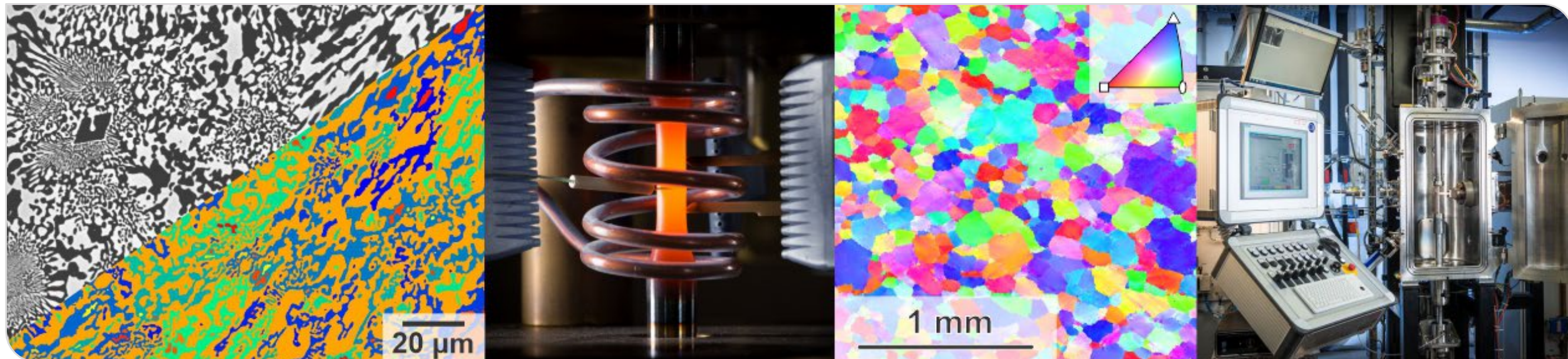


Phase Transformations in Materials

Lecture for “Mechanical Engineering” and “Materials Science and Engineering”
Dr.-Ing. Alexander Kauffmann (Bldg. 10.91, R. 375)
Dr. Sandipan Sen (Bldg. 10.91, R. 311)

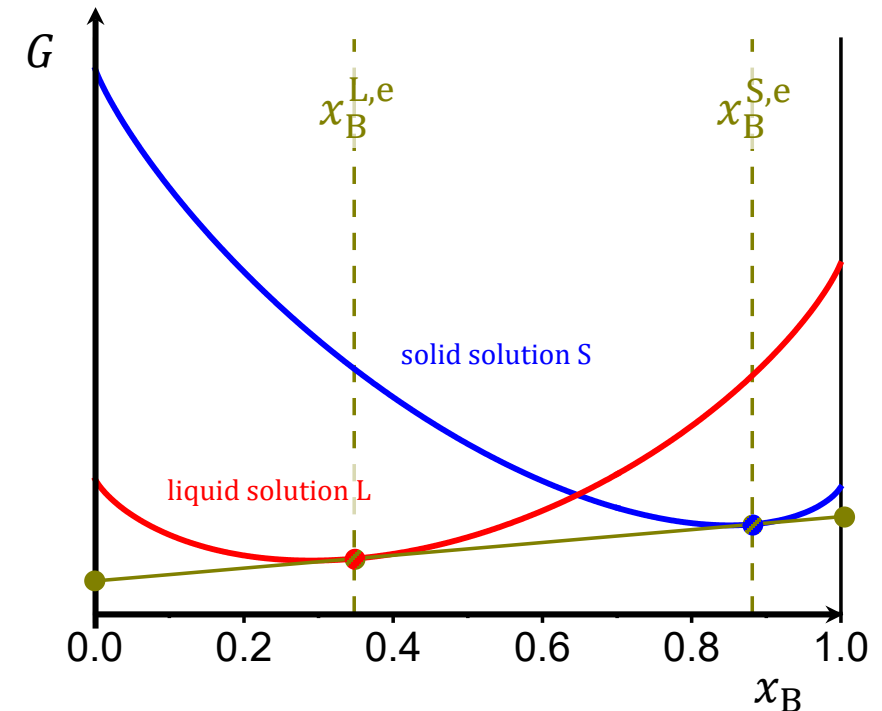
Version 24-01-23



- Solidification with Complete Miscibility
 - Impact of Interfaces
 - Boundary Conditions:
 - Fast Diffusion in both, the Liquid and the Solid
 - Fast Diffusion in the Liquid only
 - Limited Diffusion in both, the Liquid and the Solid

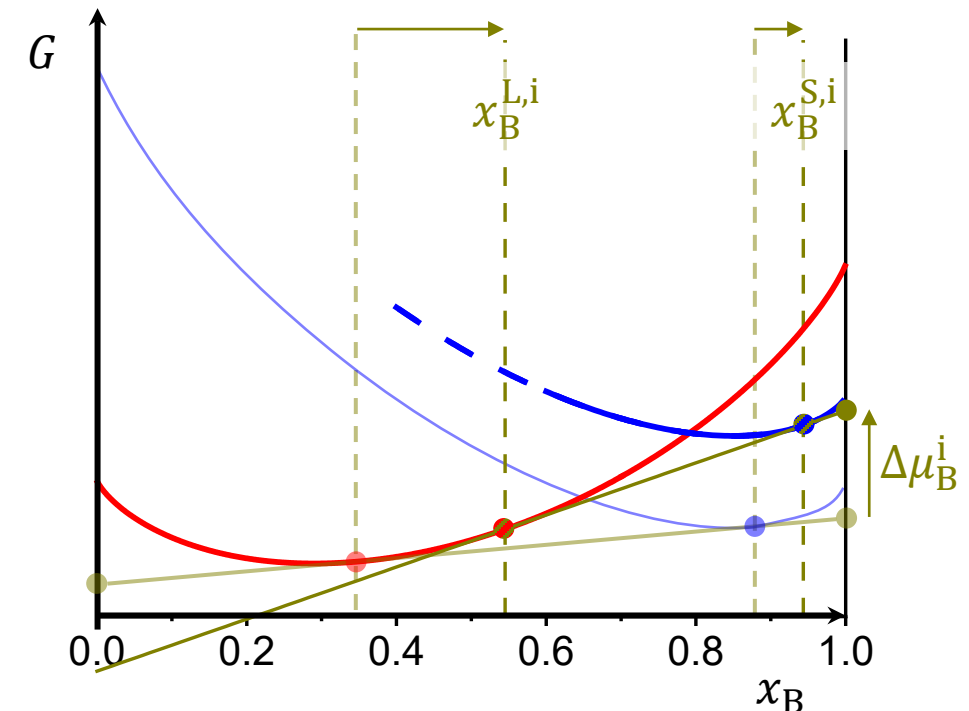
Impact of Interfaces

- In the two-phase region, the two phases in equilibrium are obtained by the common tangent to the G curves.
- For atoms are transferred from one phase into the other, an increase of chemical potential is observed due to the presence of the interface.



Impact of Interfaces

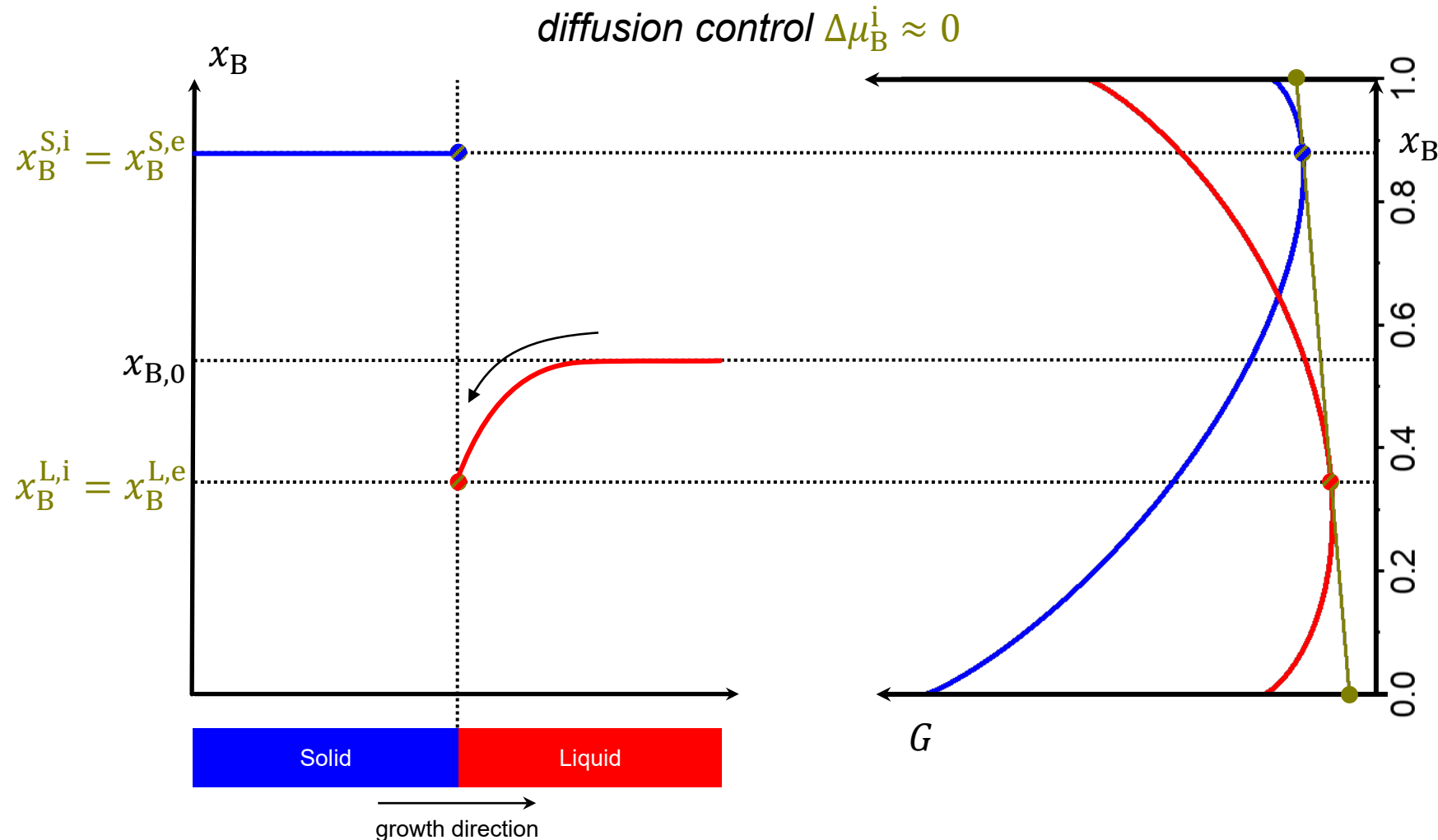
- In the two-phase region, the two phases in equilibrium are obtained by the common tangent to the G curves.
- For atoms are transferred from one phase into the other, an increase of chemical potential is observed due to the presence of the interface.



