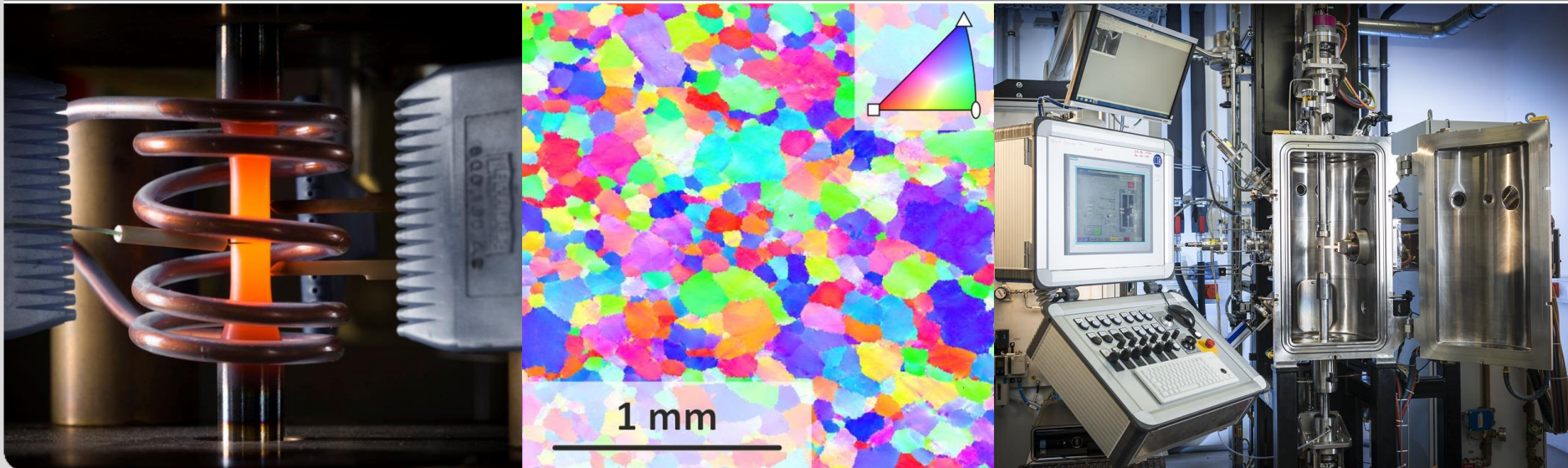


Phase Transformations

Lecture for “Mechanical Engineering” and “Materials Science and Engineering”
Dr.-Ing. Alexander Kauffmann (Bldg. 10.91, R. 375)

Version 23-01-12

Institute for Applied Materials (IAM-WK)

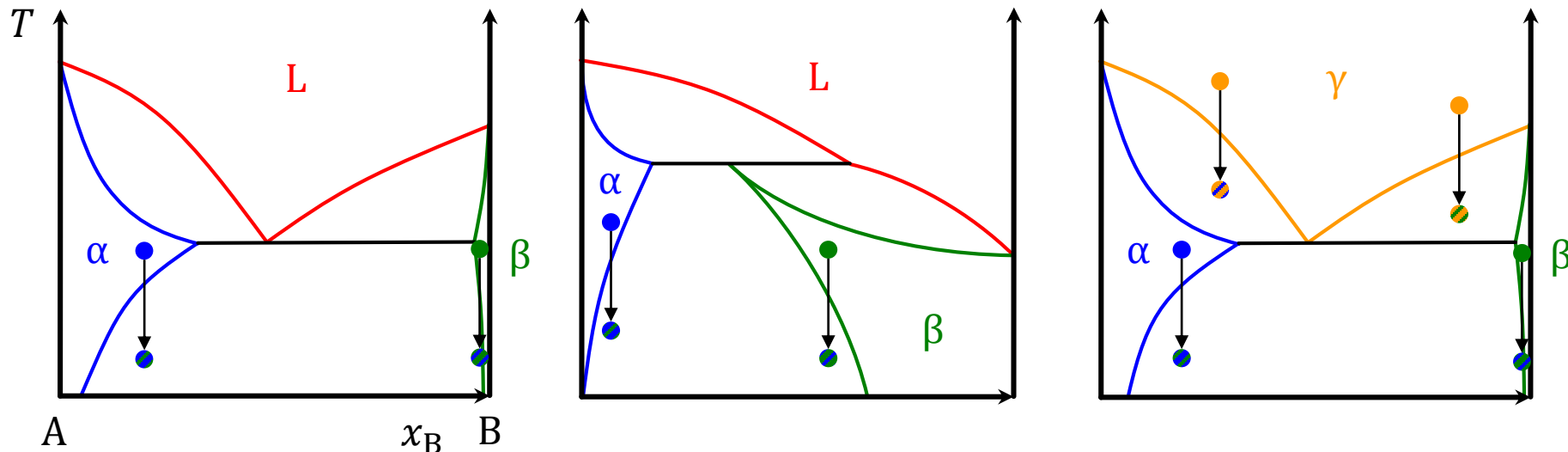


Topics

- Solid State Transformations in Multi-Component Systems
 - Overview
 - Long-range diffusion
 - Precipitation
 - Spinodal Decomposition (spontaneous)
 - Eutectoid and Peritectoid
 - Absence of long-range diffusion
 - Ordering
 - Massive transformation
 - Precipitation
 - Nucleation
 - Homogeneous
 - Heterogeneous
 - Growth
 - Coarsening

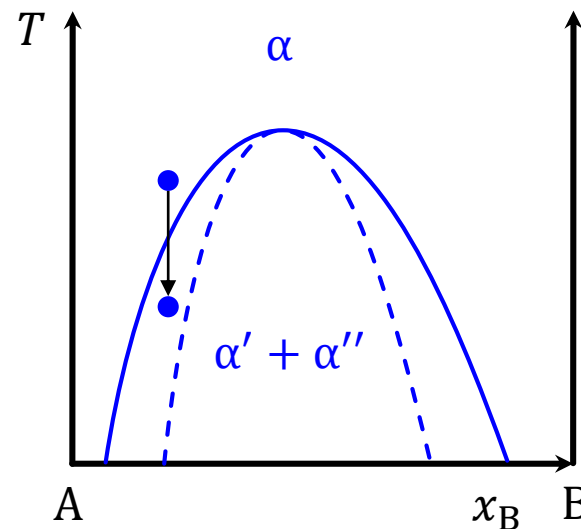
Precipitation

- Precipitation reactions occur from a super-saturated condition into a two-phase state by a thermally activated nucleation and growth process and are controlled by long-range diffusion. Subsequent to precipitation to maximum volume fraction, coarsening is obtained to further reduce total interface energy of the system.



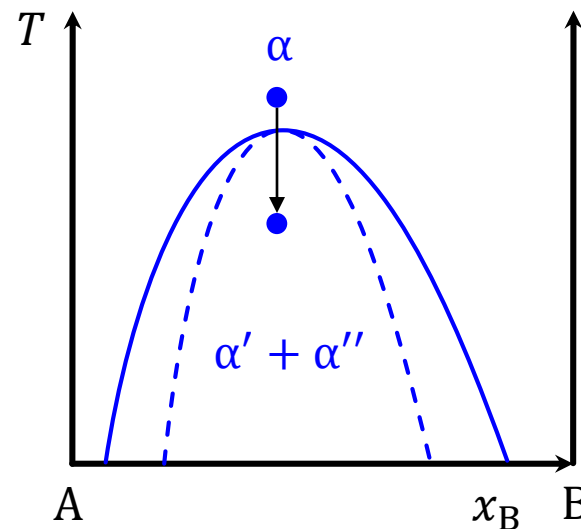
Precipitation

- Precipitation reactions occur from a super-saturated condition into a two-phase state by a thermally activated nucleation and growth process and are controlled by long-range diffusion. Subsequent to precipitation to maximum volume fraction, ageing is obtained to further reduce total interface energy of the system.



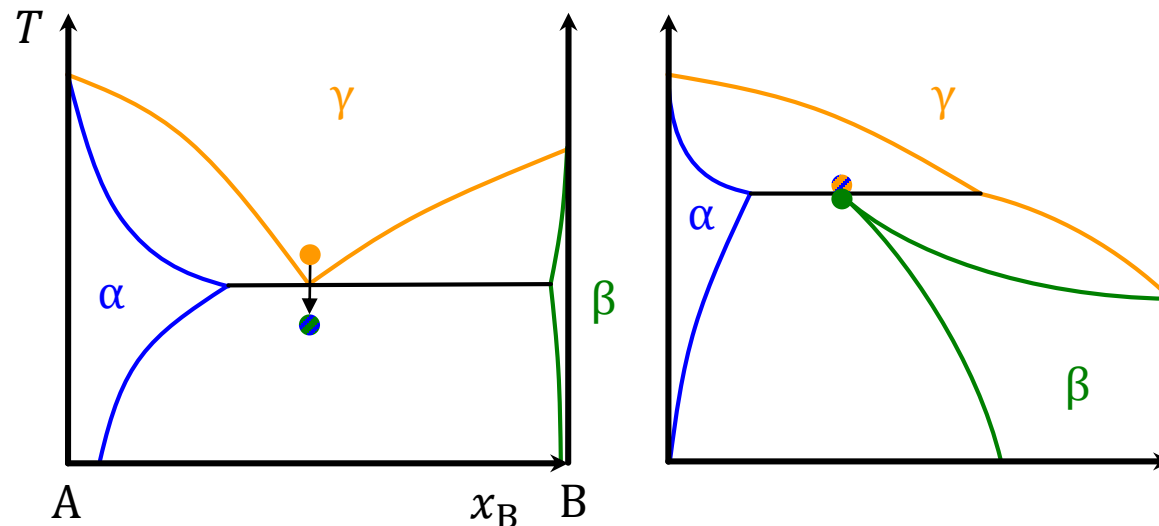
Spinodal Decomposition

- As already seen in Ch. 4c, the spinodal decomposition is a reaction free of nucleation and growth, only involving long-range “up-hill” diffusion. It occurs spontaneously.



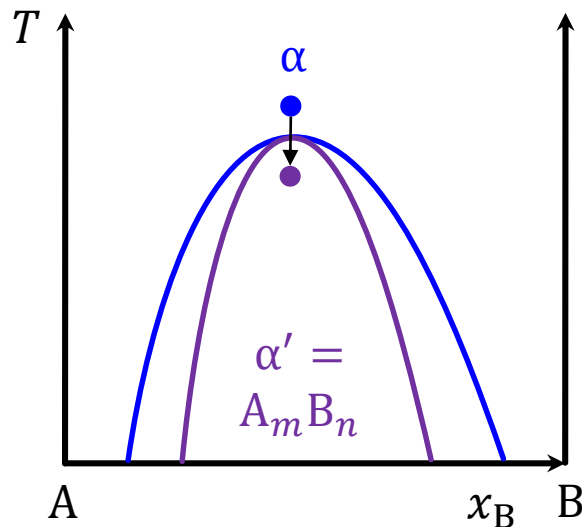
Eutectoid and Peritectoid Reactions

- Other diffusion-controlled reactions involving thermally activated nucleation and growth are obtained by eutectoid and peritectoid reactions. During the eutectoid decomposition, the metastable high temperature phase is replaced by the stable two-phase condition. During the peritectoid reaction, the stable phase is formed at the interface of the metastable high temperature phase with the aforementioned (Ch. 4e) restrictions of atomic flux through the formed phase.

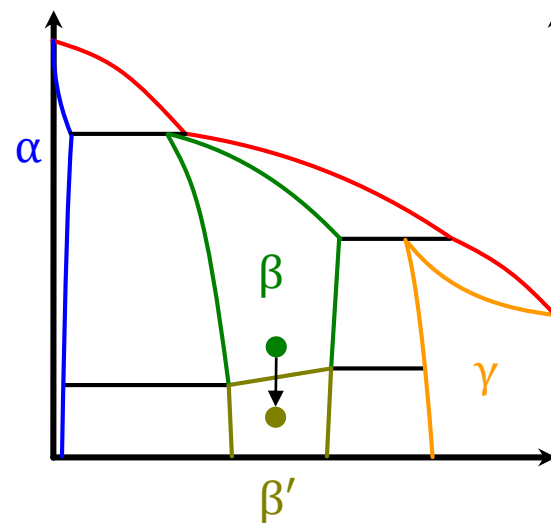


Ordering

- Disordered phases might undergo crystallographic ordering below certain temperatures. Since only rearrangement of atoms within unit cells are required to obtain the different site occupations, no long-range diffusion is required. The reaction can be discontinuous (1st order) by thermal activation due to domain growth or continuous (2nd order, see Ch. 3e).



