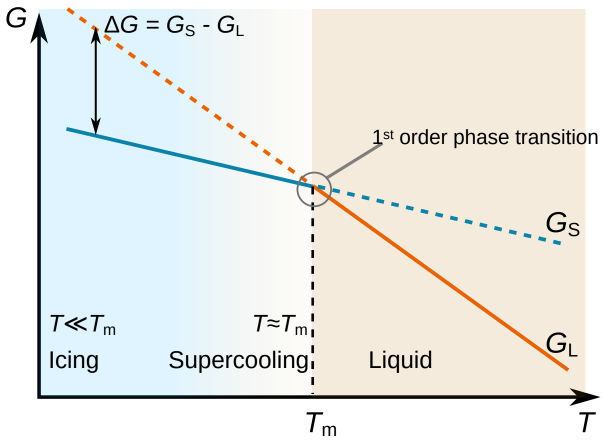


Transformation driving force in single-component phase diagram

- Cooling from liquid to solid provides driving force

$$\Delta G^{\text{L->S}} = \frac{\Delta H^{\text{L->S}}(T_m - T)}{T_m} < 0$$

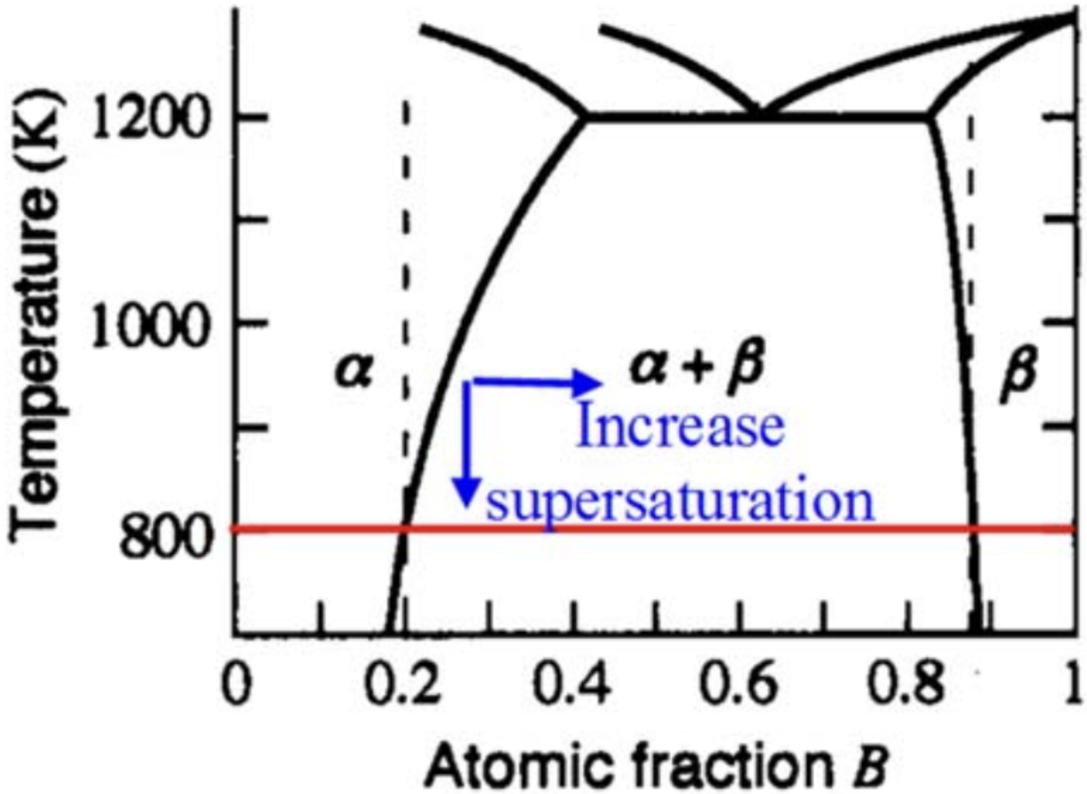
- Why doesn't ice form spontaneously?