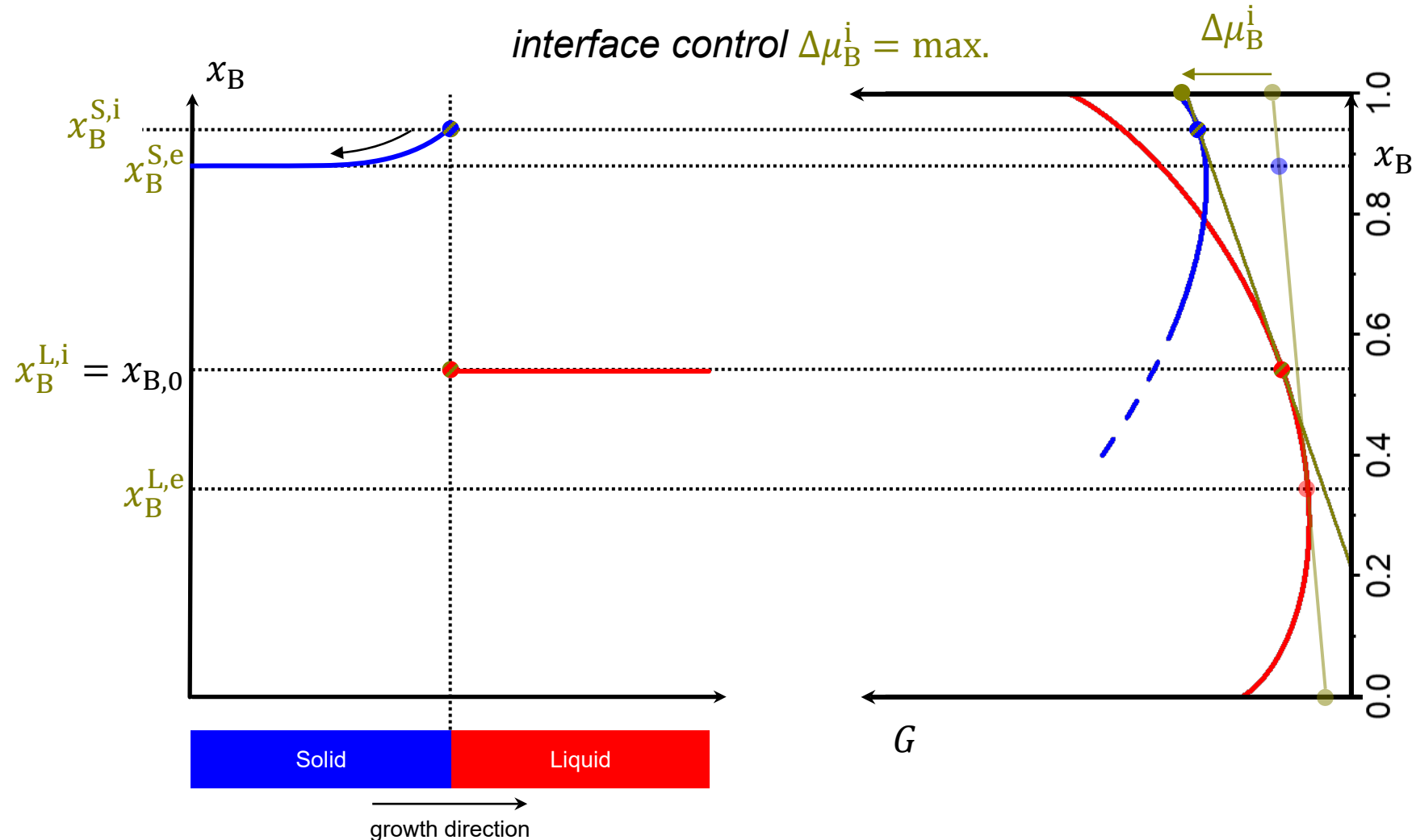
Impact of Interfaces

- 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 $x_B^{L,e}$ in the liquid.
 - (2) When $\Delta\mu_B^i$ is large (interface mobility is low, coherent interface), the situation is practically *interface-controlled* with $x_B^{L,i} = x_{B,0}$. A small concentration gradient in the solid occurs from $x_B^{S,i}$ to $x_B^{S,e}$.
 - (3) In reality, an intermediate situation is obtained.

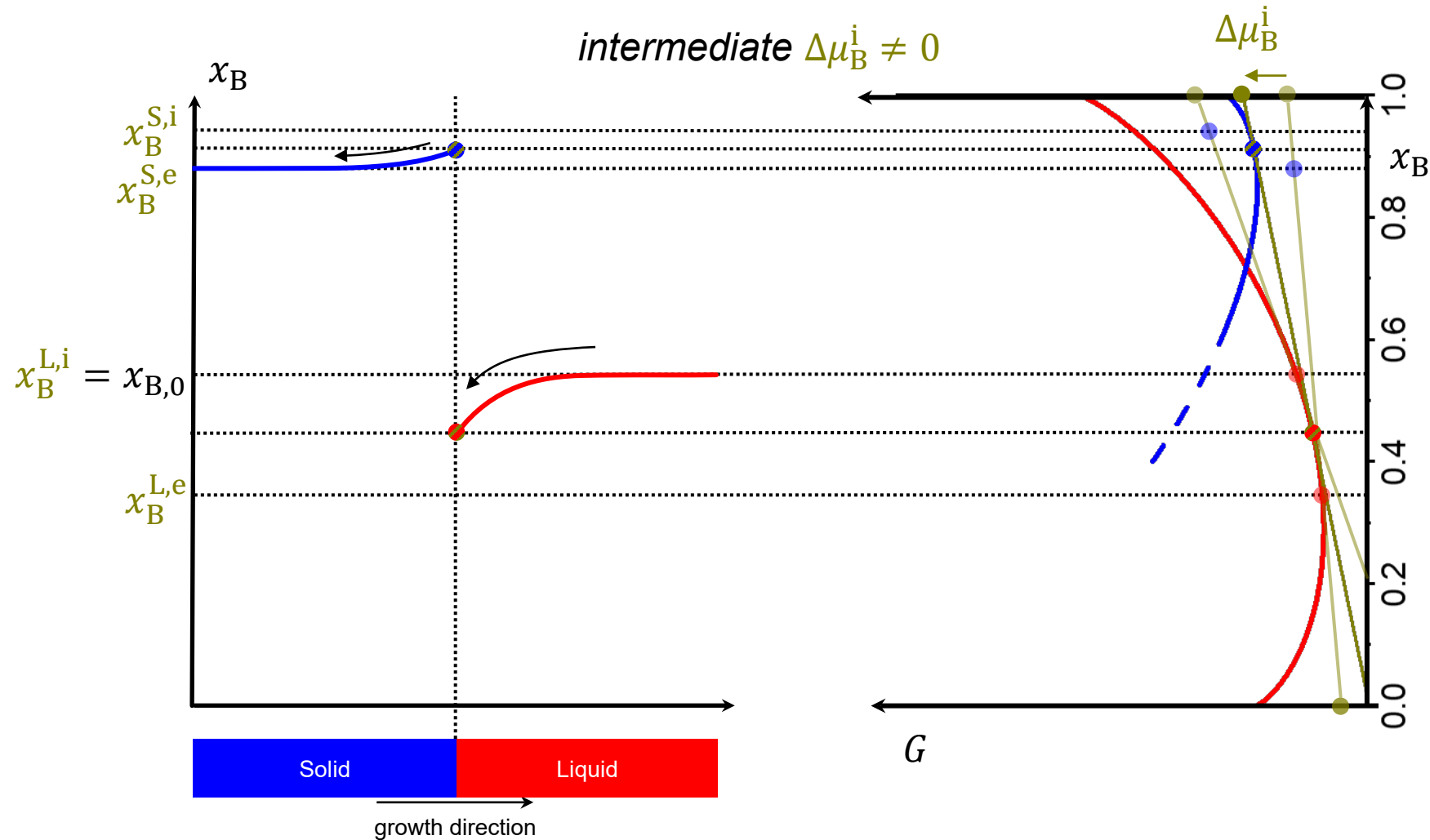
Impact of Interfaces – Case (1)



Impact of Interfaces – Case (2)



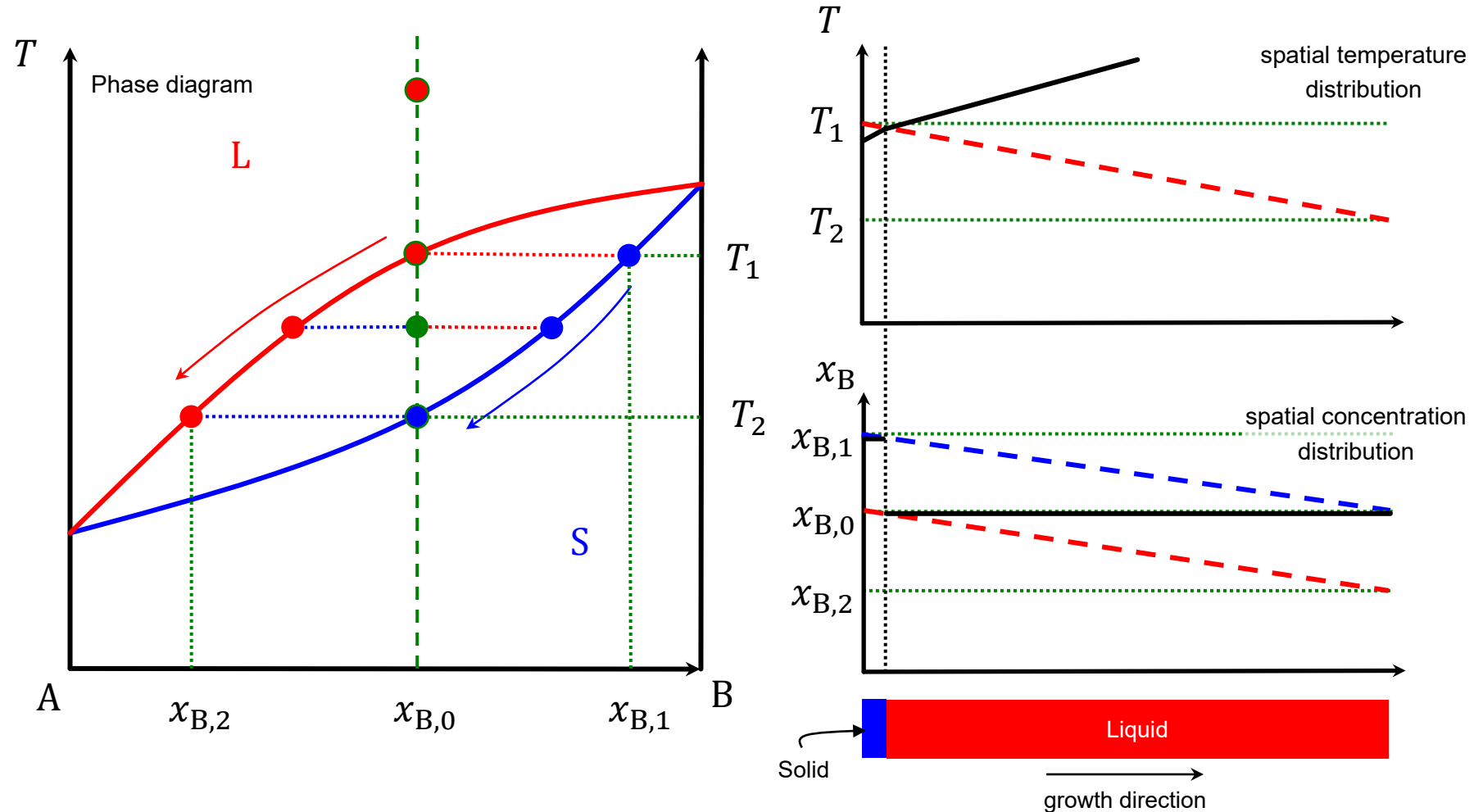
Impact of Interfaces – Case (3)