1st order with
two-phase region

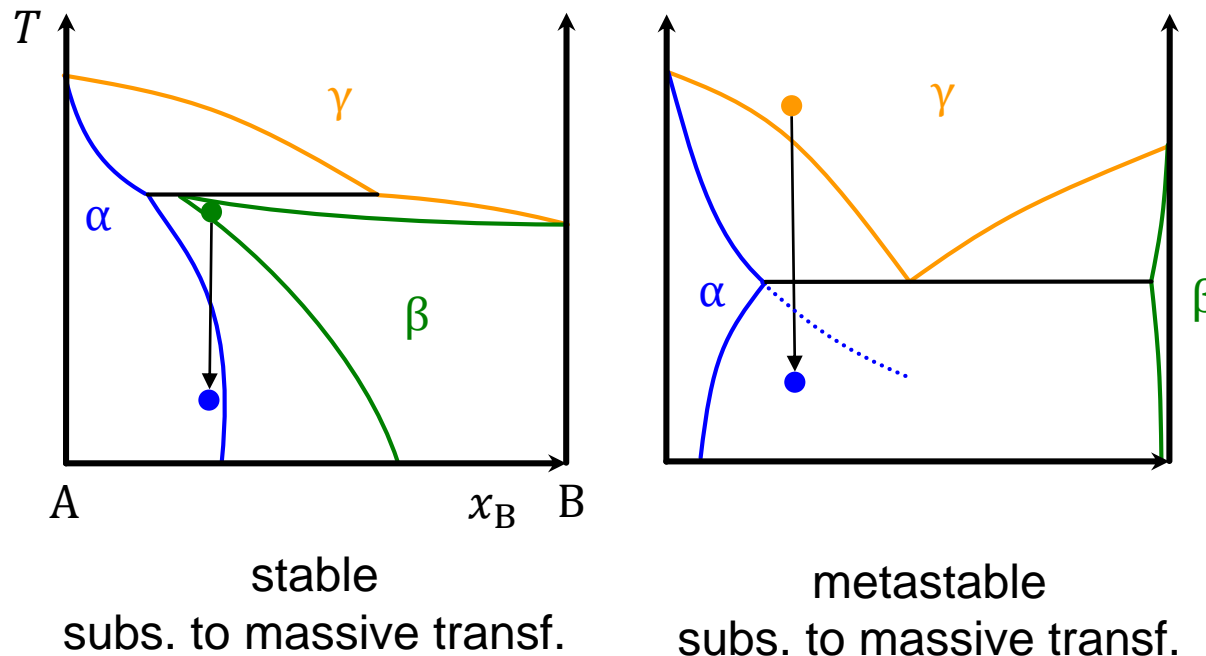


2nd order

Note that apart from variation in site occupation, slight modifications of the crystal structure (symmetry, dimensions) might be obtain as well. In contrast to pure elements (allotropic transf.), the transition from one crystal structure to another in alloys is usually referred to as polymorphic transformation.

Massive Transformation

- During massive transformation, a single-phase condition transforms into one or several phases of the same composition. In contrast to the martensitic transformation where the structural change is obtained by deformation, the restructuring occurs by thermally activated short-range rearrangement of atoms during massive transformation.



Precipitation: Nucleation

- When nucleation is considered, the same principles as discussed in the previous Chs. 3c & 3d on solid state transformations need to be discussed in the framework of a multi-component system:
 - Thermodynamic Assessment of Nucleation:
 - Driving Force
 - Interface Energy
 - Strain Energy

$$\Delta G^{\text{hom}} = -V^{\text{N}} \Delta g^{\text{D}} + V^{\text{N}} \Delta g^{\text{S}} + A^{\text{I}} \gamma^{\text{I}}$$

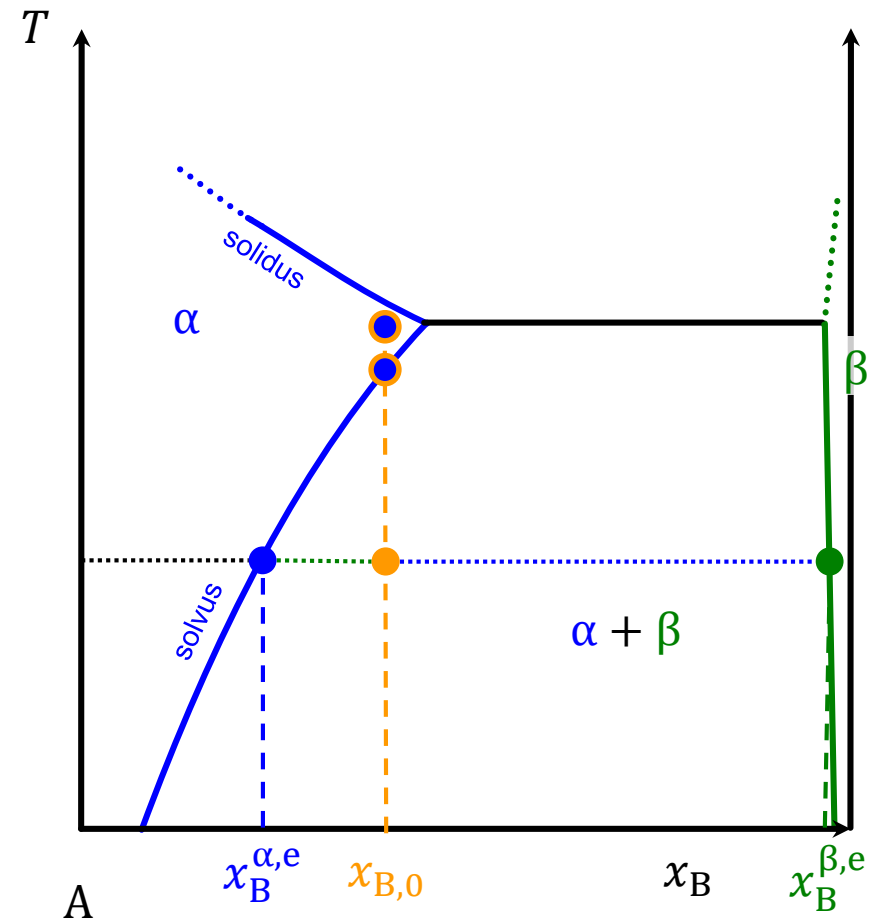
$$\Delta G^{\text{het}} = f(\theta) \Delta G^{\text{hom}}$$

- Kinetic Assessment of Nucleation:
 - Diffusion flux to obtain nuclei of critical size:

$$\eta \propto \exp -\frac{\Delta G^{\text{diff}}}{k_{\text{B}} T} \exp -\frac{\Delta G^{\text{hom/het}}(T)}{k_{\text{B}} T}$$

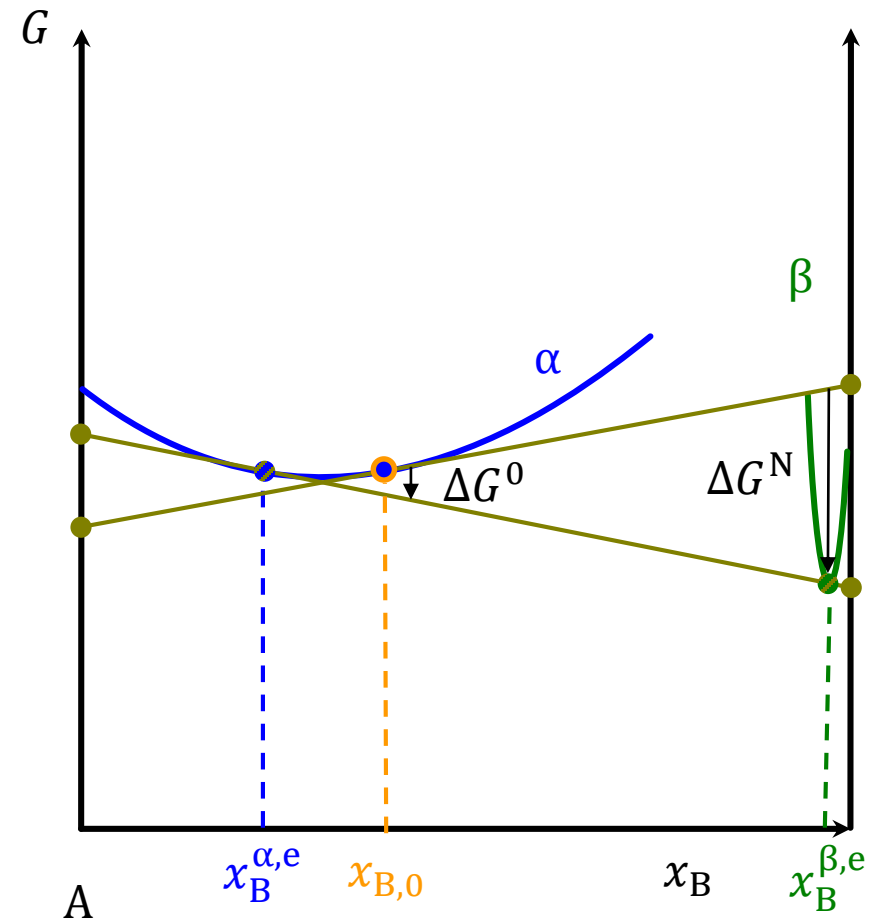
Precipitation: Homogeneous Nucleation

- An alloy of the composition $x_{B,0}$ might be quenched from the homogeneous α region into the stable two-phase region $\alpha + \beta$.
- The driving force Δg^0 for the reaction is provided by the G difference from the quenched homogeneous state (at $x_{B,0}$) to the fully decomposed state.
- However, the driving force for nucleation Δg^N (of β at $x_B^{\beta,e}$) is much higher due to the differences in chemical potential from the quenched state to β .

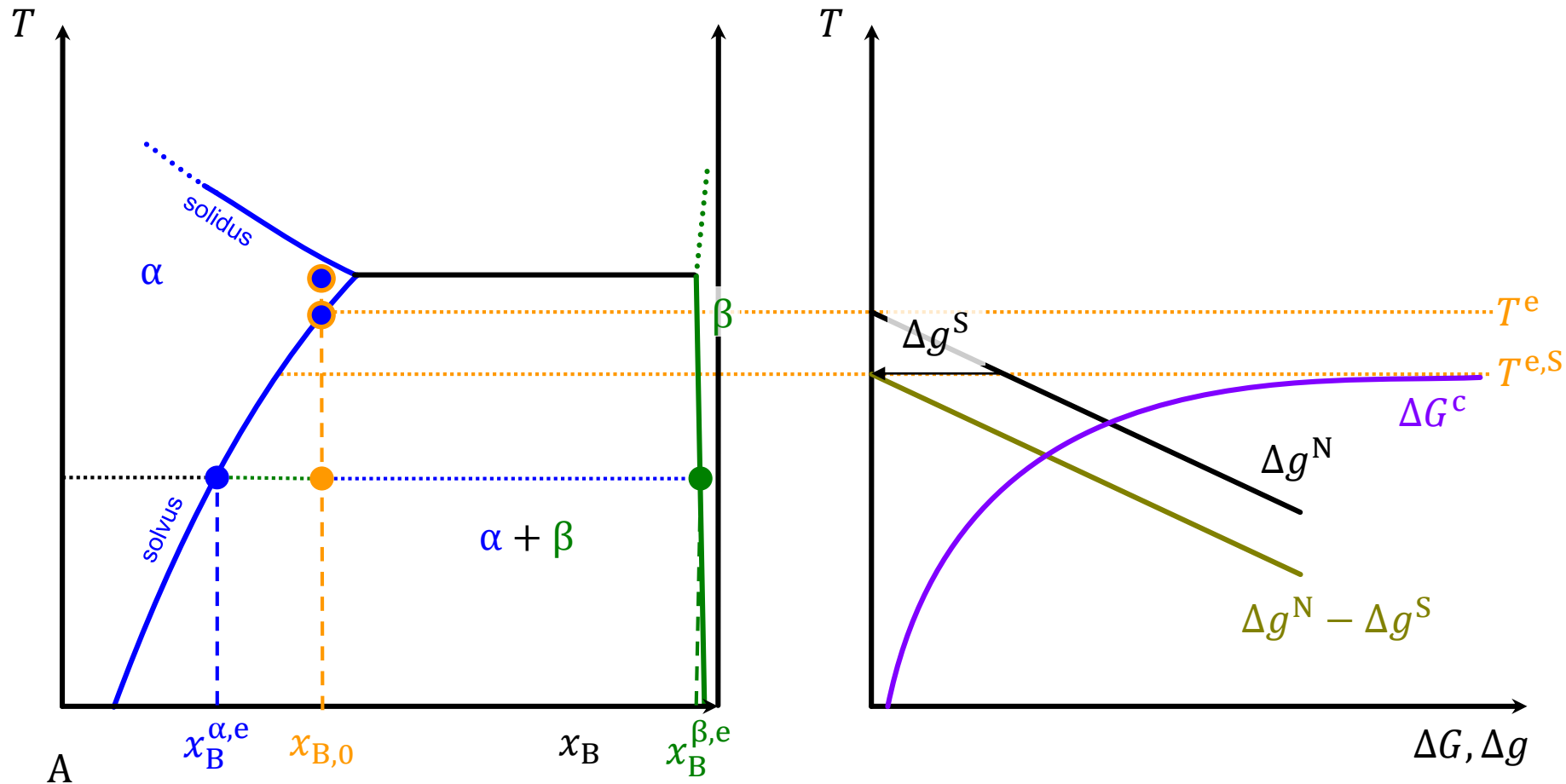


Precipitation: Homogeneous Nucleation

- An alloy of the composition $x_{B,0}$ might be quenched from the homogeneous α region into the stable two-phase region $\alpha + \beta$.
- The driving force $\Delta g^0 = \frac{\Delta G^0}{V_m^\alpha}$ for the reaction is provided by the G difference from the quenched homogeneous state (at $x_{B,0}$) to the fully decomposed state.
- However, the driving force for nucleation $\Delta g^N = \frac{\Delta G^0}{V_m^\beta}$ (of β at $x_B^{\beta,e}$) is much higher due to the differences in chemical potential from the quenched state to β .