Phase transformation in binary phase diagram ($T - X_B$)

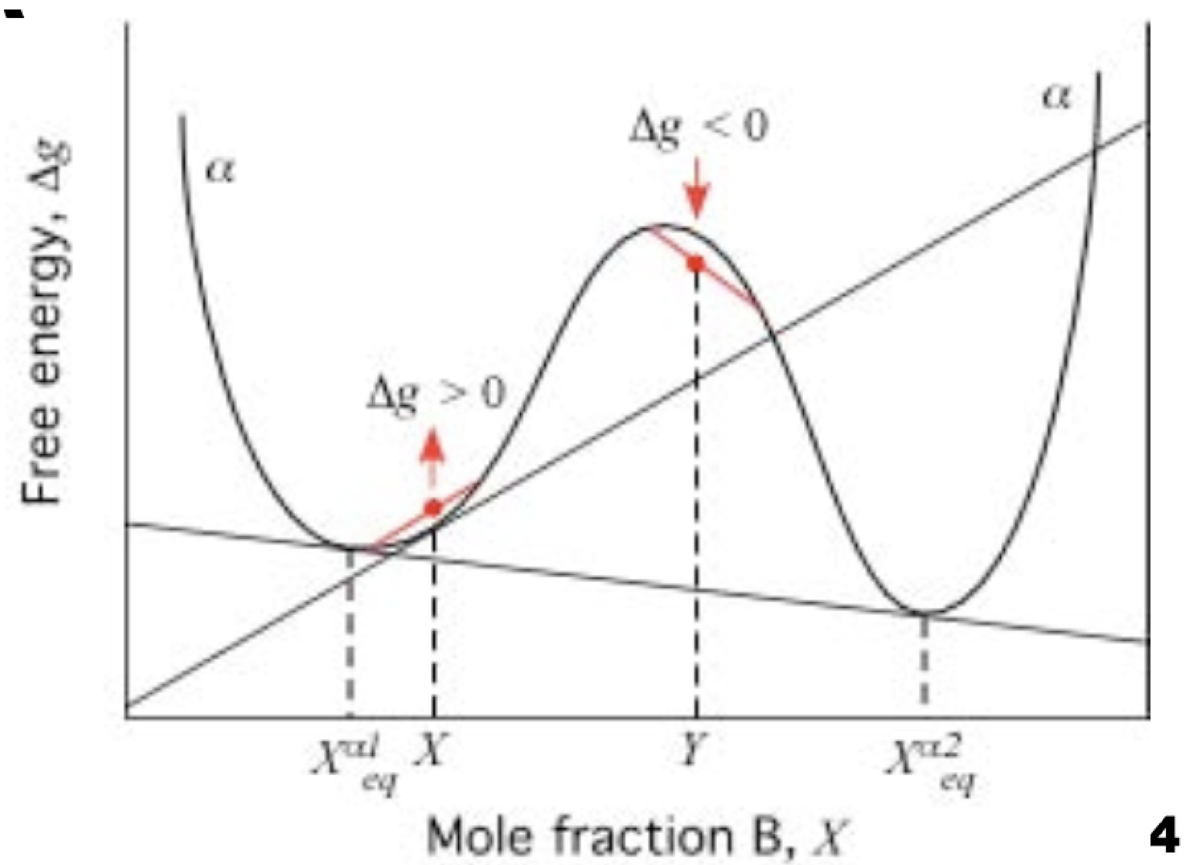
Ways to introduce driving force:

- (Super)saturation
- (Super)cooling



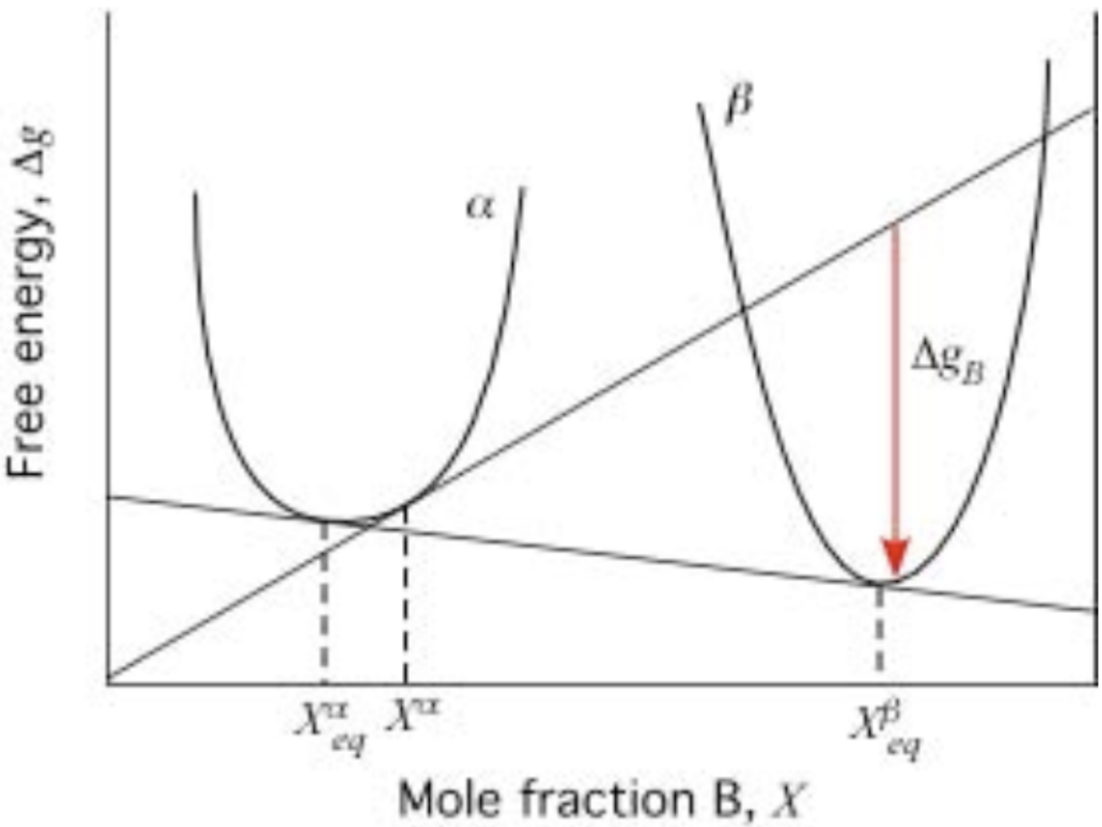
Phase transformation in binary phase diagram ($G - X_B$)

- Metastable regions in binary phase diagram (nucleation)
- Unstable regions (spinodal decomposition)