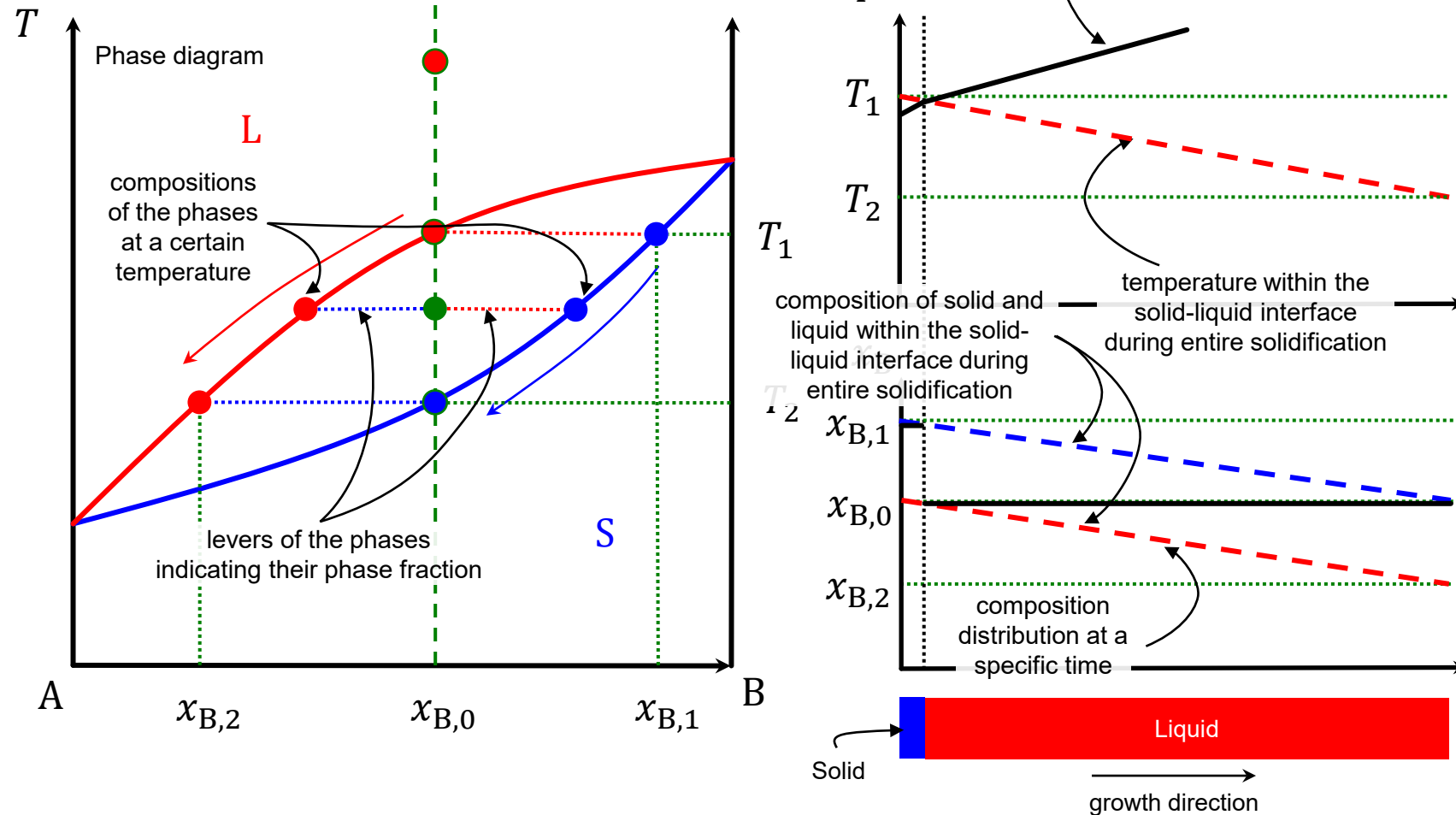
Impact of Diffusion

- In the following, we will discuss three important cases of solidification of miscible systems under the following considerations:
 - Close-to-equilibrium solidification (fast diffusion in liquid and solid, long time scales)
 - Limited diffusion in the solid (segregation)
 - Limited diffusion in both, the liquid and the solid (constitutional super cooling)
- For simplification, we assume the other relevant aspects to be simple:
 - a planar solidification front (see Ch. 3b)
 - heat transfer through the solid
(stable solidification condition for pure elements, see Ch. 3b)
 - the impact of the interface energy is neglected