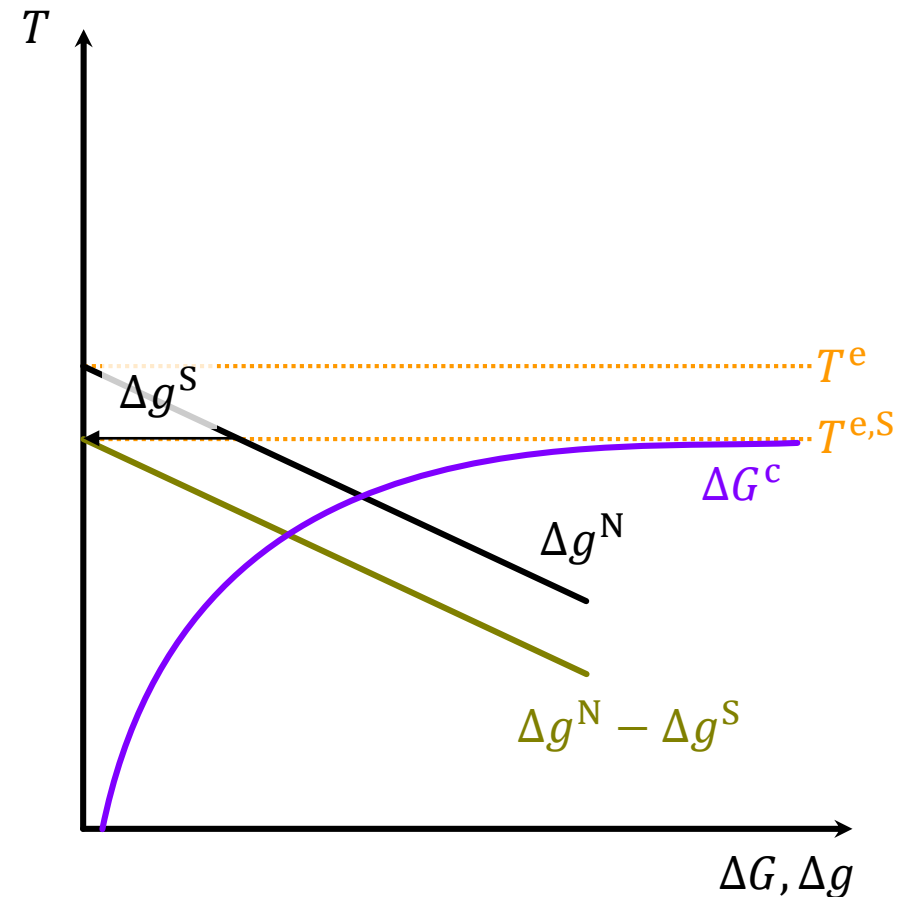
Precipitation: Homogeneous Nucleation



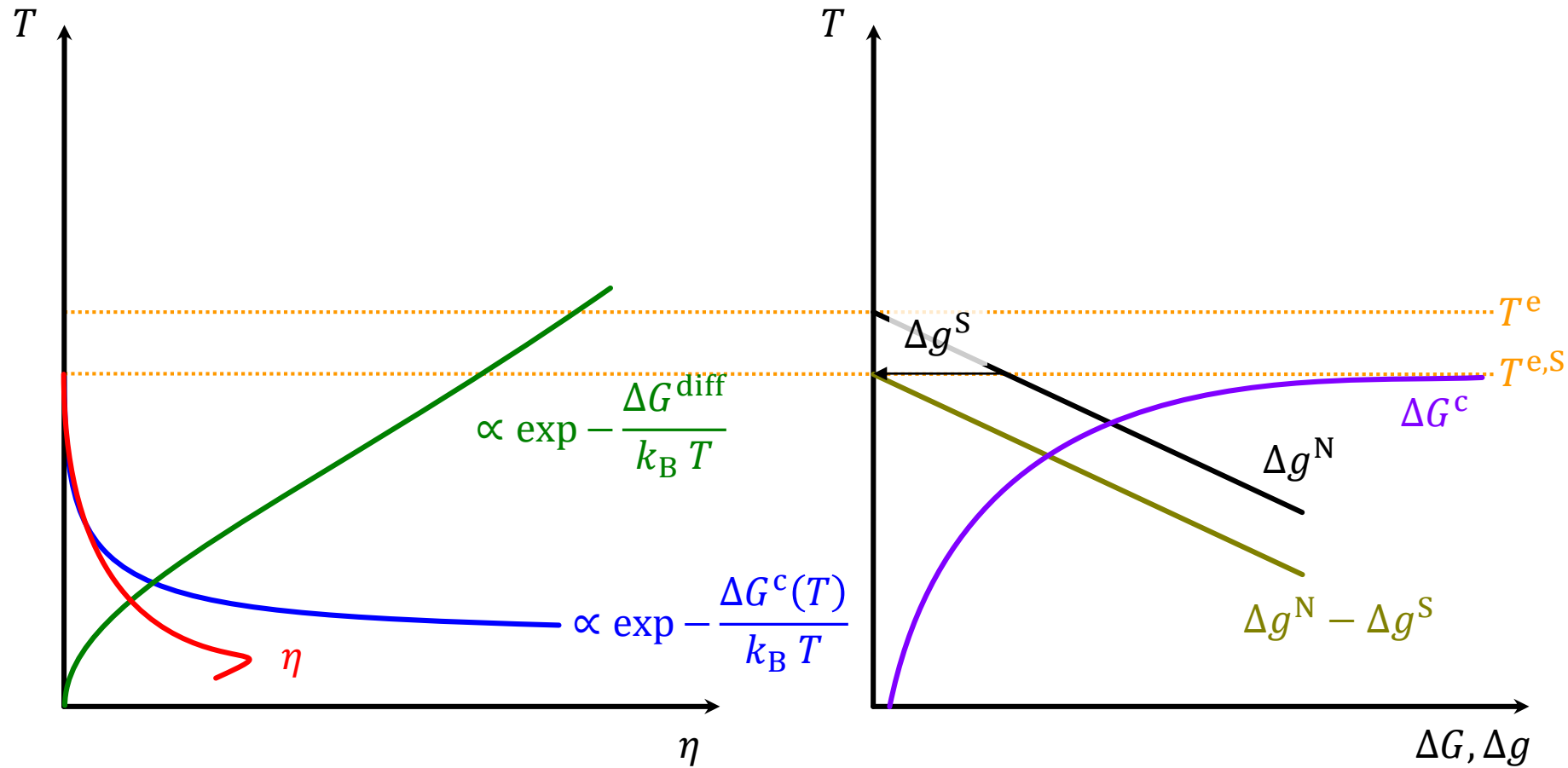
Precipitation: Homogeneous Nucleation

- The driving force for nucleation Δg^N continuously increases with increasing super cooling.
- With taking the important strain energy Δg^S (temperature-insensitive) into account, the activation barrier for nucleation can be calculated by $\Delta G^c =$

$$\frac{16\pi}{3} \frac{\gamma I^3}{(\Delta g^D - \Delta g^S)^2} \text{ (Ch. 3c).}$$



Precipitation: Homogeneous Nucleation

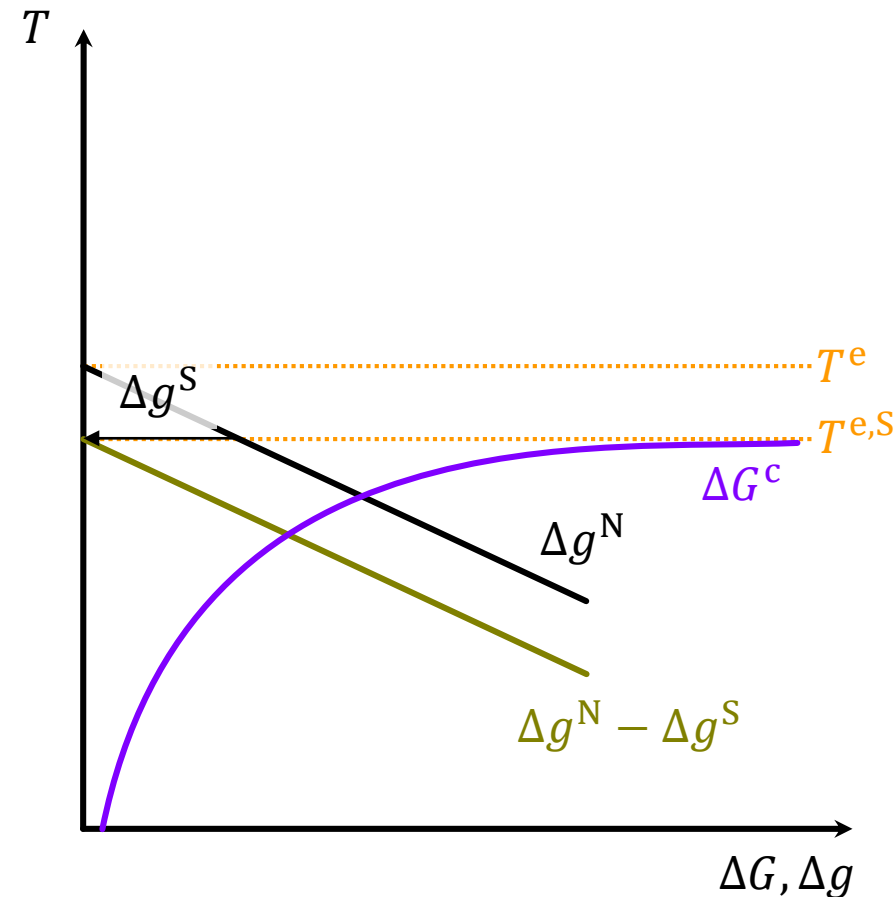


Precipitation: Homogeneous Nucleation

- Similar to Ch. 3d, the nucleation rate depends on the thermal activation of critical nuclei *and* the diffusion to form these nuclei:

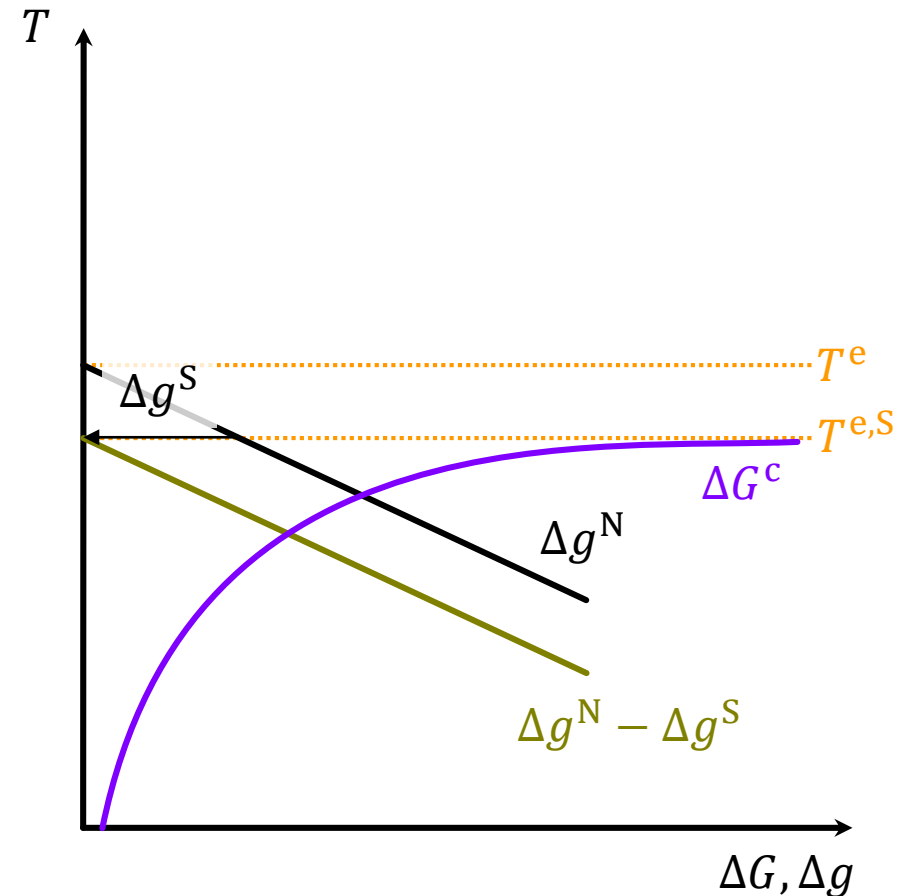
$$\eta \propto \exp - \frac{\Delta G^{\text{diff}}}{k_B T} \exp - \frac{\Delta G^c(T)}{k_B T}$$

- Again, a maximum nucleation rate is obtained at intermediate temperatures. Further, a critical super cooling is needed.
- In the solid, a strong competition between interface and strain terms is obtained.