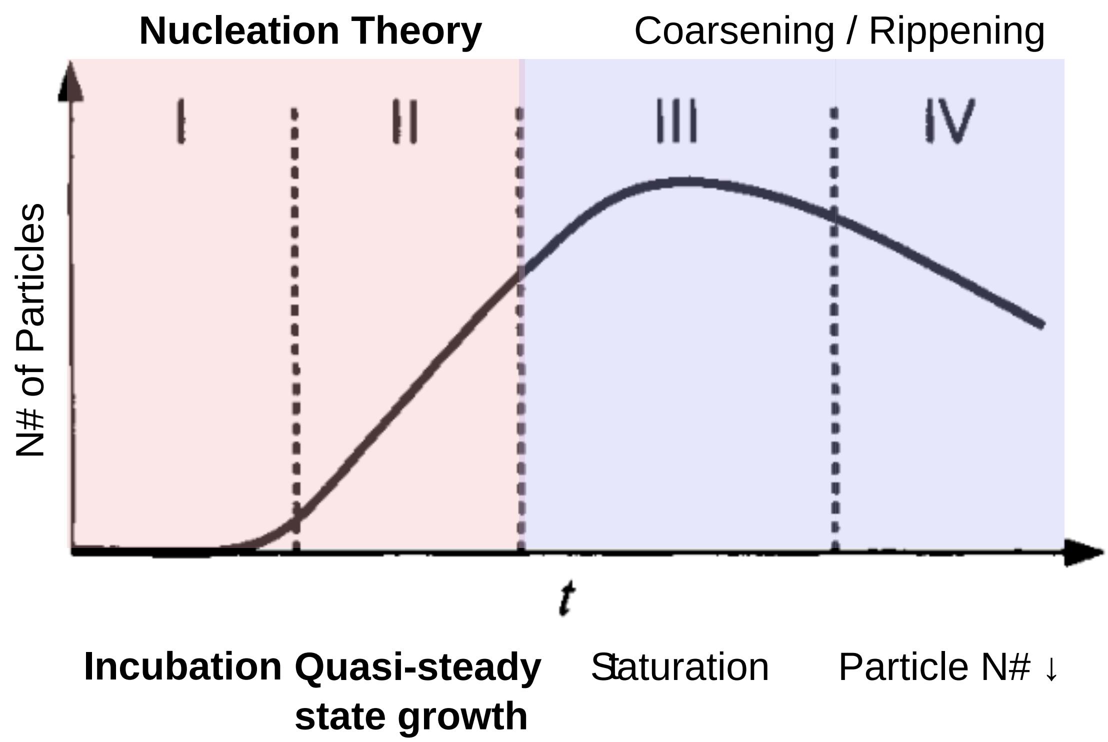
Phase transformation in binary phase diagram ($G - X_B$)

- Metastable regions in binary phase diagram
- *Tangent-to-line* method: driving force ΔG_B (molar)



Nucleation theory in a nutshell

- Crystal growth can be divided in 4 regions
- Nucleation theory deals with regions I and II (incubation & pseudo-steady-state)

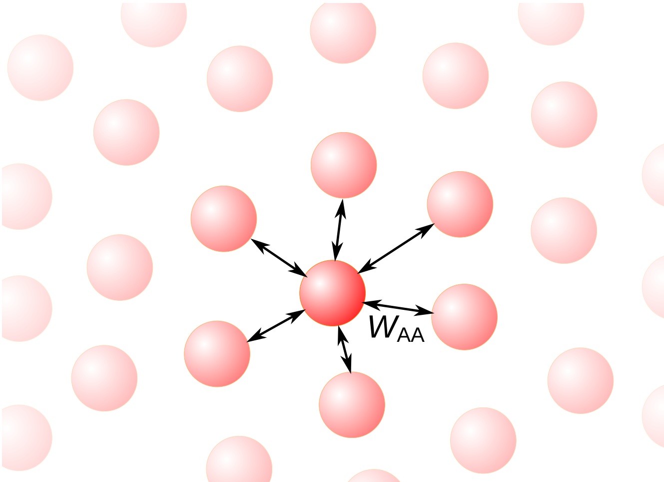


Introducing interfacial energy (1)

- Creating interfaces between different atoms causes energy to change!
- Surface energy γ_A (vacuum, unit J/m^2 or N/m)

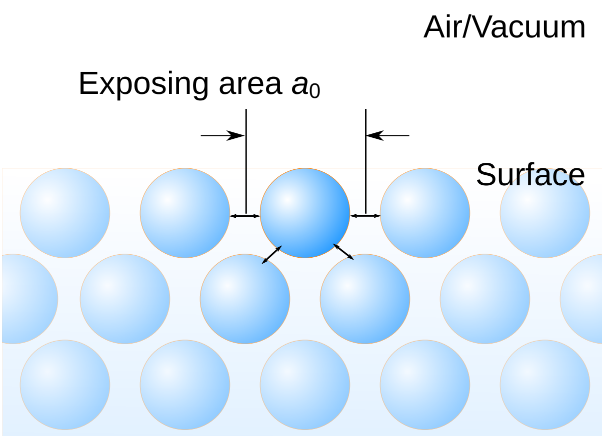
$$\gamma_A = \frac{1}{2a_0} w_{AA}(Z_s - Z_b)$$