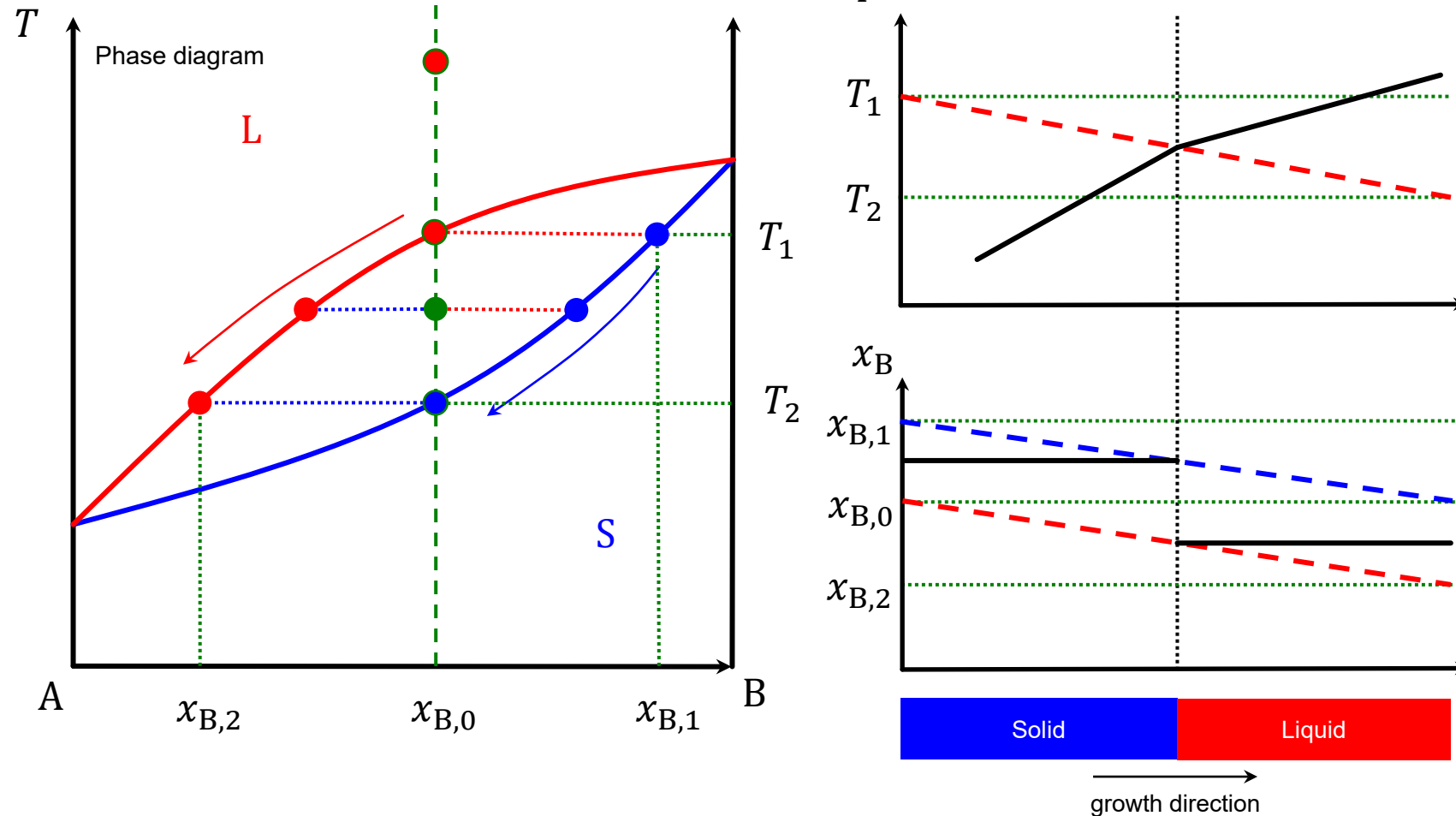
Solidification: Close-to-Equilibrium



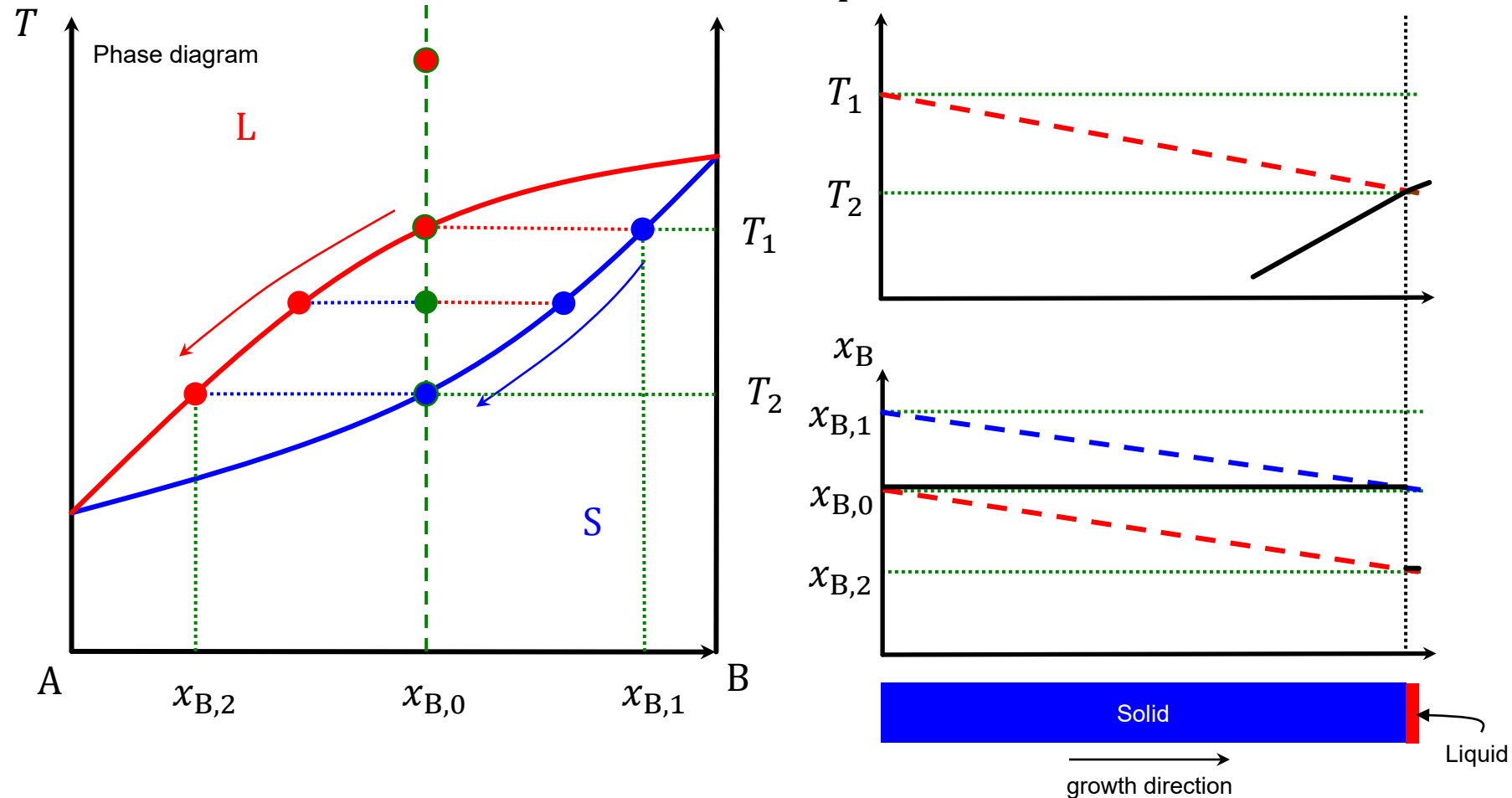
Solidification: Close-to-Equilibrium



Solidification: Close-to-Equilibrium



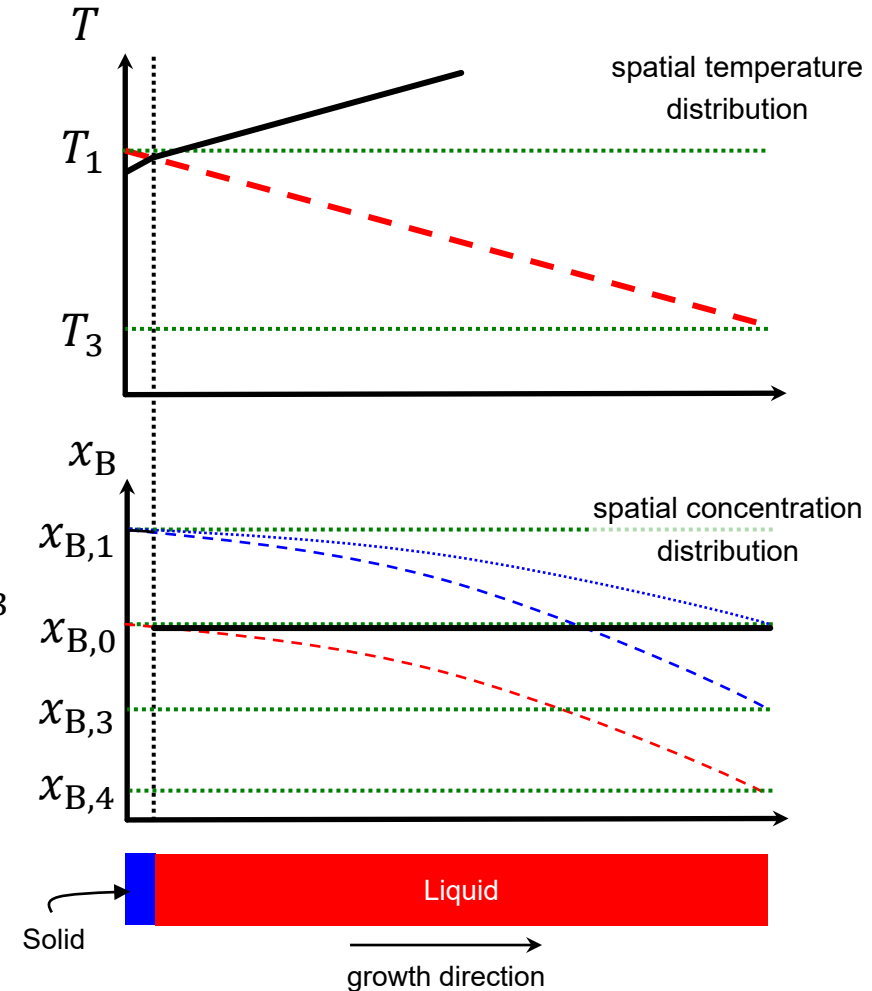
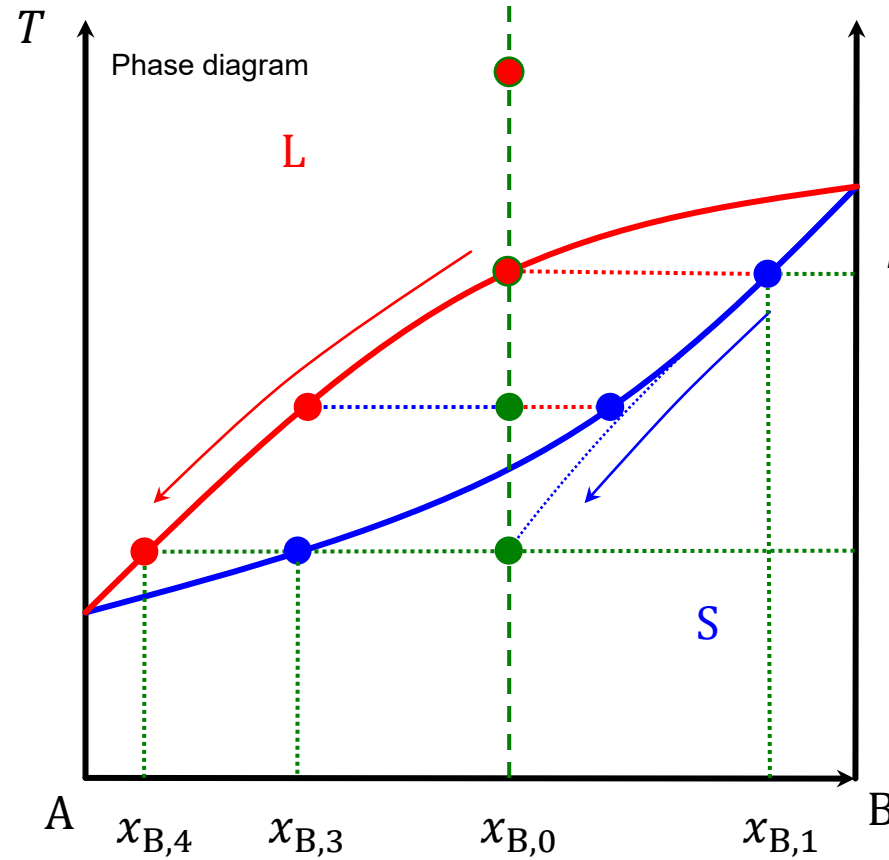
Solidification: Close-to-Equilibrium



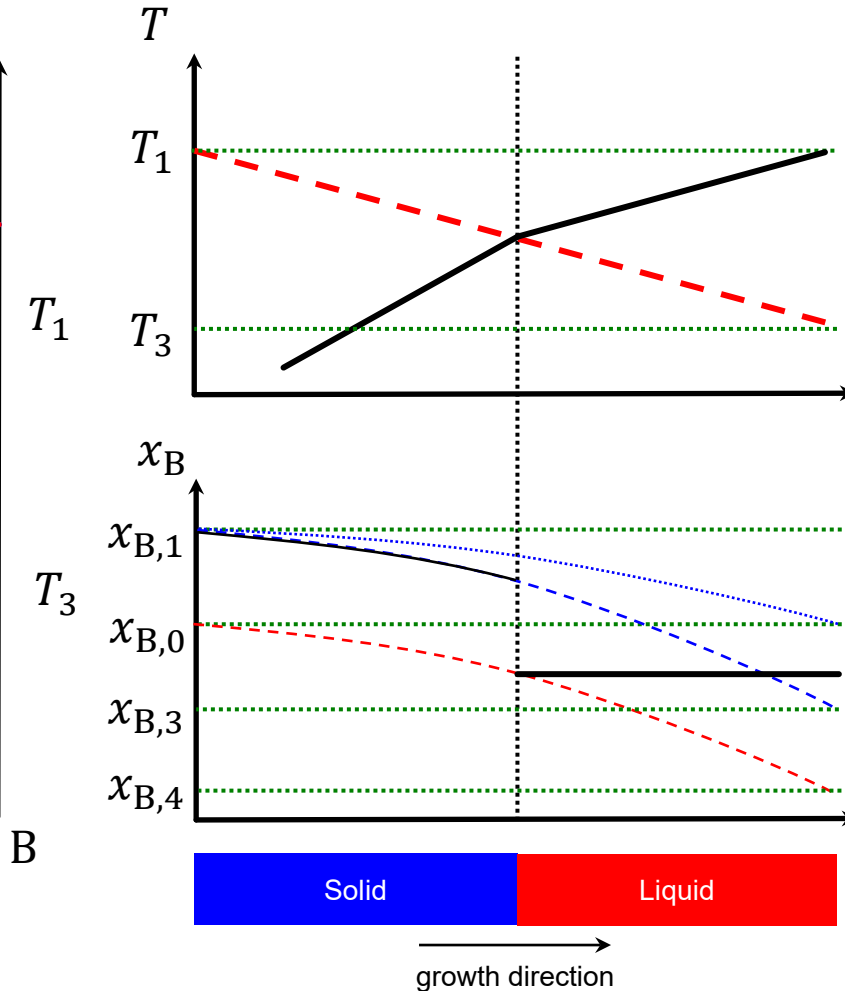
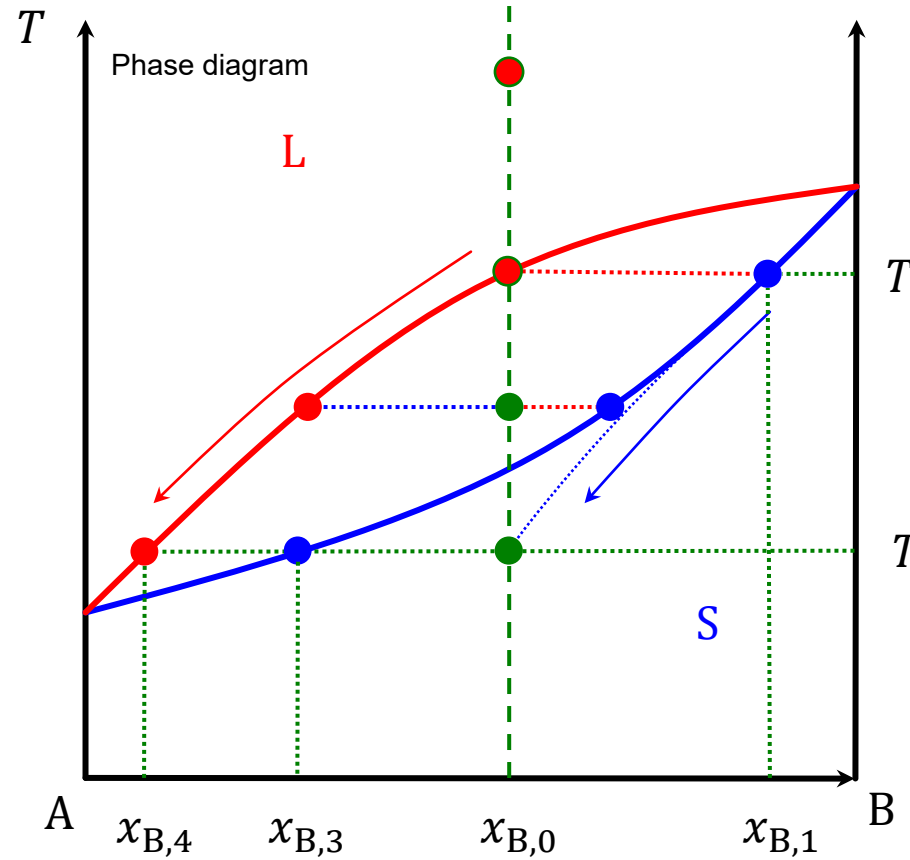
Solidification: Close-to-Equilibrium

- Solidification starts when nucleation is initiated below the liquidus temperature.
- The solid can grow into the liquid when heat is dissipated through the solid in a way that the temperature within the solidification front decreases. In the solid-liquid interface, the liquidus temperature is maintained.
- Fast diffusion and/or sufficient time allows for complete concentration equilibration in both phases. According to the liquidus and solidus temperature provided by the phase diagram, the composition of the liquid departs from and the composition of the solid approaches the alloy composition.
- Solidification is finished when the composition of the solid is the same as the alloy composition.