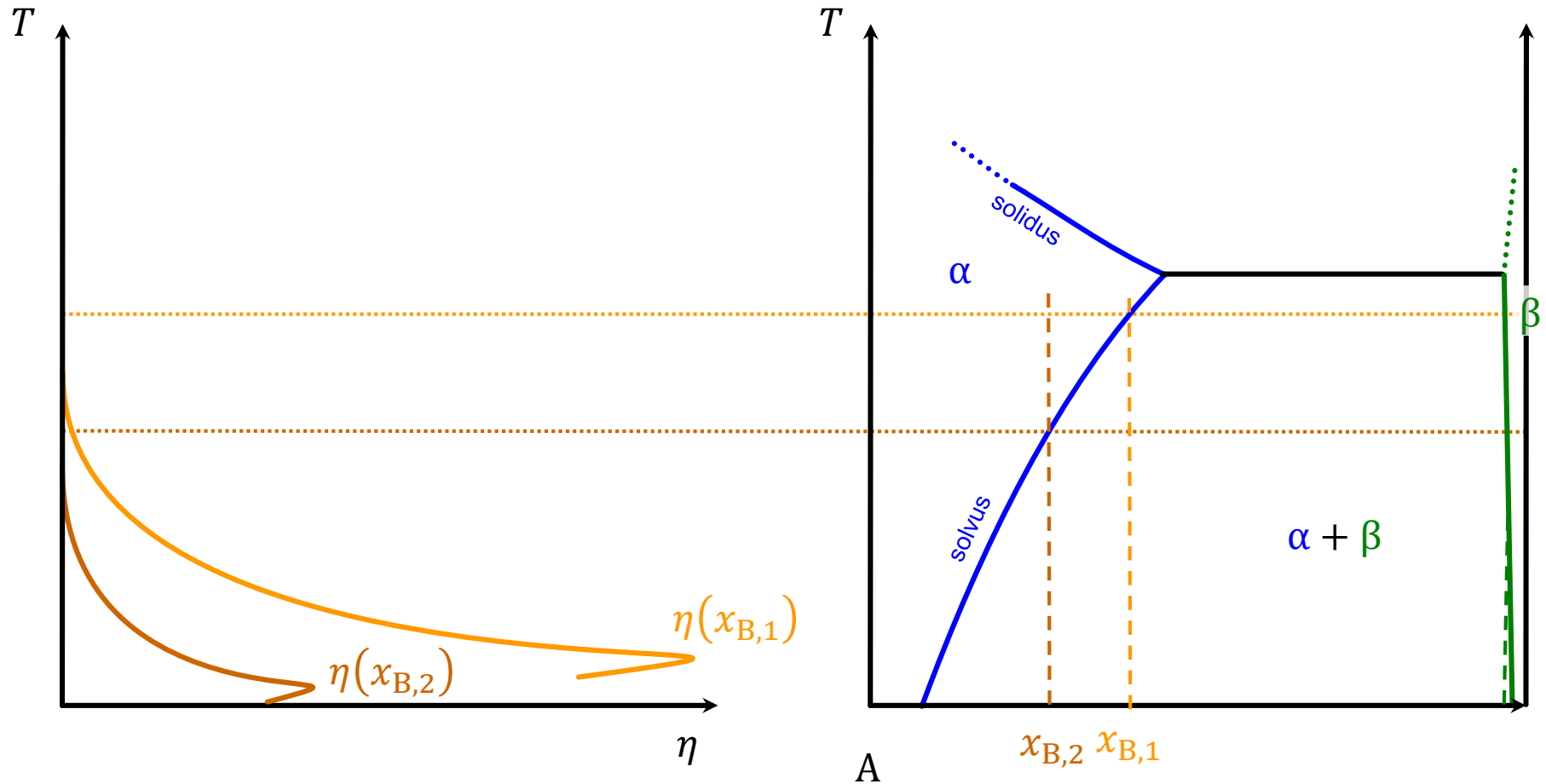


Precipitation: Homogeneous Nucleation

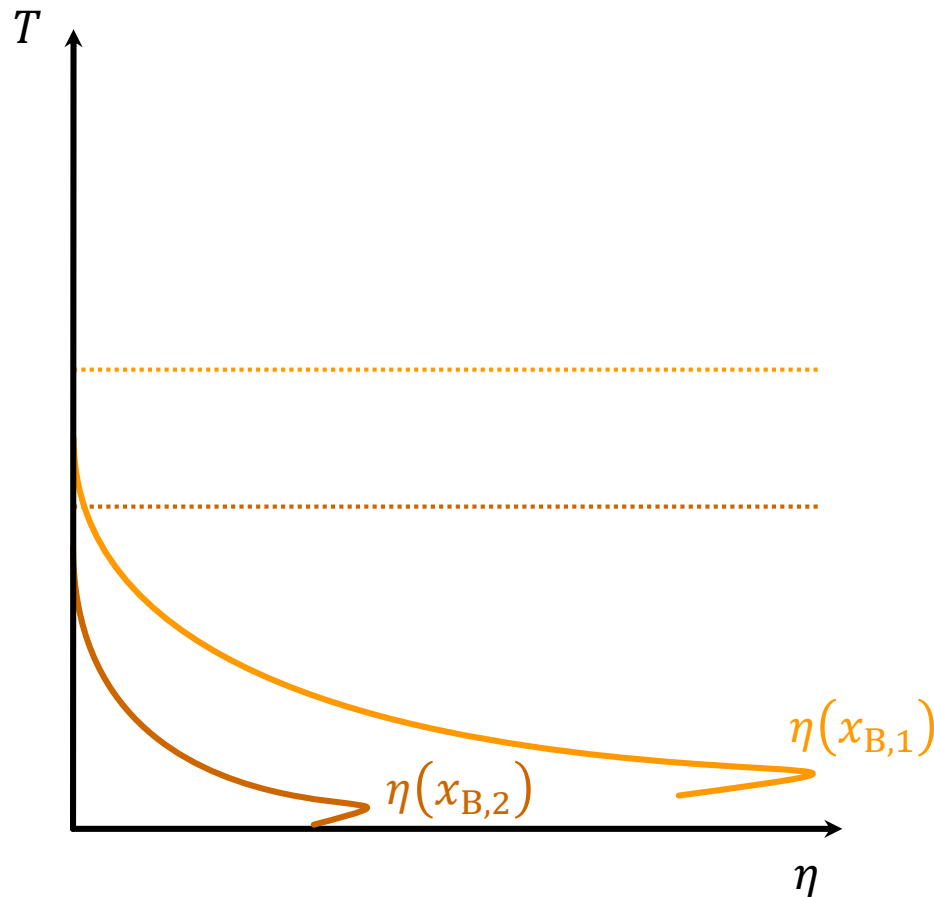
- In many cases, incoherent, high energy interfaces are omitted in the nucleation state by the expense of coherency stresses.
- In some cases, this even leads to the formation of metastable transition phases that are otherwise not obtained during close-to-equilibrium precipitation, for example Guinier-Preston zones in Al-Cu.



Precipitation: Homogeneous Nucleation



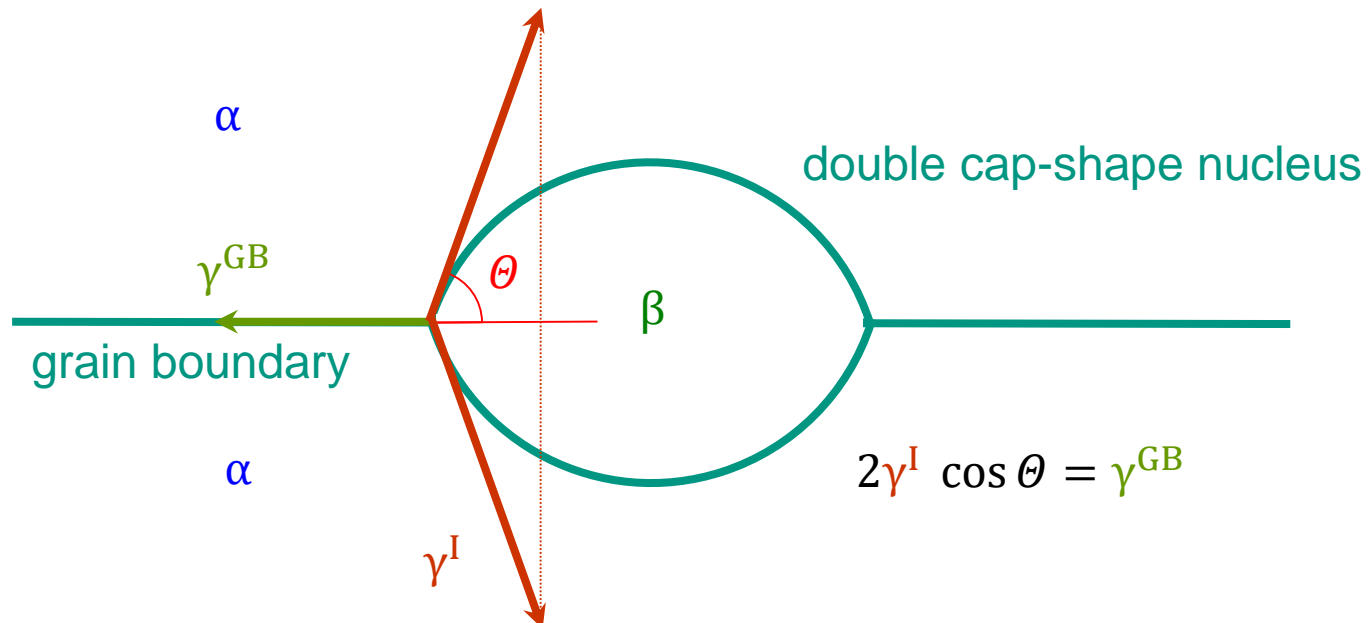
Precipitation: Homogeneous Nucleation



- Even when nucleation occurs homogeneously, the nucleation rate won't be constant during the precipitation since the amount of super saturation decreases during the precipitation.
- After some incubation time (due to the necessary diffusion to form early clusters), the nucleation will rise and, finally, decrease.

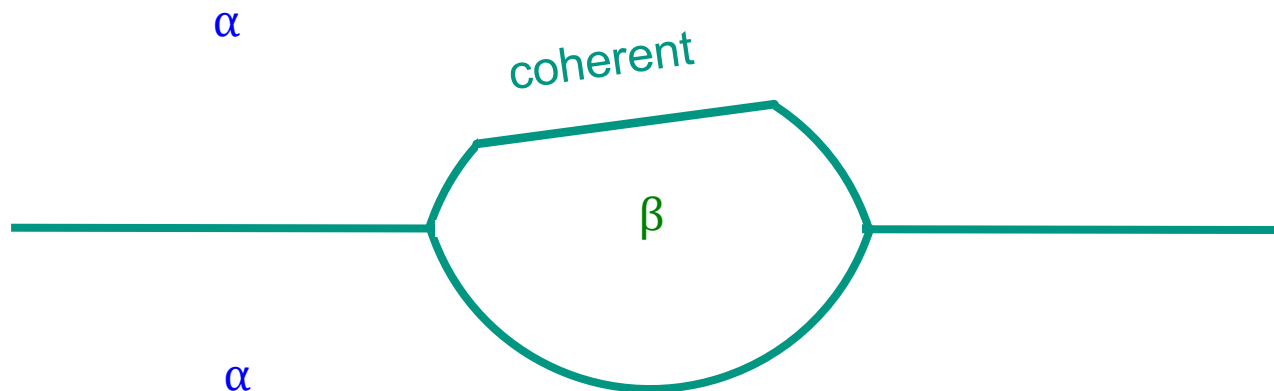
Precipitation: Heterogeneous Nucleation

- Nucleation in the solid is often heterogeneous involving several different defects assisting nucleation.
- As seen in Ch. 3c, grain boundaries are potent by energetic reasons. Coherent portions of the interface might contribute to a further reduction in nucleation energy:



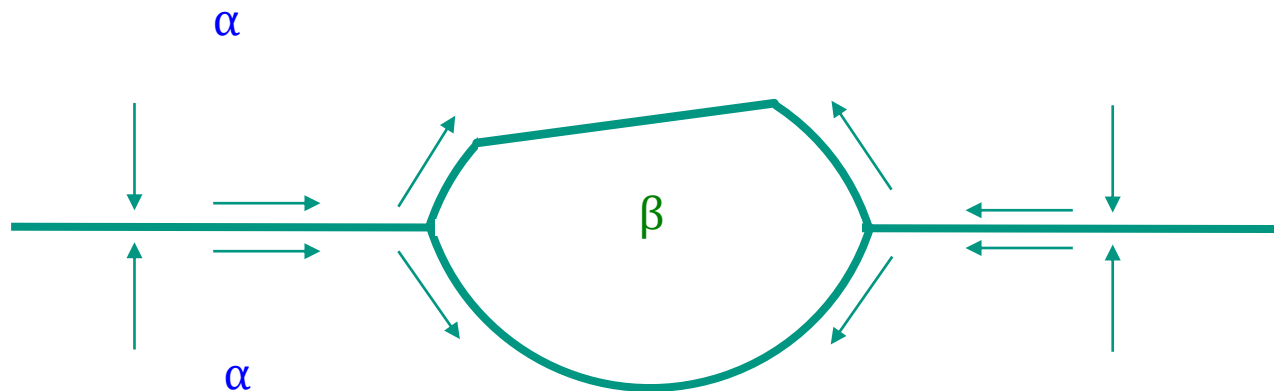
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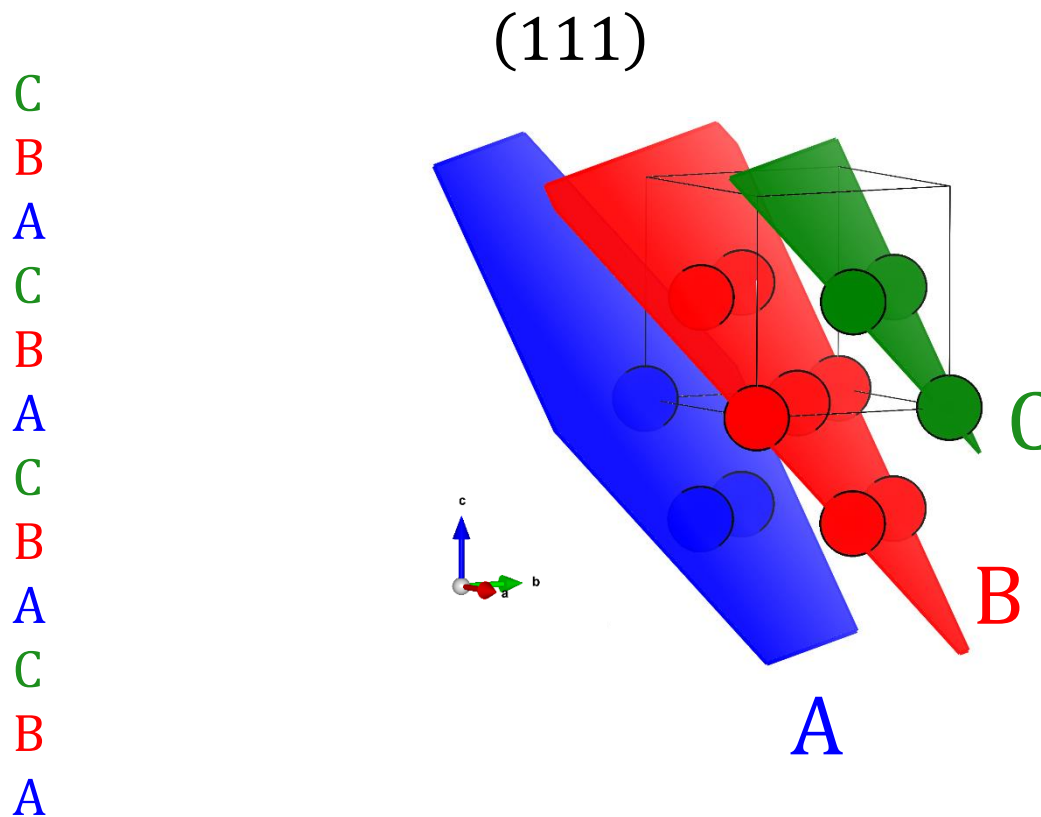
- They also contribute to the kinetics of the precipitation due to enhanced diffusion along the grain boundary and interfaces.

Precipitation: Heterogeneous Nucleation

- Nucleation in the solid is often heterogeneous involving several different defects assisting nucleation. The ratio of heterogeneous vs. homogeneous can be tailored by the amount of heterogeneous nucleation sites (for example artificial coarsening of the single-phase microstructure prior to precipitation).
- As seen in Ch. 3c, grain boundaries are potent by energetic reasons. Coherent portions of the interface might contribute to a further reduction in nucleation energy.
- They also contribute to the kinetics of the precipitation due to enhanced diffusion along the grain boundary and interfaces.
- Similar considerations are valid for dislocations, planar faults, excess vacancies (or clusters of them), etc. In some cases, these defects act as orientation precursors for coherent nucleation (stacking faults in fcc A1 for hcp A3 precipitates).
- When the defect is removed by the nucleation of the secondary phase, the nucleation is facilitated.

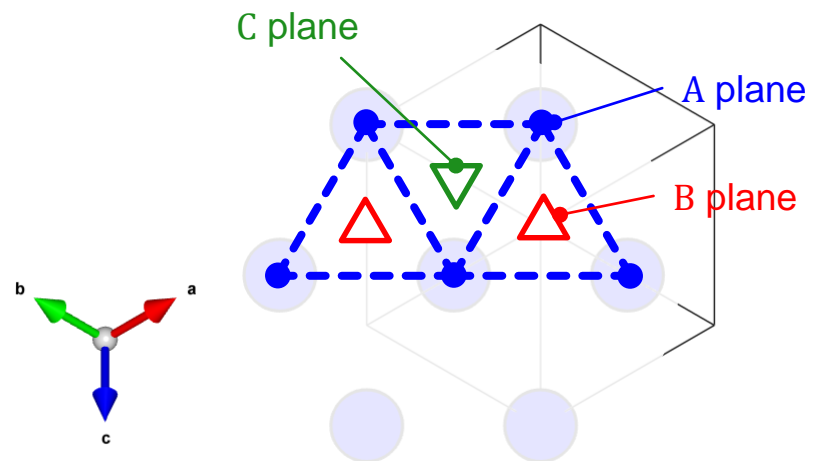
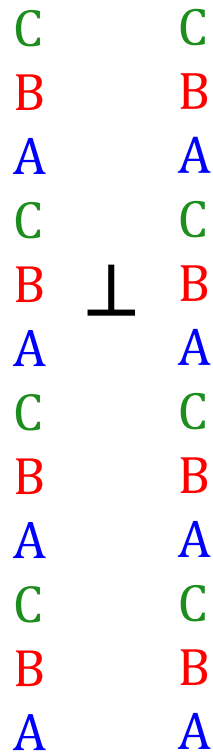
Precipitation: Heterogeneous Nucleation

- Undistorted stacking sequence in A1 metals and alloys:



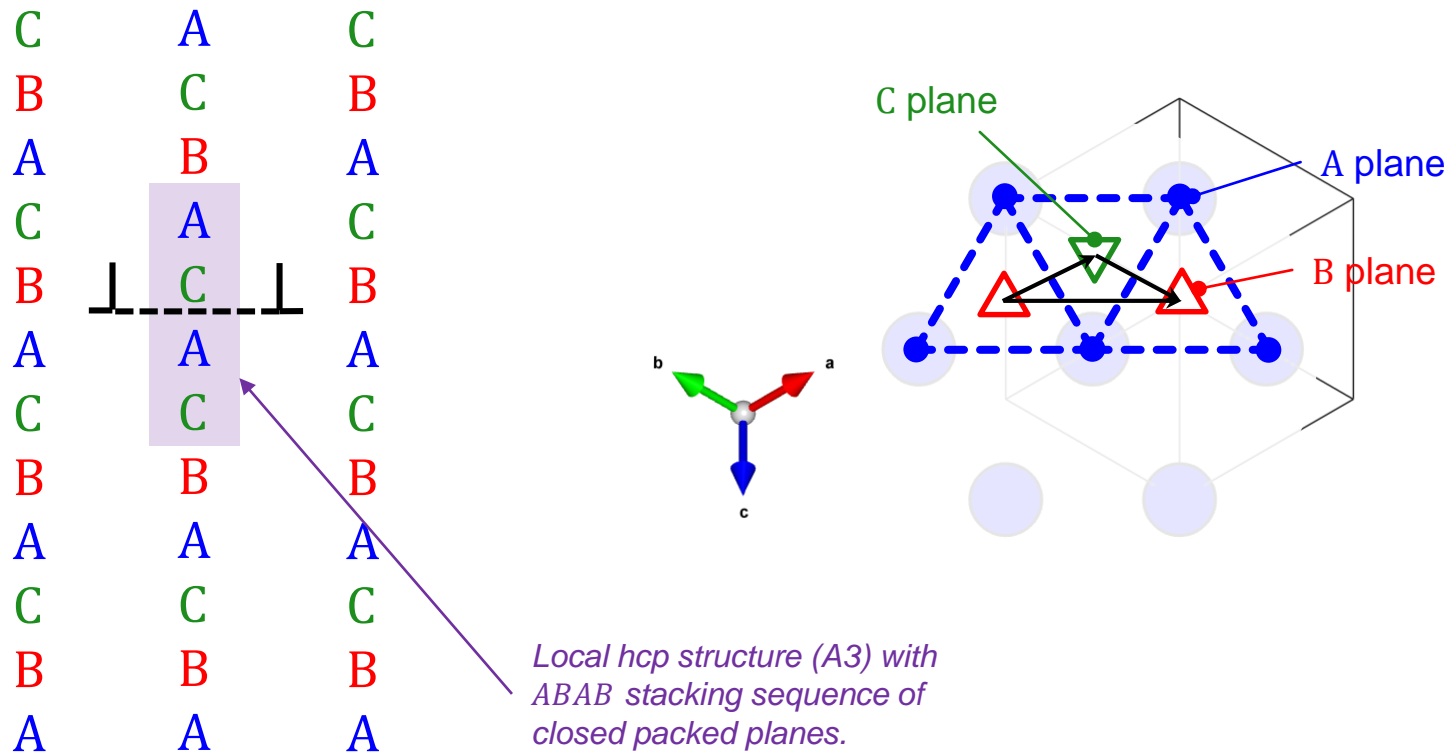
Precipitation: Heterogeneous Nucleation

- Full dislocation in A1 metals and alloys:



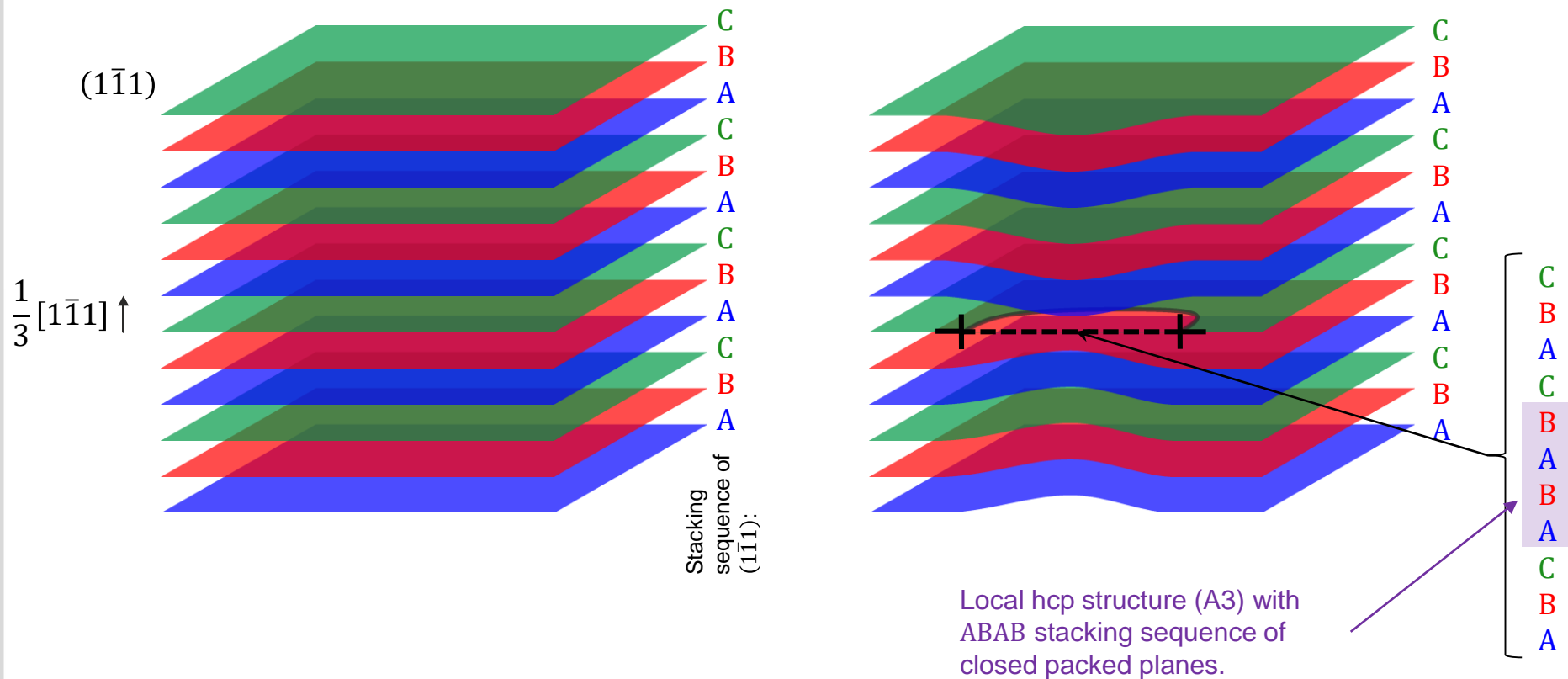
Precipitation: Heterogeneous Nucleation

- Dissociation of dislocations into Shockley partials in A1 metals and alloys. The leading partial dislocation opens the stacking fault by shifting from B to C. The trailing partial closes the stacking fault by shifting from C to B. In the region bordered by the partial dislocations, an intrinsic stacking fault is formed:



Precipitation: Heterogeneous Nucleation

- Condensation of vacancies (for example subsequent to quenching or radiation) leads to the formation of prismatic Frank loops with enclosed intrinsic stacking fault:



Precipitation: Growth

- Similar to what was presented in Ch. 4a, several types of growth can be distinguished.
- Two extreme cases of concentration profile can exist (1) and (2) while reality is an intermediate situation between the two:
 - (1) When $\Delta\mu_B^i \approx 0$ (interface mobility is high, incoherent interface), *local equilibrium* within the interface is obtained. The reaction is *controlled by diffusion* along the concentration gradient from $x_{B,0}$ to $x_B^{\beta,e}$ in the matrix phase.
 - (2) When $\Delta\mu_B^i$ is large (interface mobility is low, coherent interface), the situation is practically *interface-controlled* with $x_B^{\beta,i} = x_{B,0}$.
 - (3) In reality, an intermediate situation is obtained.

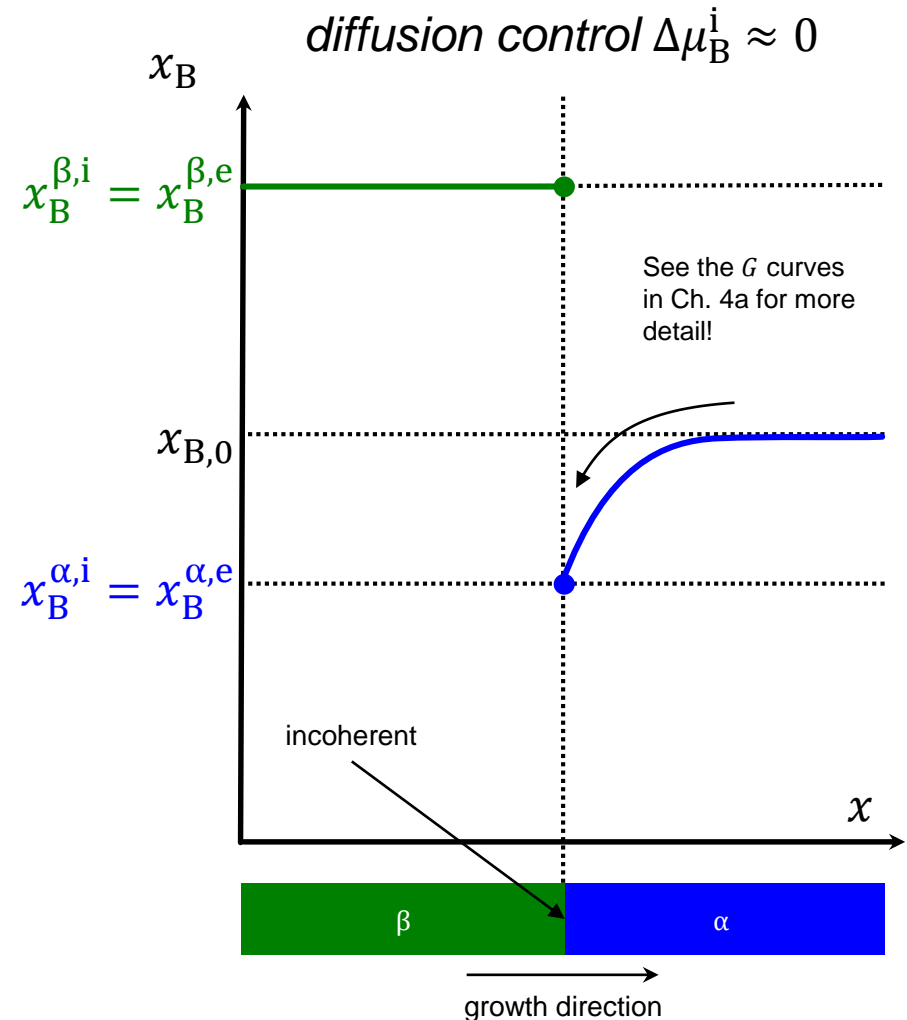
Precipitation: Growth (Incoherent Slab)

- As previously shown in Ch. 4a, the movement of the interface occurs by converting α of $c_B^{\alpha,i}$ to β of $c_B^{\beta,i}$.
- The advancement of the interface requires

$$\left(c_B^{\beta,i} - c_B^{\alpha,i} \right) dV^\beta = V^\alpha dc_B^\alpha$$
- Assuming similar molar volumes $V_m^\beta \approx V_m^\alpha$, a constant interface area and a constant supply of B atoms j_B^α at the interface by diffusion in the diffusion controlled situation (see figure), leads to:

$$\left(x_B^{\beta,e} - x_B^{\alpha,e} \right) dx \approx j_B^{\alpha,i} dt$$

$$\left(x_B^{\beta,e} - x_B^{\alpha,e} \right) dx = D \left. \frac{dx_B^\alpha}{dx} \right|_i dt$$



Precipitation: Growth (Incoherent Slab)

- The situation might be approximated linear:

$$\left(x_B^{\beta,e} - x_B^{\alpha,e} \right) \frac{dx}{dt} \approx D \frac{x_{B,0} - x_B^{\alpha,e}}{L}$$

- Conservation of the total composition yields the equality of the two shaded regions:

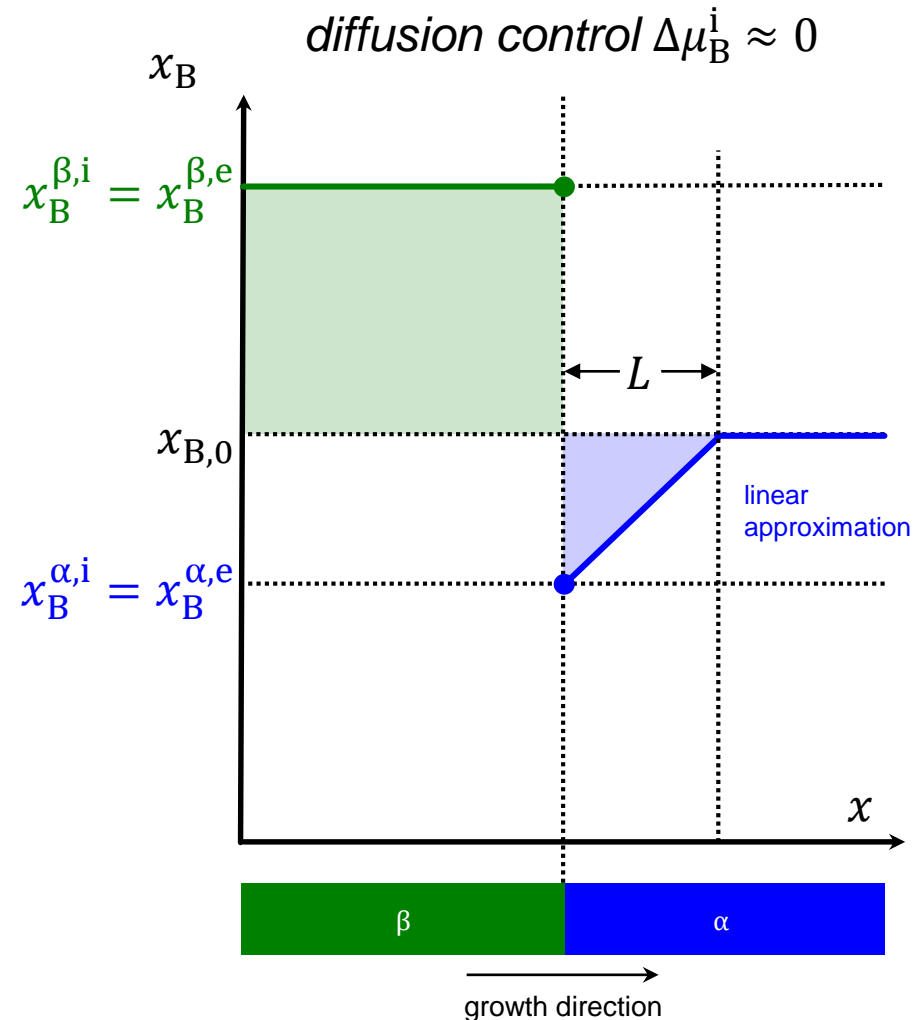
$$\left(c_B^{\beta,e} - c_{B,0} \right) x = \frac{1}{2} L \left(c_{B,0} - c_B^{\alpha,e} \right)$$

$$\left(x_B^{\beta,e} - x_{B,0} \right) x = \frac{1}{2} L \left(x_{B,0} - x_B^{\alpha,e} \right)$$

- The progression of the interface occurs with:

$$v = \frac{dx}{dt} = \frac{D}{x_B^{\beta,e} - x_B^{\alpha,e}} \frac{x_{B,0} - x_B^{\alpha,e}}{L}$$

$$\approx \frac{D \left(x_{B,0} - x_B^{\alpha,e} \right)^2}{2 \left(x_B^{\beta,e} - x_B^{\alpha,e} \right) \left(x_B^{\beta,e} - x_{B,0} \right) x}$$



Precipitation: Growth (Incoherent Slab)

- Integration yields (further assuming

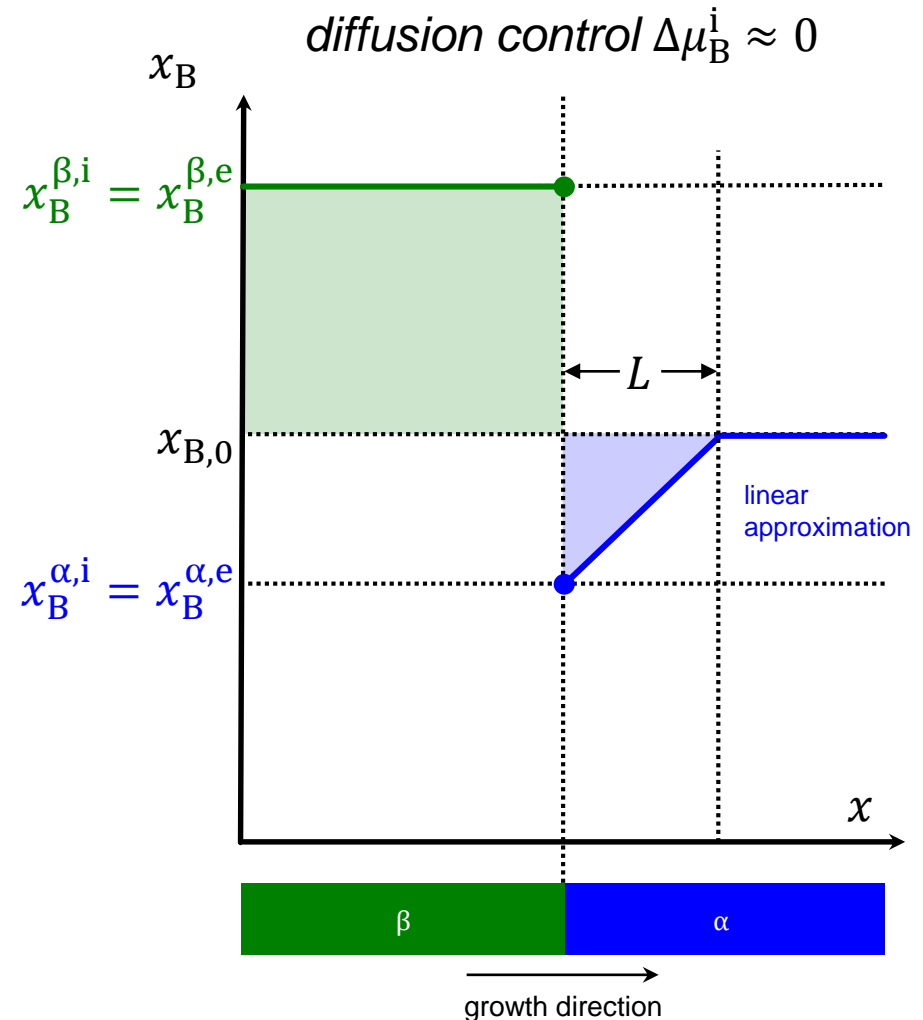
$$x_B^{\beta,e} - x_{B,0} \approx x_B^{\beta,e} - x_B^{\alpha,e}:$$

$$x(t) = \frac{x_{B,0} - x_B^{\alpha,e}}{x_B^{\beta,e} - x_B^{\alpha,e}} \sqrt{D t}$$

$$v(t) = \frac{x_{B,0} - x_B^{\alpha,e}}{2(x_B^{\beta,e} - x_B^{\alpha,e})} \sqrt{D/t}$$