Interatomic energy in bulk



Average number of neighbors: Z_b

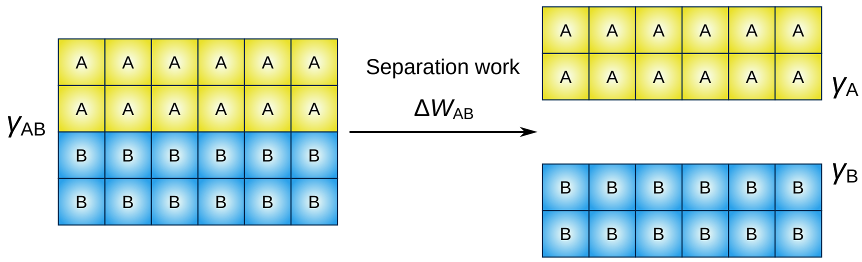
Creation of surface



Introducing interfacial energy (2)

- Interfacial energy γ_{AB} can be calculated using γ_A γ_B and ΔW_{AB}
- If adhesion between A and B are not strong, interface unlikely to form!

$$\gamma_{AB} = \gamma_A + \gamma_B - \Delta W_{AB}$$



Nucleation theory: overall nucleation free energy

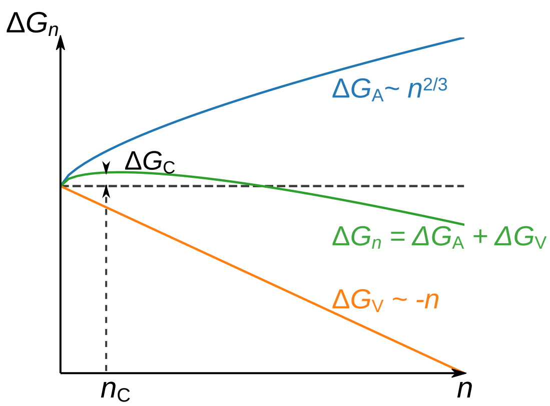
- Nucleation free energy has bulk and interface parts

$$\begin{aligned} \Delta G_N &= \Delta G_N^{\text{bulk}} + \Delta G_N^{\text{interfacial}} & (1) \\ &= n(\mu^\beta - \mu^\alpha) + \eta n^{2/3} \gamma_{\alpha\beta} & (2) \\ & & (3) \end{aligned}$$

- Shape factor $\eta = (36\pi)^{1/3} \Omega^{2/3}$

Different scaling between bulk & interfacial F.E.

- $\Delta G^{\text{bulk}} \propto -n^{1.0}$
- $\Delta G^{\text{interfacial}} \propto +n^{2/3}$
- Maximum ΔG_c at n_c.
- $\partial G_c / \partial n|_{n=n_c} = 0$