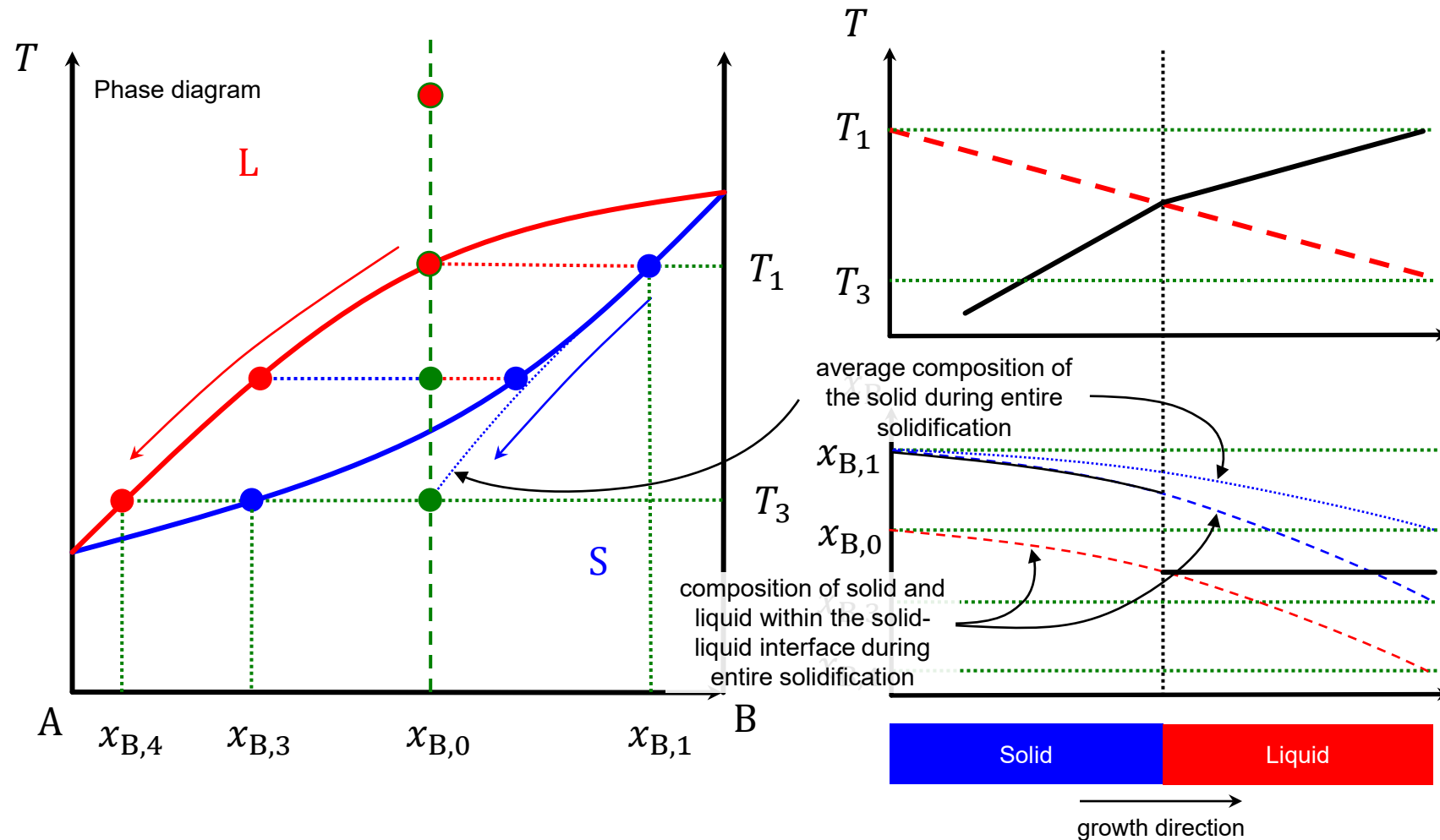
Solidification: Segregation



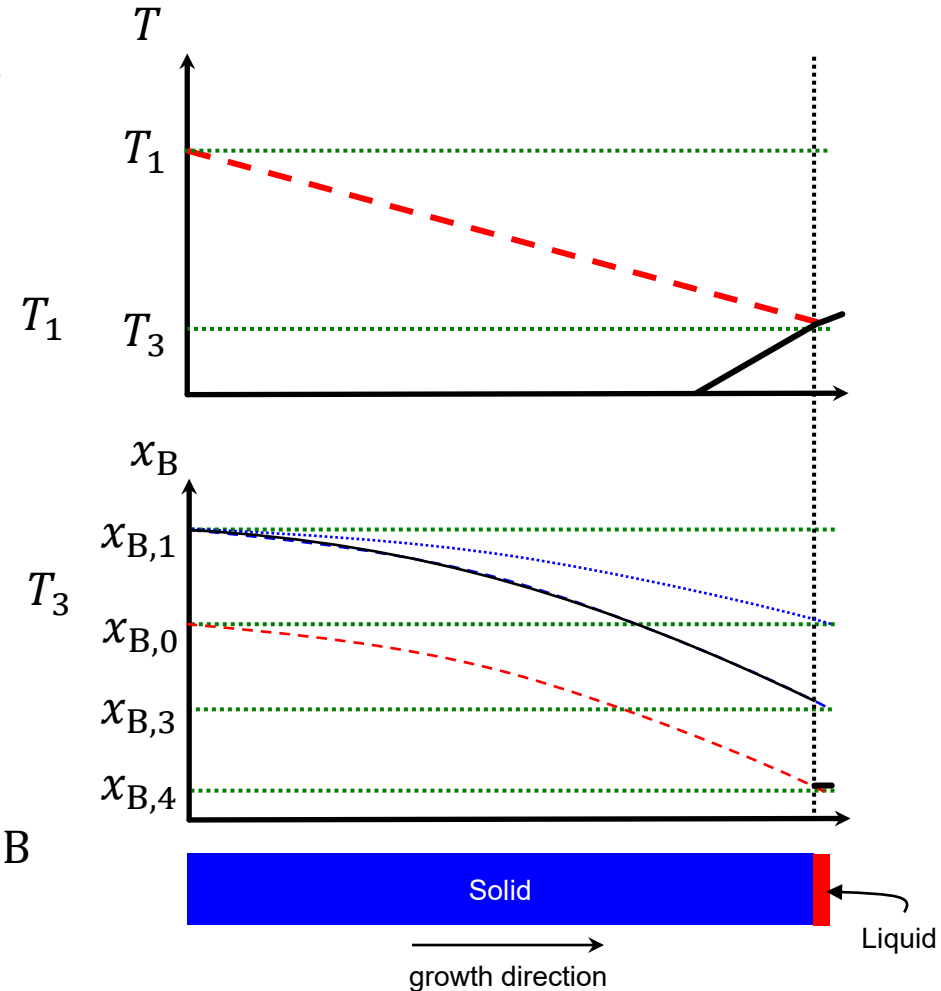
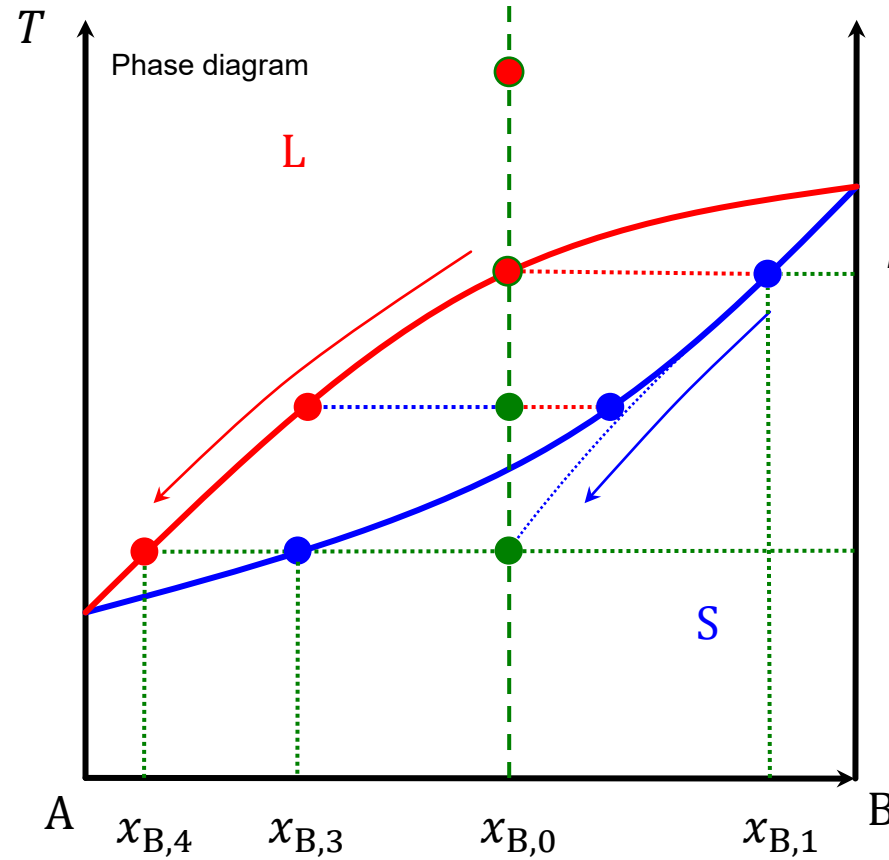
Solidification: Segregation



Solidification: Segregation



Solidification: Segregation

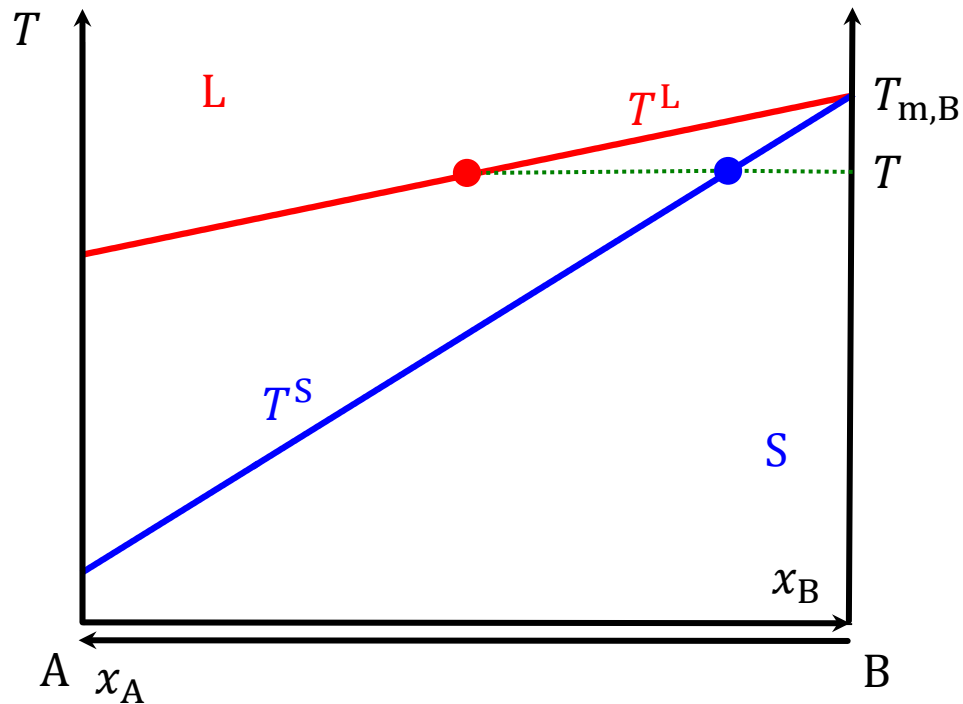


Solidification: Segregation

- Solidification starts when nucleation is initiated below the liquidus temperature.
- The solid can grow into the liquid when heat is dissipated through the solid in a way that the temperature within the solidification front decreases. In the solid-liquid interface, the liquidus temperature is maintained.
- Fast diffusion allows for complete concentration equilibration in the liquid. According to solidus line some portion of new solid is formed with the equilibrium composition. There is no equilibration of the composition within the solid. A concentration gradient in the solid builds up.
- Solidification is finished when the total composition of the solid is the same as the alloy composition. Complete solidification is obtained at lower temperatures than for equilibrium conditions.

Solidification: Segregation

- The situation can be simplified by the using the Scheil scheme:



- We consider linear liquidus and solidus lines with:

$$T^L = T_{m,B} - k m x_A^L$$

$$T^S = T_{m,B} - m x_A^S$$

- In the interface between liquid and solid a certain temperature might be achieved (thermal equilibrium) with:

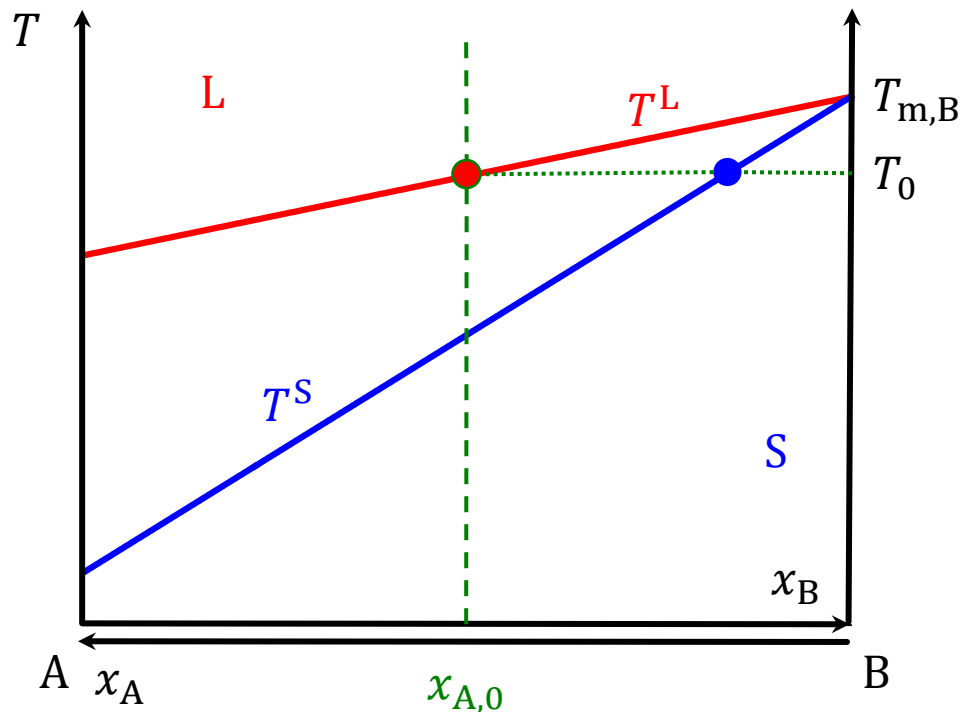
$$T = T^L = T^S$$

$$T_{m,B} - k m x_A^L = T_{m,B} - m x_A^S$$

$$k = \frac{x_A^S}{x_A^L} < 1 = \text{const.}$$

Solidification: Segregation

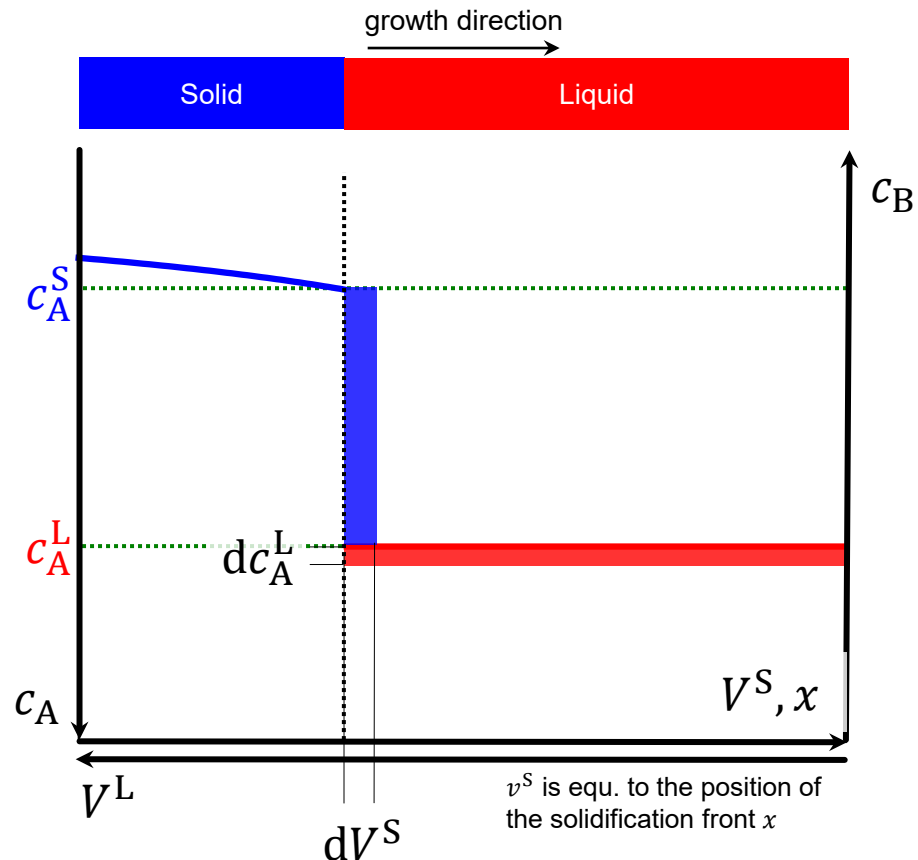
- The situation can be simplified by the using the Scheil scheme:



- When solidification of an alloy of $x_{A,0}$ starts at T_0 , the composition of the liquid is $x_A^L = x_{A,0}$ and the volume fractions of the two phases are $v^L = 1$ and $v^S = 0$.
- The composition of the solid is $x_A^S = k x_{A,0}$ at T_0 .

Solidification: Segregation

- The situation can be simplified by the using the Scheil scheme:



- A concentration gradient in the solid builds up. The liquid remains homogenous.
- For the formation of a small portion of solid dV^S , $(c_A^L - c_A^S) dV^S$ atoms are repelled to the liquid and enrich the liquid. dc_A^L is distributed along V^L .
- Both needs to be balanced by:

$$(c_A^L - c_A^S) dV^S = V^L dc_A^L$$

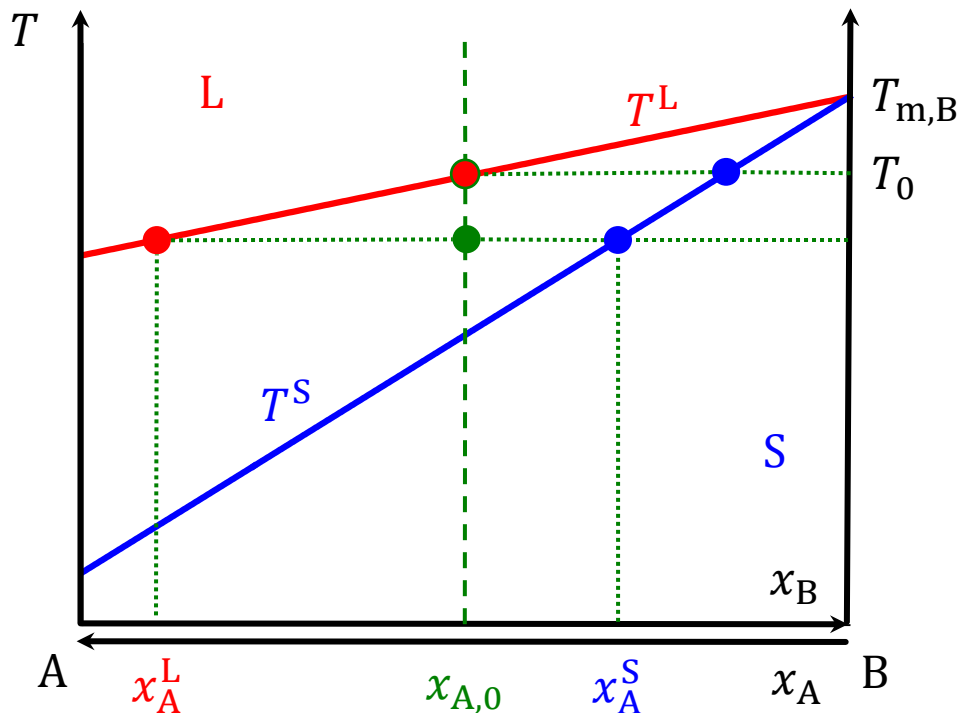
- Considering the different molar volumes yields:

$$\left(\frac{x_A^L}{V_m^L} - \frac{x_A^S}{V_m^S} \right) \frac{dV^S}{V} = \frac{V^L}{V} \frac{dx_A^L}{V_m^L}$$

$$\left(\frac{x_A^L}{V_m^L} - \frac{x_A^S}{V_m^S} \right) dv^S = v^L \frac{dx_A^L}{V_m^L}$$

Solidification: Segregation

- The situation can be simplified by the using the Scheil scheme:



- The molar volumes might be approximated the same $V_m^L \approx V_m^S$:

$$(x_A^L - x_A^S) dv^S \approx v^L dx_A^L$$

- Following integration can be performed with $x_A^S = k x_A^L$:

$$(x_A^L - x_A^S) dv^S = (1 - v^S) dx_A^L$$

$$\frac{dv^S}{1 - v^S} = \frac{dx_A^L}{x_A^L (1 - k)}$$

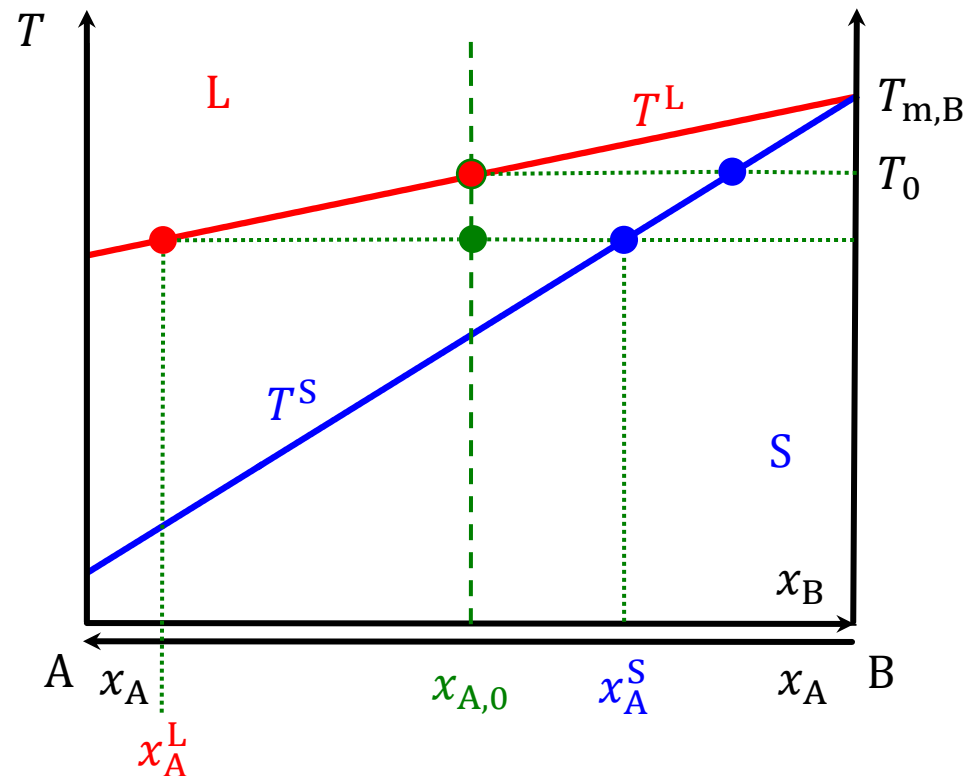
$$\int_0^{v^S} \frac{dv^S}{1 - v^S} = \frac{1}{1 - k} \int_{x_{A,0}}^{x_A^L} \frac{dx_A^L}{x_A^L}$$

$$[-\ln(1 - v^S)]_0^{v^S} = \frac{1}{1 - k} [\ln x_A^L]_{x_{A,0}}^{x_A^L}$$

$$(k - 1) \ln v^L = \ln \frac{x_A^L}{x_{A,0}}$$

Solidification: Segregation

- The situation can be simplified by the using the Scheil scheme:



- Hence, the composition of the liquid develops with:

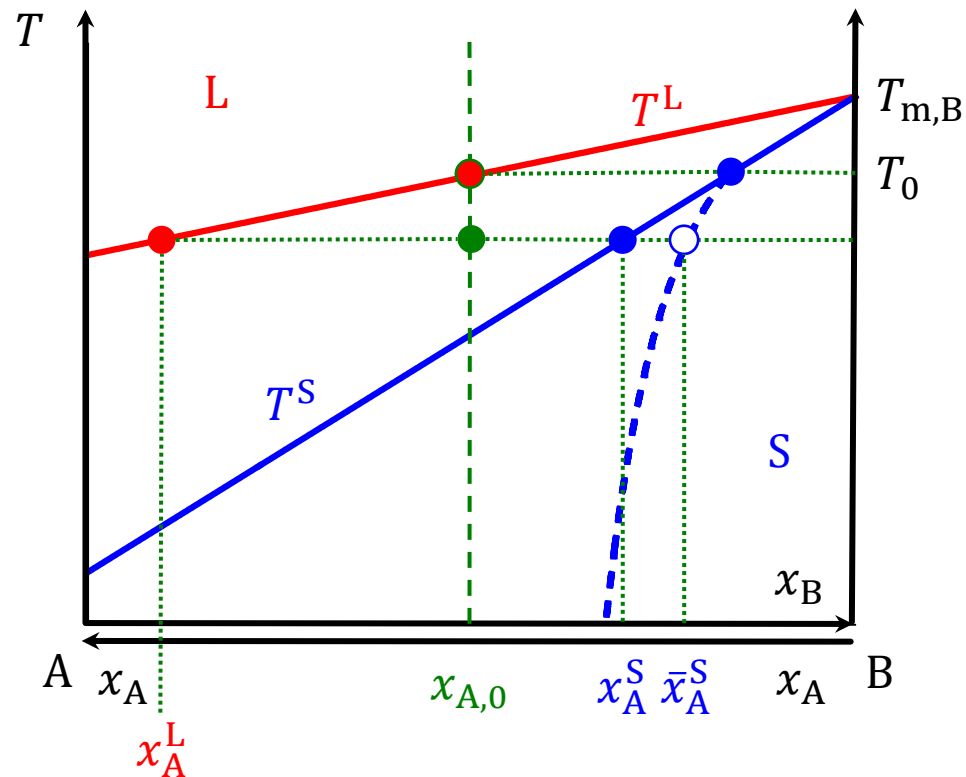
$$x_A^L = x_{A,0} v^{L^{k-1}}$$

- The small solidifying portion of solid has a composition of:

$$x_A^S = k x_A^L = k x_{A,0} (1 - v^S)^{k-1}$$

Solidification: Segregation

- The situation can be simplified by the using the Scheil scheme:



- The total number of particles in the system remains constant:

$$n_A^S + n_A^L = n_A^0$$

$$c_A^S V^S + c_A^L V^L = c_{A,0} V$$

$$\frac{\bar{x}_A^S}{V_m^S} v^S + \frac{x_A^L}{V_m^L} v^L = \frac{x_{A,0}}{V_m^0}$$

- Considering similar molar volumes $V_m^S \approx V_m^L \approx V_m^0$:

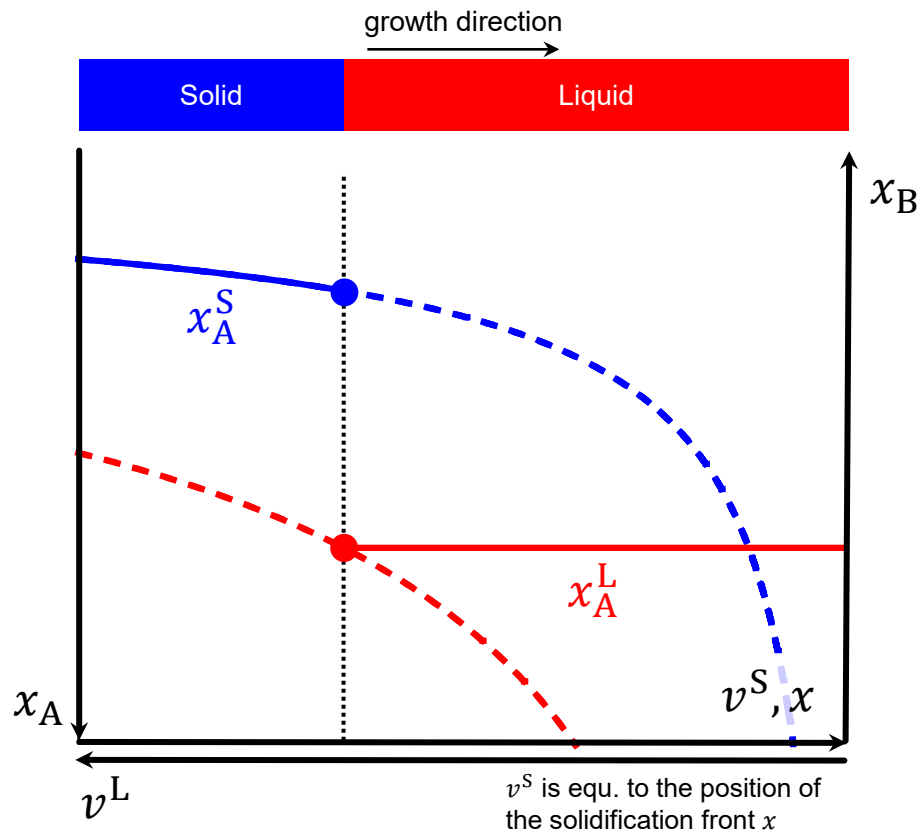
$$\bar{x}_A^S v^S + x_A^L v^L = x_{A,0}$$

- The total composition of the (inhomogeneous) solid is:

$$\bar{x}_A^S = \frac{x_{A,0} - x_A^L v^L}{v^S}$$

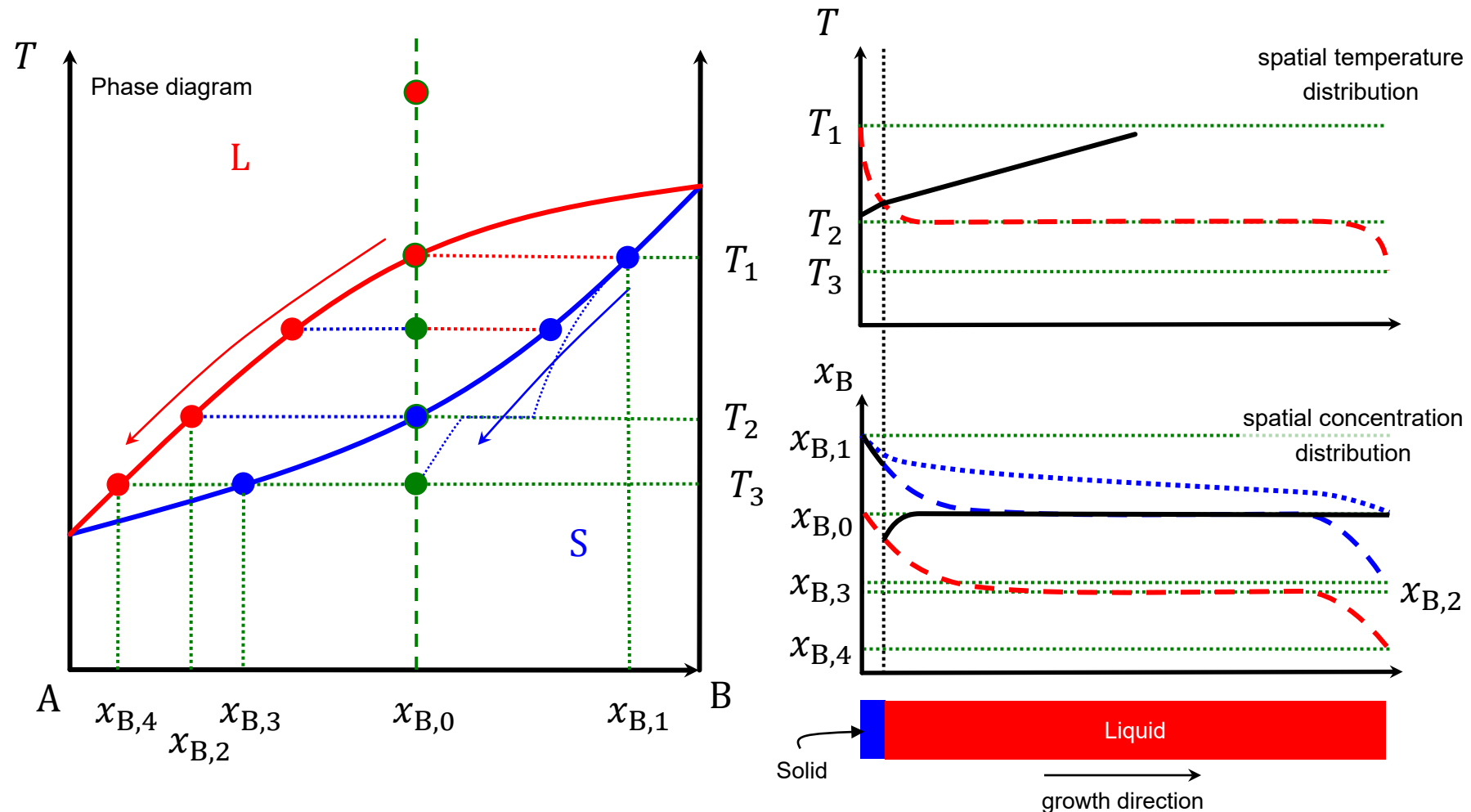
Solidification: Segregation

- The situation can be simplified by the using the Scheil scheme:



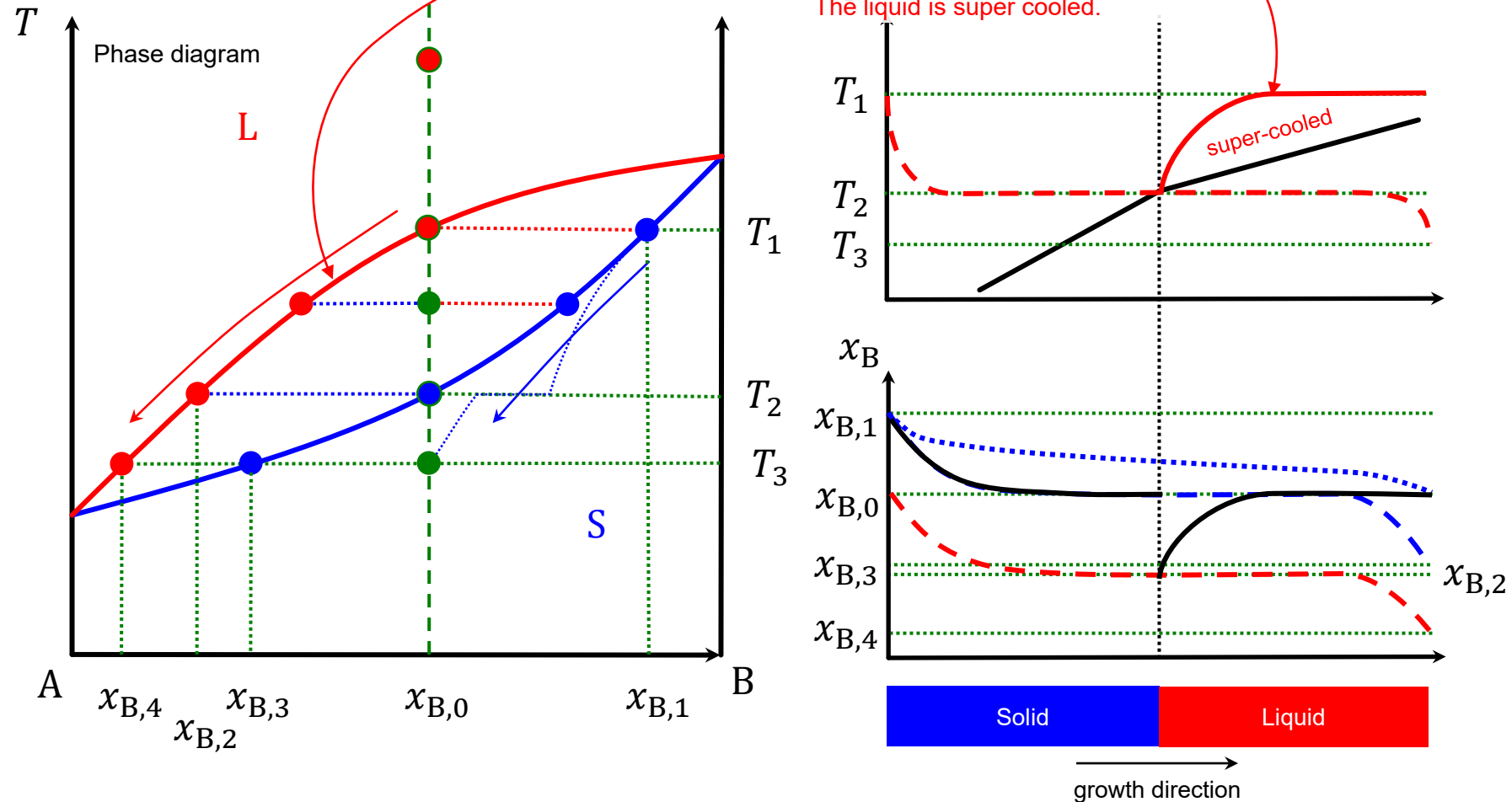
- Note that solidification under these simple assumptions is stopped by reaching an invariant reaction (immediate solidification of the liquid), e.g. solidification of pure A or a eutectic reaction.
- In reality, k becomes closer to 1, slowing down the reaction in the end of solidification.

Solidification: Constitutional Super Cooling

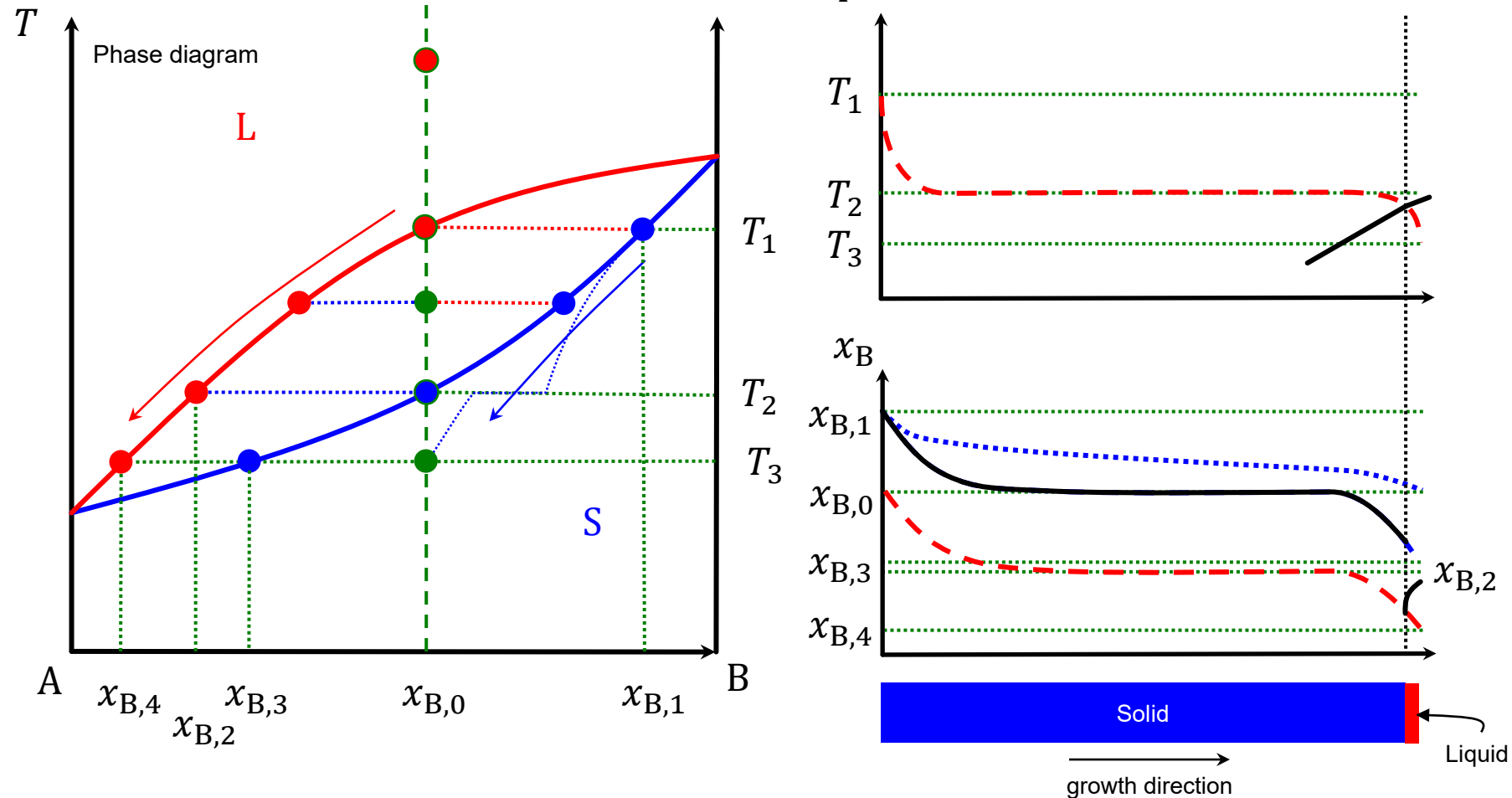


Solidification: Constitutional Super Cooling

Liquidus temperature of the liquid according to the composition profile. Note that the actual temperature is lower than the liquidus temperature. The liquid is super cooled.