- Hence:

- Growth follows a parabolic law $x \propto \sqrt{D t}$
- Growth rate is proportional to supersaturation $v \propto (x_{B,0} - x_B^{\alpha,e})$
- Growth slows down $v \propto \sqrt{D/t}$

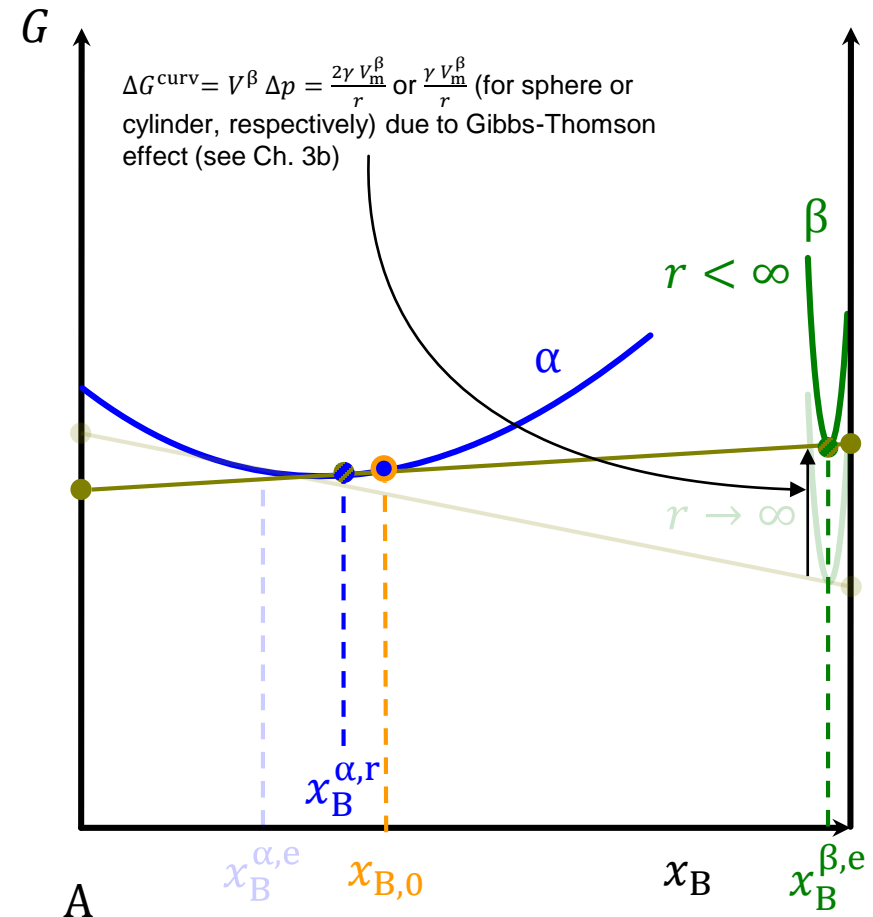


Precipitation: Growth (Incoherent Plate or Needle Tip)

- At a sharp tip of radius r , the situation is altered due to Gibbs-Thompson effect.
- Interface equilibrium is changed to $x_B^{\alpha,r}$ instead of $x_B^{\alpha,e}$.
- Radial diffusion (cylindrical geometry) in conjunction with a similar approach as seen before provides approximately:

$$v \approx \frac{D}{x_B^{\beta,e} - x_B^{\alpha,r}} \frac{x_{B,0} - x_B^{\alpha,r}}{k r}$$

- k is dimensionless in the order of 1



Precipitation: Growth (Incoherent Plate or Needle Tip)

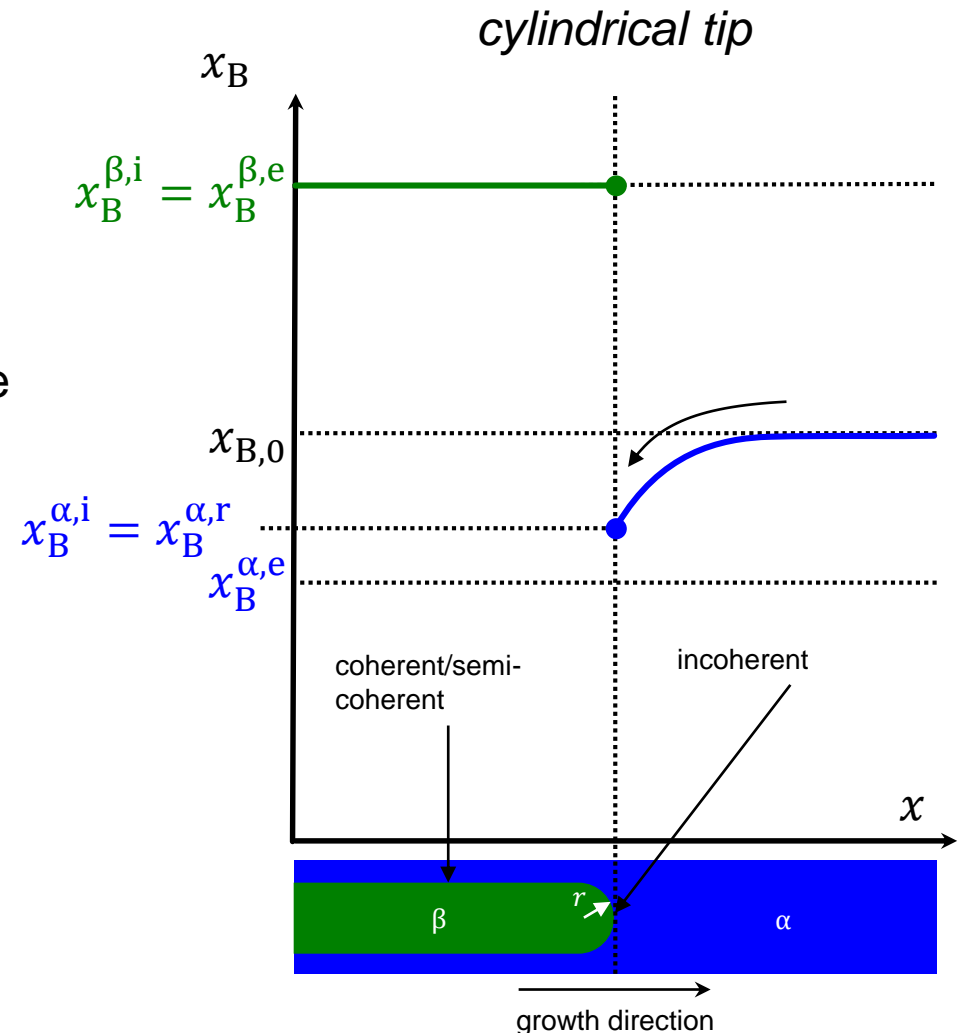
- $x_{B,0} - x_B^{\alpha,r}$ might be approximated by:

$$x_{B,0} - x_B^{\alpha,r} \approx (x_{B,0} - x_B^{\alpha,e}) \left(1 - \frac{r^*}{r}\right)$$

- Finally, the balance at the interface and conservation of total composition yield:

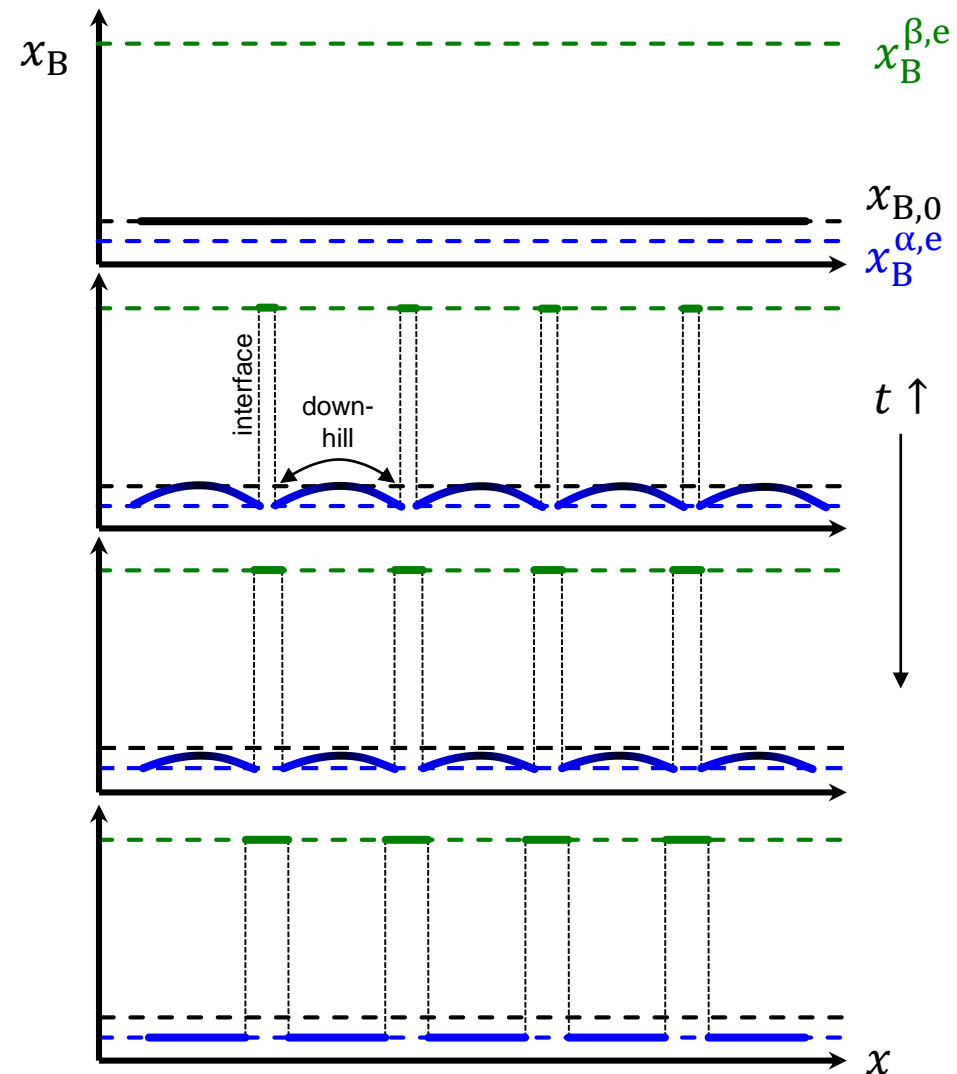
$$v \approx \frac{D (x_{B,0} - x_B^{\alpha,e})}{k (x_B^{\beta,e} - x_B^{\alpha,r})} \frac{1}{r} \left(1 - \frac{r^*}{r}\right)$$

- It yields, that:
 - Growth follows a linear law $x \propto t$ (no x in the equation to integrate!)



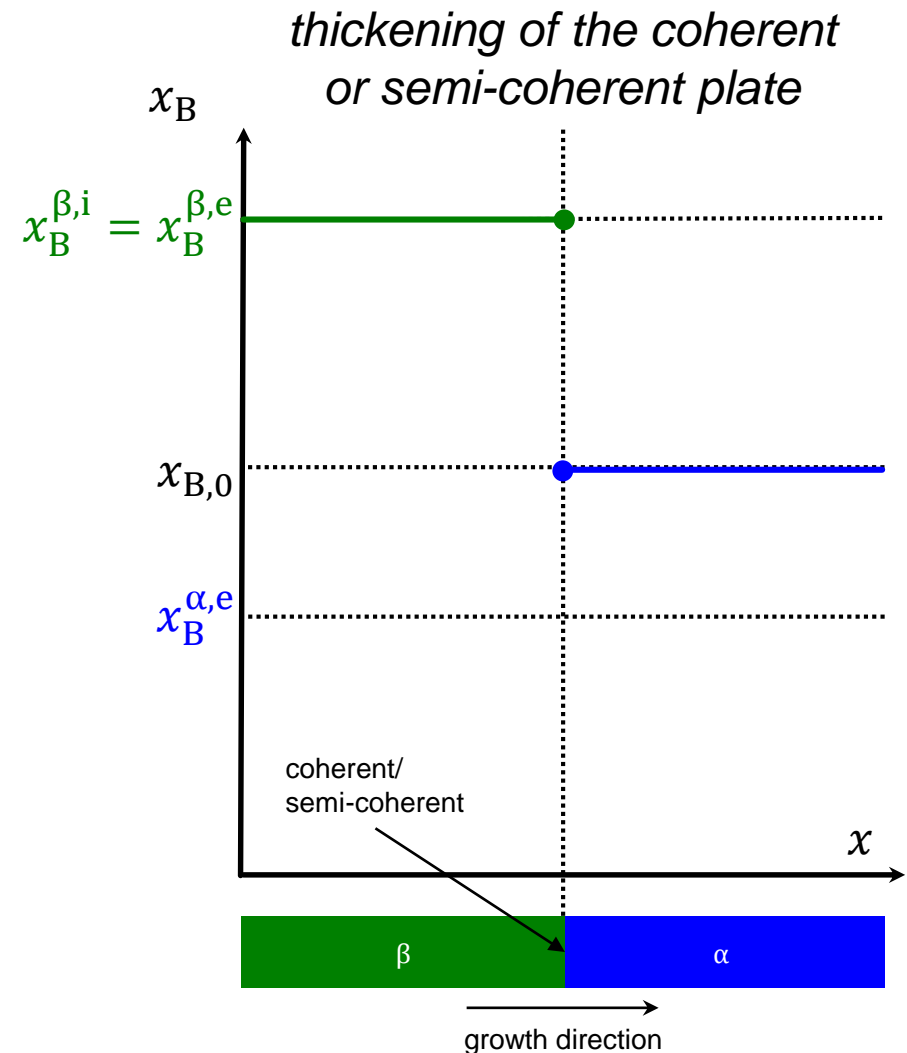
Precipitation: Growth (Diffusion Control)

- For both situations, the composition profiles across many precipitates are similar.
- The aforementioned conditions are valid as long as the diffusion profiles in the vicinity of the interfaces do not meet.



Precipitation: Growth (Coherent Plate Thickening)

- The interface-controlled situation of a coherent or semi-coherent plate that thickens can be treated in a similar way as the growing tip.
- The composition profile is altered by a very high $\Delta\mu_B^i = \max.$ (see Ch. 4a).



Precipitation: Growth (Coherent Plate Thickening)

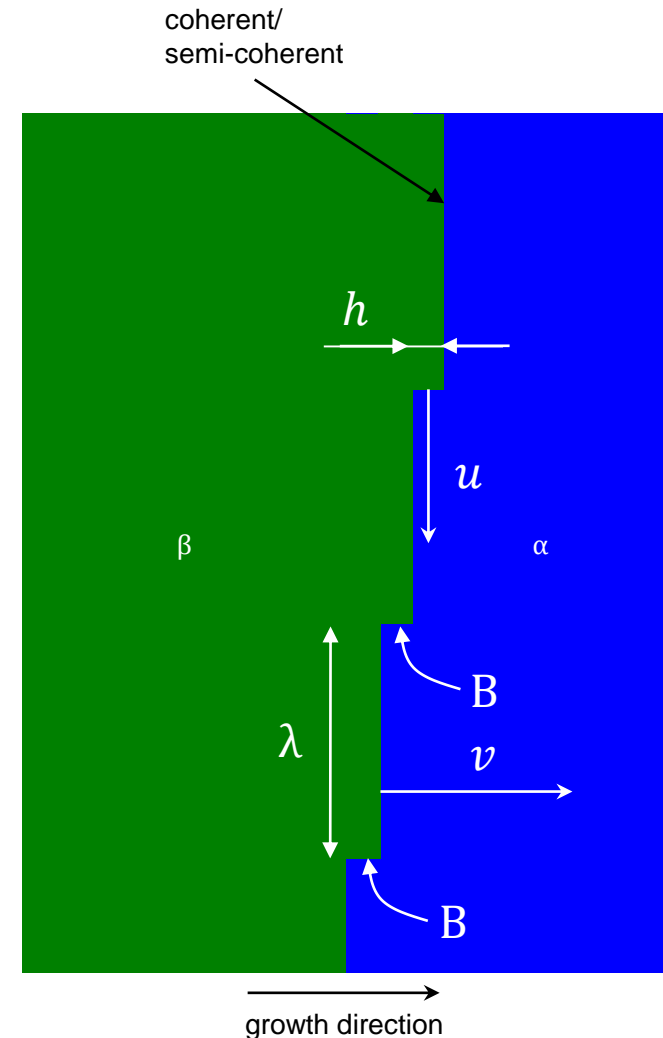
- The thickening occurs by the growth of ledges at a velocity u :

$$v \approx \frac{u h}{\lambda}$$

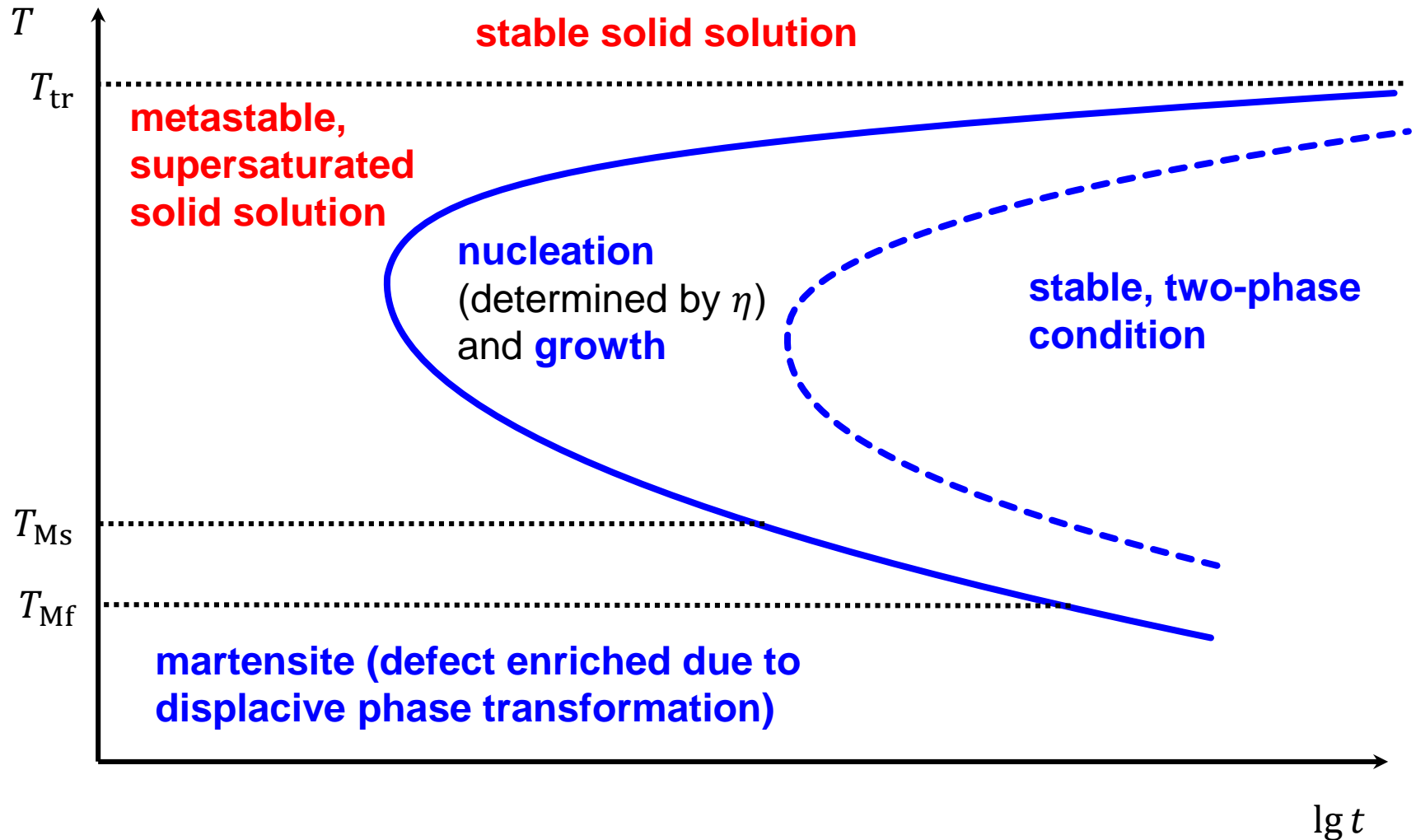
- Similar to the tip ($h \approx r$):

$$u \approx \frac{D}{x_B^{\beta,e} - x_B^{\alpha,e}} \frac{x_{B,0} - x_B^{\alpha,e}}{k h}$$

$$v \approx \frac{D}{x_B^{\beta,e} - x_B^{\alpha,e}} \frac{x_{B,0} - x_B^{\alpha,e}}{k \lambda}$$



Precipitation: Growth (time evolution)



Precipitation: Growth

- As presented in Chs. 3b and 3d, four situations regarding the temporal evolution of precipitation might be distinguished.
- In case of low equilibrium volume fractions, almost all precipitates grow free to the maximum volume fraction. Hence, the polynomial estimates as for solidification from Ch. 3b can be used:

- For constant nucleation rate η ($[\eta] = \frac{1}{\text{m}^3 \text{s}}$) and growth velocity v ($[v] = \text{m/s}$):

$$v^\beta = \frac{V^\beta}{V} = \frac{\pi}{3} v^3 \eta t^4$$

- For constant site density η ($[\eta] = \frac{1}{\text{m}^3}$) from the beginning of the precipitation process and constant growth velocity v ($[v] = \text{m/s}$):

$$v^\beta = \frac{4}{3} \pi v^3 \eta t^3$$

- In case, precipitates grow to a volume fraction where the individual growth of the precipitates is limited by other precipitates, a JMAK approach from Ch. 3d is necessary:

- For constant nucleation rate η and growth velocity v :

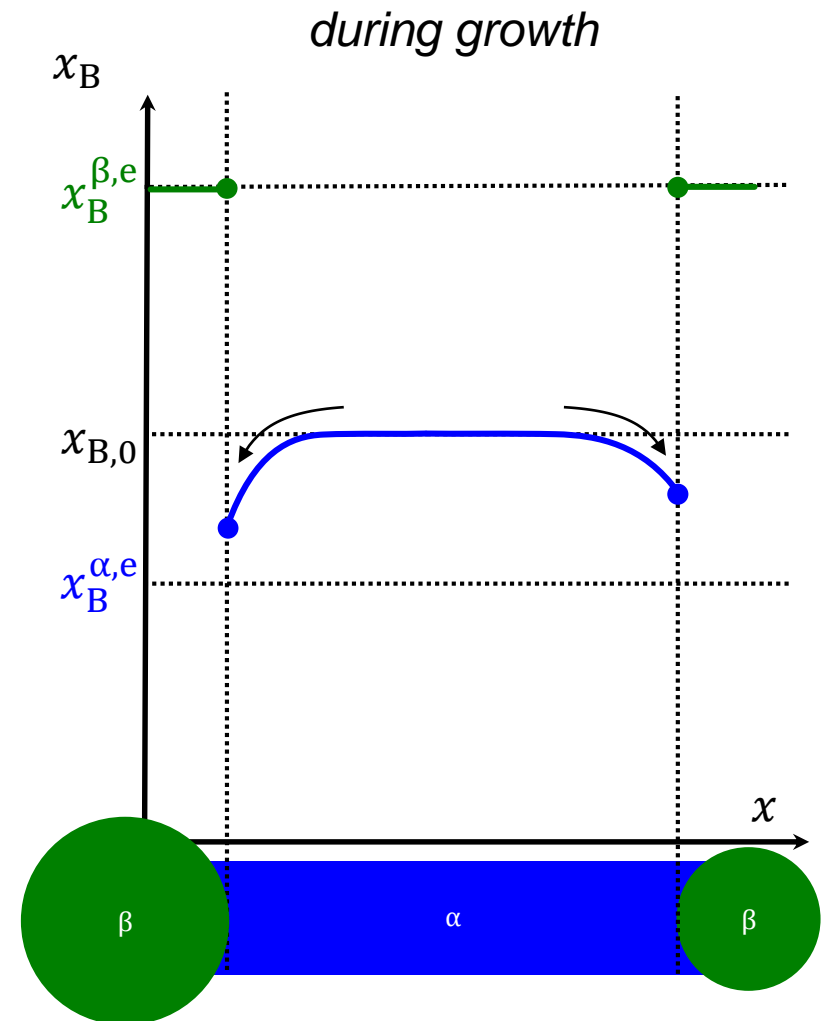
$$v^\beta = 1 - \exp - \frac{\pi}{3} v^3 \eta t^4$$

- For constant site density η from the beginning of the precipitation process and constant growth velocity:

$$v^\beta = 1 - \exp - \frac{4\pi}{3} v^3 \eta t^3$$

Precipitation: Coarsening

- Precipitation occurs until maximum volume fraction of precipitates are formed (according to the lever rule).



Precipitation: Coarsening

- Beyond that, interface energy is reduced by preferential growth of particles with less curvature by the expense of high-curvature particles (different nucleation times).
- The size distribution changes with:

$$\bar{r}^3 - \bar{r}_0^3 \propto D \gamma x_B^{\alpha,e} t$$

- The rate of coarsening is:

$$\frac{d\bar{r}}{dt} \propto \frac{1}{\bar{r}^2}$$