The critical nucleus size n_c

Classical homogeneous nucleation gives

- Critical nucleus size

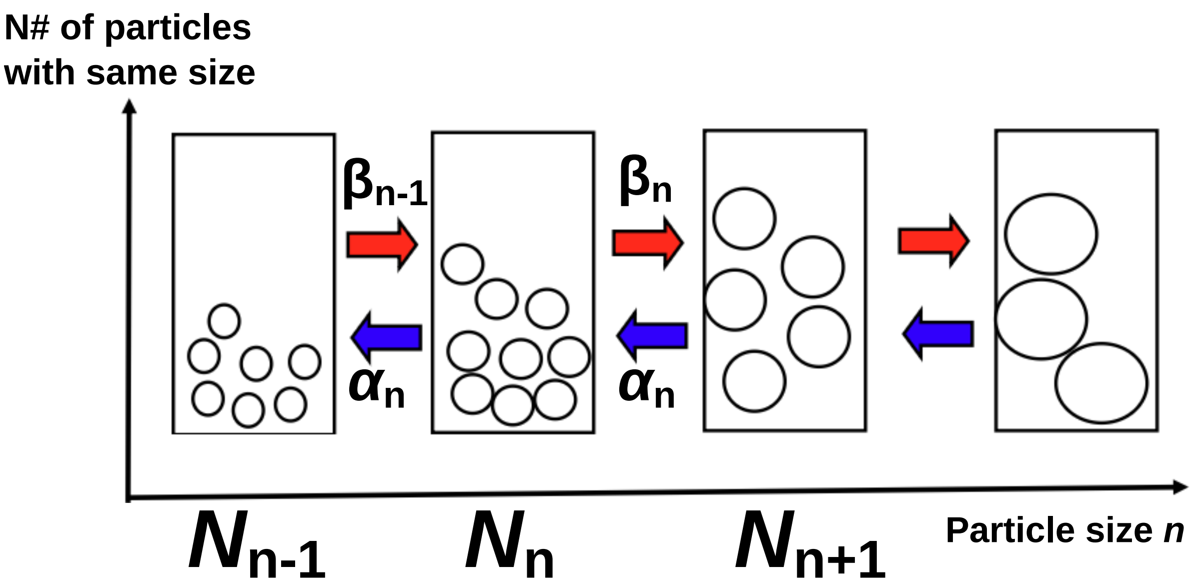
$$n_c = -\frac{8}{27}\left[\frac{\eta\gamma_{\alpha\beta}}{\mu_\beta - \mu_\alpha}\right]^3$$

- Nucleation free energy barrier

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

Pseudo-steady-state nucleation theory

- Consider the "quasi-diffusion" in n-landscape!



Q.S.S. governing equations

- "Quasi flux" of $n \to n+1$: J_n
- Can also model $\partial N_n/\partial t$ from assignment 2
- At equilibrium, detailed balance follows:

$$J_n(t) = \beta_n N_n(t) - \alpha_{n+1} N_{n+1}(t) = 0$$

- The nucleation rate at quasi-pseudo-state can be computed using a known N_n distribution

Q.S.S. assumptions

- In a constrained equilibrium system, N_n follows the Boltzmann distribution

$$\frac{N_n^{\text{ceq}}}{N_t} \approx \exp\left(-\frac{\Delta G_n}{k_B T}\right)$$

- Result:

$$J_n(t) = -\beta_n \left[\frac{\partial N_n}{\partial n} + \frac{N_n}{k_B T}\frac{\partial \Delta G_n}{\partial n}\right]$$

- Analog: diffusion in external potential

$$J = -L_{11}\nabla(\mu_1 + \phi) = -D_1\left(\frac{\partial c}{\partial x} + \frac{c}{k_B T}\frac{\partial \phi}{\partial x}\right)$$

Q.S.S. nucleation rate: final results

- Assuming the nucleation rate is determined by $J \approx J_{n_c}$
- Z is the Zeldovich factor (~0.1)

$$J = Z\beta_c n_t \exp(-\frac{\Delta G_c}{k_B T}) \tag{4}$$

$$Z = \sqrt{\frac{\Delta G_c}{3\pi n_c^3 k_B T}} \tag{5}$$

Implication of Q.S.S. nucleation rate

- Zeldovich factor 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

$$J = Z \beta_c n_t \exp(-\frac{\Delta G_c}{k_B T}) \tag{6}$$

$$Z = \sqrt{\frac{\Delta G_c}{3\pi n_c^3 k_B T}} \tag{7}$$

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

What to learn next

Is homogeneous nucleation the whole picture? Maybe not. Consider the following examples

Sugar crystal formation

- *Heterogeneous nucleation*

Snow formation

- *Diffusion-controlled growth*