Solidification: Constitutional Super Cooling

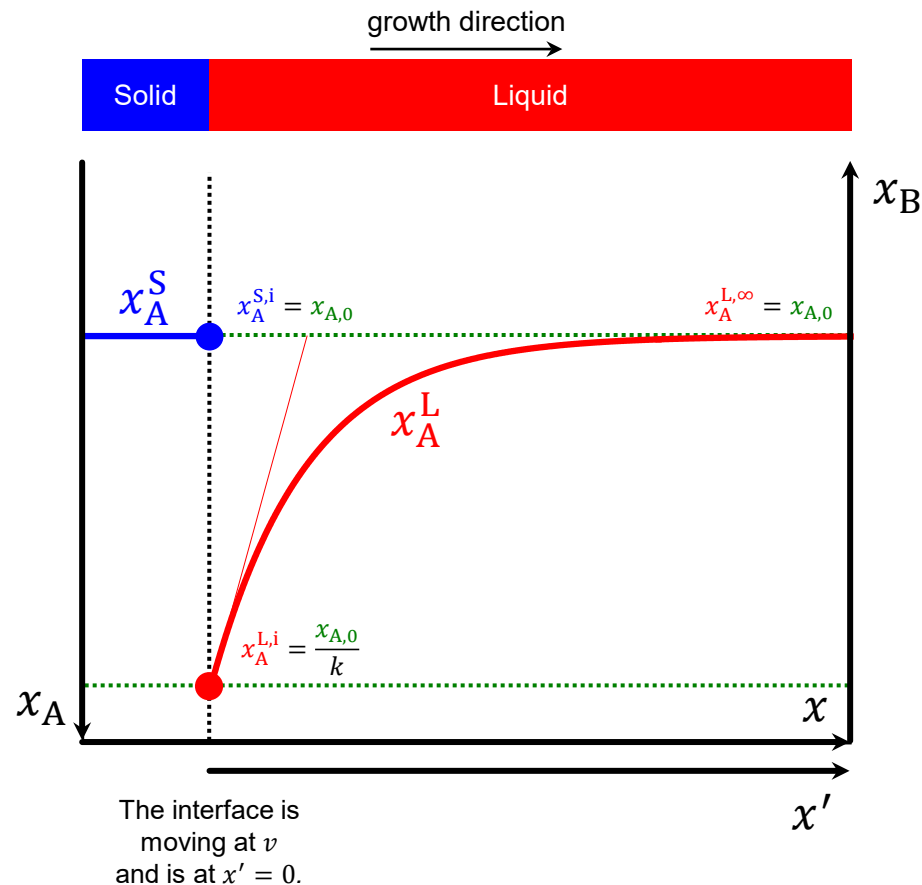


Solidification: Constitutional Super Cooling

- There is no equilibration in both phases, the solid and the liquid.
- Due to the formation of B rich solid from the liquid, a significant depletion in B occurs in the liquid ahead of the solidification front.
- A stationary condition is obtained at $T = T_2 = \text{const.}$ when the solidifying solid has the alloy composition $x_{B,0}$. The composition of the liquid at the solidification front is $x_{B,2}$.
- The composition gradient in the liquid can drive the solidification progress. Note that the actual temperature of the liquid can be lower than the corresponding liquidus temperature according to the position-depending composition in the liquid. If the temperature gradient is small, the liquid is super cooled. Even for the case of heat transfer through the liquid, the solidification front becomes unstable and dendritic growth occurs.

Solidification: Constitutional Super Cooling

- The steady-state can be approximated by:



- The diffusion flux ahead of the *moving* solidification front within the liquid need to transport away the solutes:

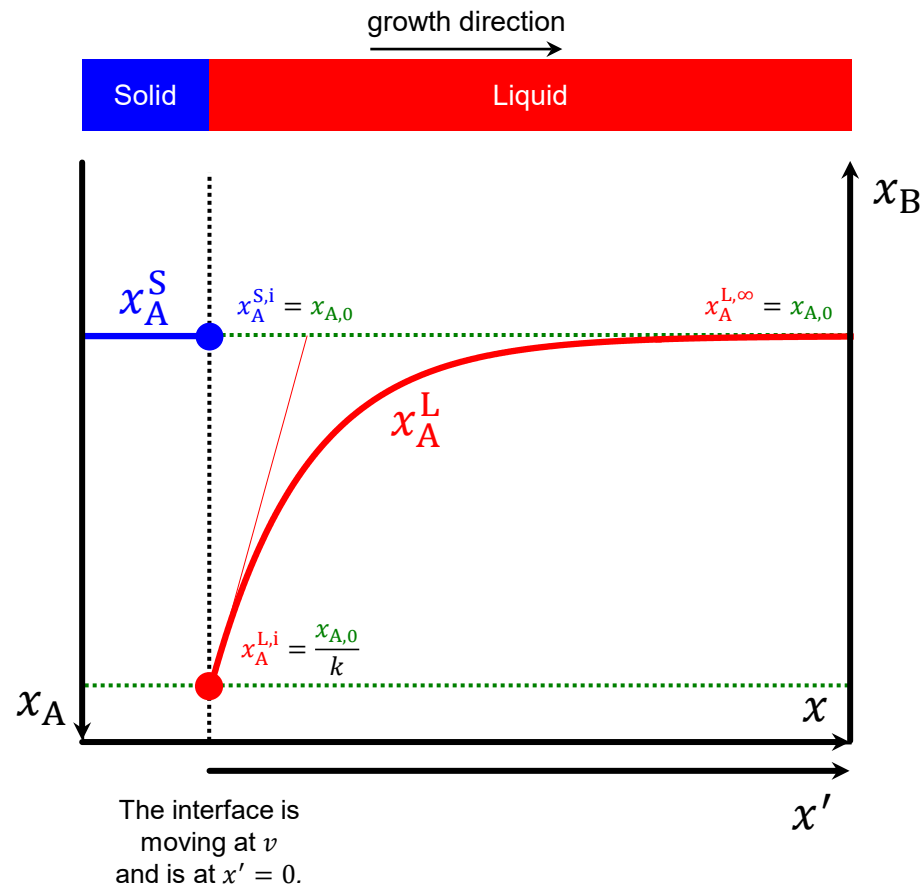
$$j_A^i = -D_A \left. \frac{dc_A^L}{dx'} \right|^i = v (c_A^{L,i} - c_A^{S,i})$$

- The molar volumes might again be considered same $V_m^S \approx V_m^L$:

$$\begin{aligned} -D_A \left. \frac{dx_A^L}{dx'} \right|^i &= v (x_A^{L,i} - x_A^{S,i}) \\ &= v \frac{k-1}{k} x_{A,0} \end{aligned}$$

Solidification: Constitutional Super Cooling

- The steady-state can be approximated by:



- Solving the stationary diffusion equation in the *moving* coordinate system can be obtained by the following transform:

$$x = x' + v t$$

$$\frac{d}{dx'} = \frac{d}{dx}$$

$$\frac{d}{dt} = v \frac{d}{dx}$$

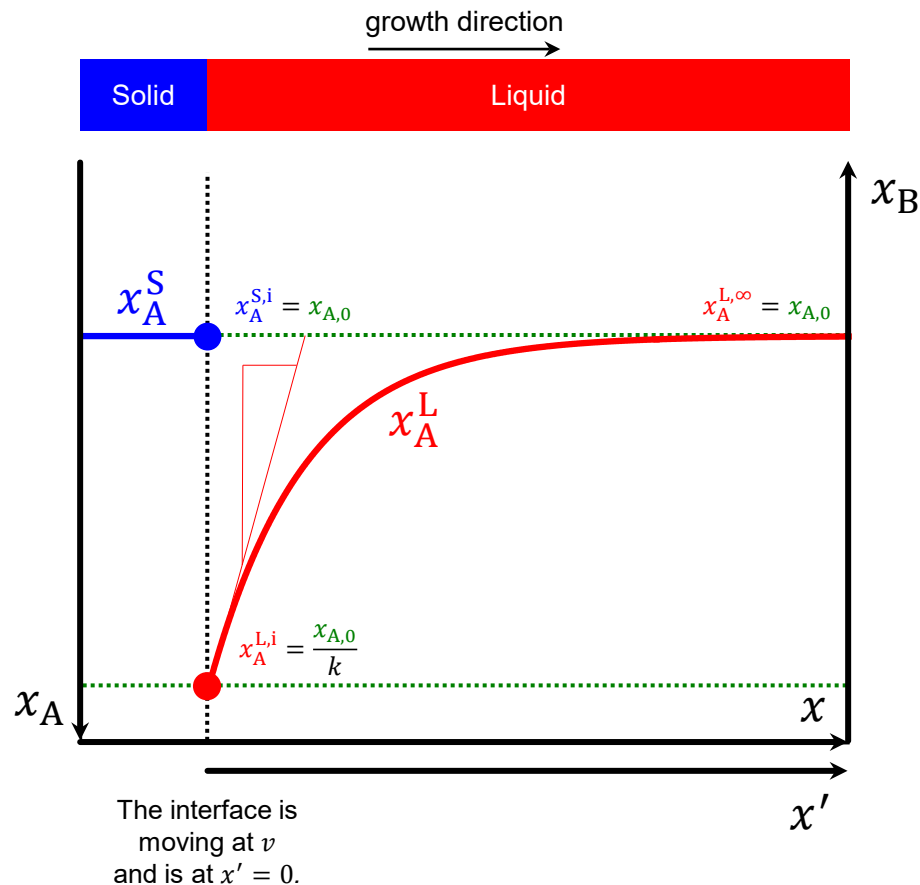
- The diffusion equation changes:

$$\frac{\partial c_A}{\partial t} = D_A \Delta c_A$$

$$\frac{\partial c_A}{\partial x'} = \frac{D_A}{v} \frac{\partial^2 c_A}{\partial x'^2}$$

Solidification: Constitutional Super Cooling

- The steady-state can be approximated by:



- Following solution can be obtained:

$$x_A^L(x') = x_{A,0} \left(1 + \frac{1-k}{k} \exp - \frac{x'}{D_A/v} \right)$$

- It meets the boundary conditions:

$$x_A^L(x' = 0) = x_A^{L,i} = \frac{x_{A,0}}{k}$$

$$x_A^L(x' \rightarrow \infty) = x_{A,0}$$

$$\frac{dx_A^L}{dx'}(x' = 0) = \left. \frac{dx_A^L}{dx} \right|^i = \frac{v}{D_A} \frac{k-1}{k} x_{A,0}$$

Note that still $k < 1$.

Solidification: Constitutional Super Cooling

- The steady-state can be approximated by:

