Karlsruhe Institute of Technology

IAM
Institute for Applied Materials

Phase Transformations in Materials

Lecture for “Mechanical Engineering” and “Materials Science and Engineering”
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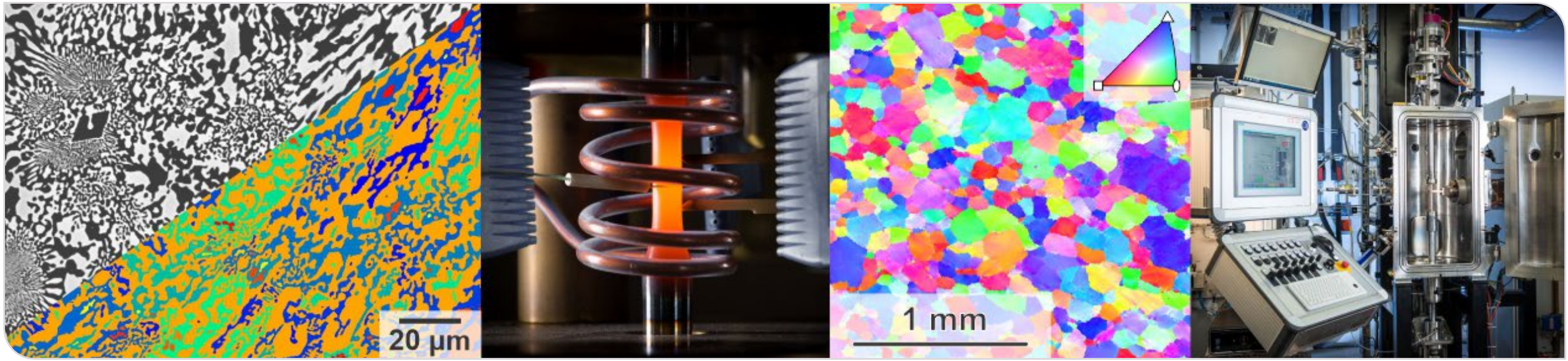
Version 24-01-14



Topics

- Spinodal Decomposition (Miscibility Gap)
  - Regular Solutions with $\Delta H_{\mathrm{mix}} \neq 0$
  - Order, Clustering, Decomposition
  - Extrema of the Liquidus Line
  - Miscibility Gap
  - Continuous and Discontinuous Decomposition

Thermodynamic Considerations

- As seen in Ch. 4a, G of the alloy can be obtained based on a linear superposition of the G of the individual elements, G_A and G_B, and an excess term ΔG^mix:

$$G = x_\mathrm{A}\, G_\mathrm{A} + x_\mathrm{B}\, G_\mathrm{B} + \Delta G^\mathrm{mix}$$

- ΔG^mix refers to ΔH^mix and ΔS_mix, when comparing the condition of separated elements A and B and randomly mixed A and B:

$$\Delta G^\mathrm{mix} = \Delta H^\mathrm{mix} - T\,\Delta S^\mathrm{mix}$$

- For **regular solutions**, we consider $\Delta H^\mathrm{mix} \neq 0$.

Thermodynamic Considerations

- An estimate might be to consider the change of internal energy by the different (nearest neighbor) bond energies U_{ij} depending on the binding partner:

$$U = N_{\mathrm{AA}} \cdot U_{\mathrm{AA}} + N_{\mathrm{BB}} \cdot U_{\mathrm{BB}} + N_{\mathrm{AB}} \cdot U_{\mathrm{AB}}$$

- Note that $U_{ij} < 0$ and a stronger bond is achieved for a more negative U_{ij}. In order to remove atoms from the bond, the energy of the system increases to zero.
- As for the configurational entropy, the change in internal energy by the mixing process needs to be consider to obtain $\Delta H^{\mathrm{mix}} = \Delta U^{\mathrm{mix}}\big|_p$.

Thermodynamic Considerations

- When the elements are separated in a 2D cubic crystal (Kossel crystal with the coordination number $z = 4$ and a binding energy of U_{ij}), it amounts to:

$$U^{\text{separat}} = \frac{1}{2}\, x_{\text{A}}\, z\, N \cdot U_{\text{AA}} + \frac{1}{2}\, x_{\text{B}}\, z\, N \cdot U_{\text{BB}}$$

- For random mixing, $x_{\text{A}}\, x_{\text{B}}\, z\, N$ dissimilar bonds might be created:

$$U^{\text{mixed}} = \left(\frac{1}{2}\, x_{\text{A}}\, z\, N - \frac{1}{2} x_{\text{A}}\, x_{\text{B}}\, z\, N\right) \cdot U_{\text{AA}} + \left(\frac{1}{2}\, x_{\text{B}}\, z\, N - \frac{1}{2} x_{\text{A}}\, x_{\text{B}}\, z\, N\right) \cdot U_{\text{BB}} + x_{\text{A}}\, x_{\text{B}}\, z\, N \cdot U_{\text{AB}}$$

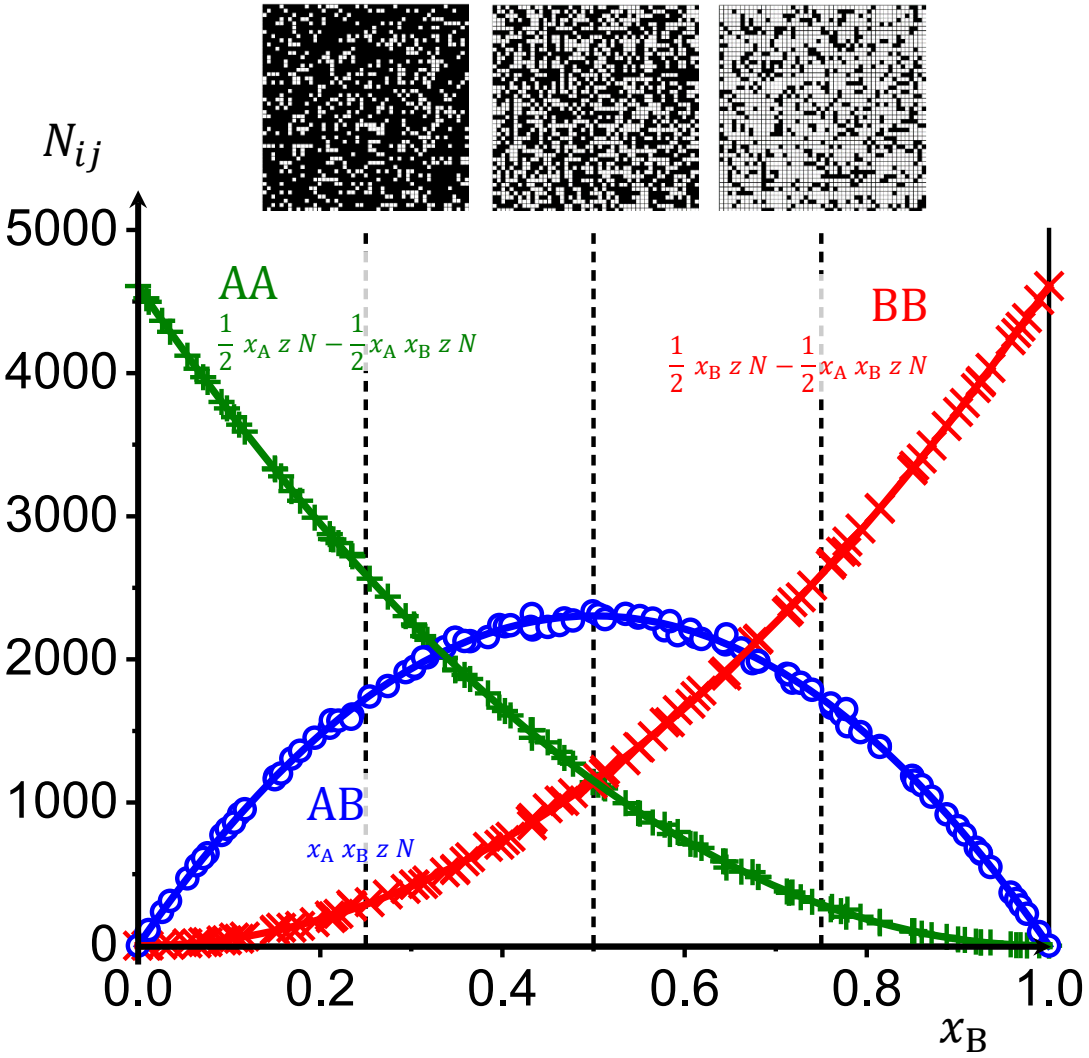
$$= \frac{1}{2}\, x_{\text{A}}\, z\, N \cdot U_{\text{AA}} + \frac{1}{2}\, x_{\text{B}}\, z\, N \cdot U_{\text{BB}} + x_{\text{A}}\, x_{\text{B}}\, z\, N \cdot \left(U_{\text{AB}} - \frac{1}{2}(U_{\text{AA}} + U_{\text{BB}})\right)$$

- Hence,

$$\Delta H^{\text{mix}} = \Delta U^{\text{mix}}\Big|_p = z\, N \cdot\, x_A\, x_B \cdot \left(U_{\text{AB}} - \frac{1}{2}(U_{\text{AA}} + U_{\text{BB}})\right) = z\, N \cdot x_A\, x_B \cdot \varepsilon$$

Number of Bonds in Random Solutions

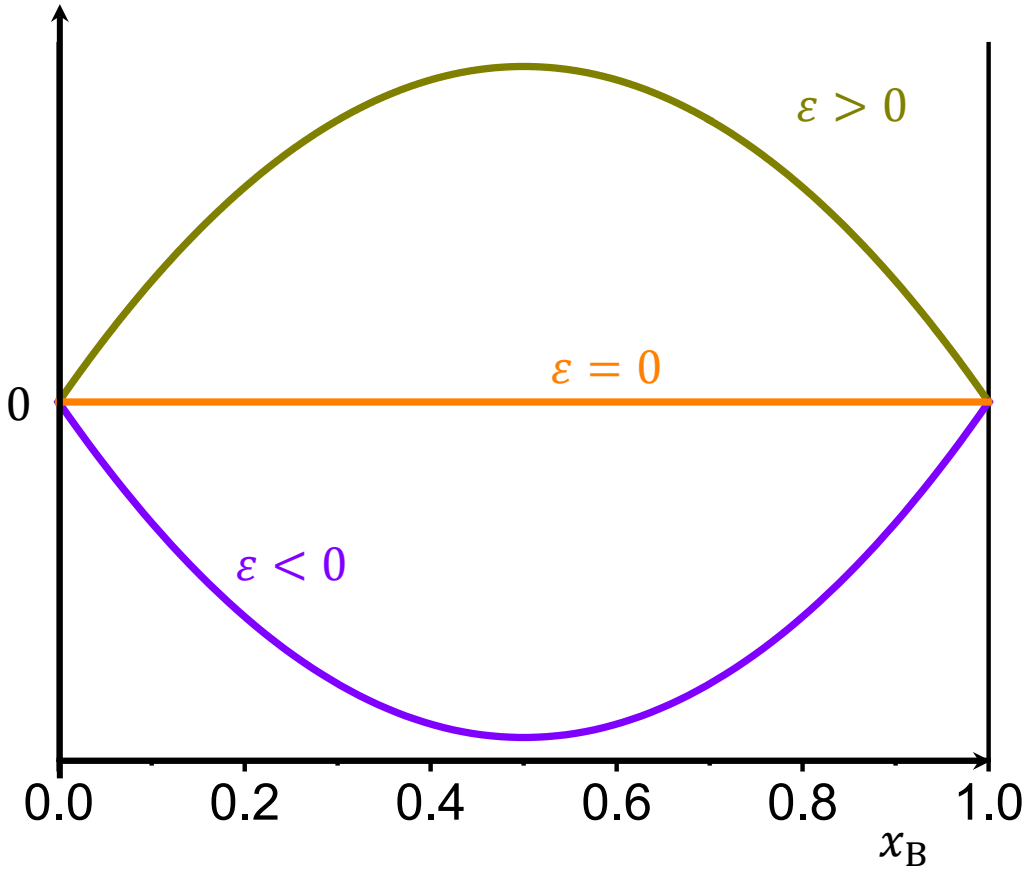
Computer generated arrangements of $N = 2304$ atoms and for $z = 4$



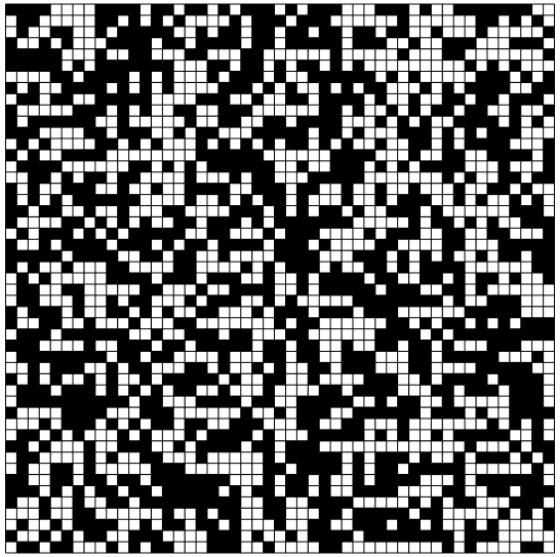
Thermodynamic Considerations

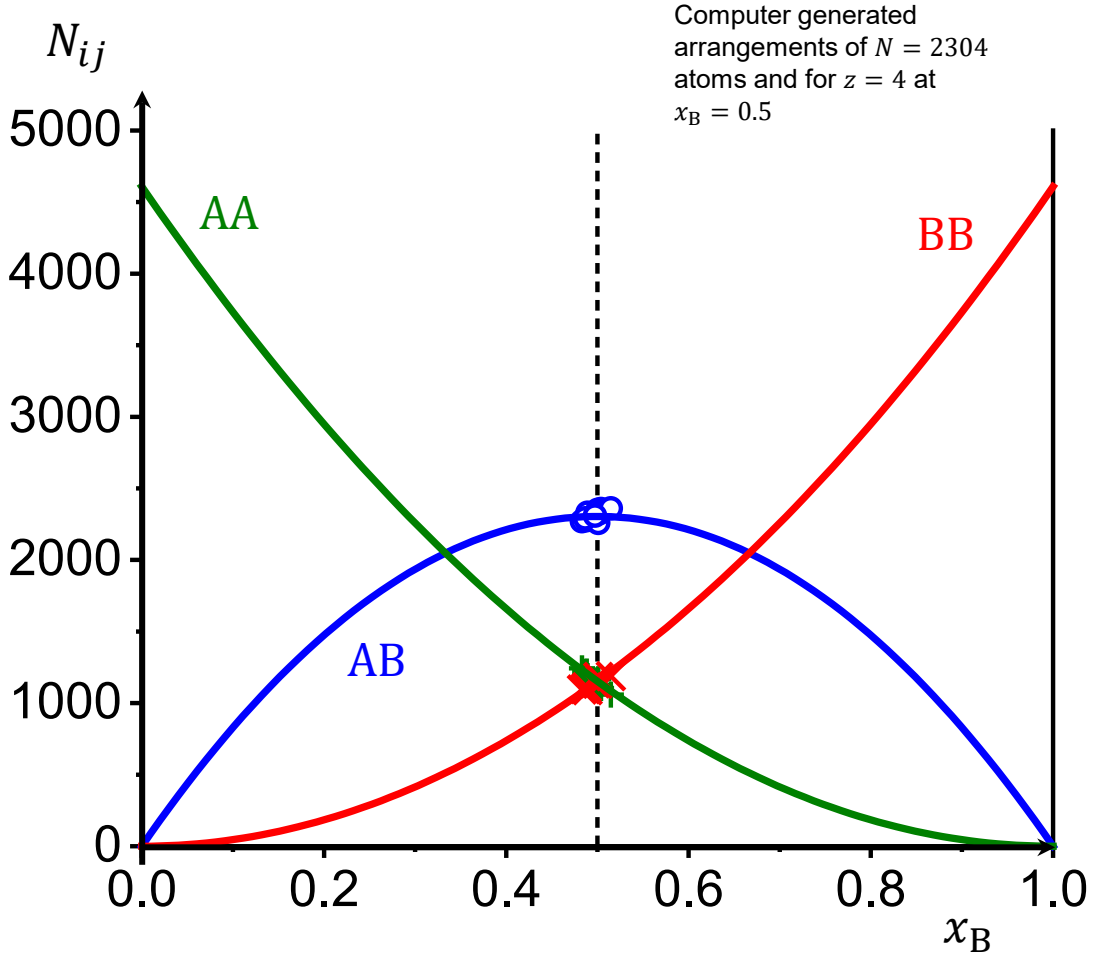
$$\Delta H^{\text{mix}} \propto \varepsilon\, x_{\text{A}}\, x_{\text{B}} = \varepsilon\, x_{\text{A}}(1 - x_{\text{B}})$$

- $\varepsilon = 0$:
  - ideal solution when no preferred interaction occurs and all bonds are of equal binding energy
  - random solutions
- $\varepsilon < 0$:
  - the mixing occurs endothermic with heat consumption and unequal AB bonds are preferred
  - U_{AB} is more negative than $\frac{1}{2}(U_{\text{AA}} + U_{\text{BB}})$
  - ordering occurs
- $\varepsilon > 0$:
  - the mixing occurs exothermic with heat release and equal AA and BB bonds are preferred
  - $\frac{1}{2}(U_{\text{AA}} + U_{\text{BB}})$ is more negative than U_{AB}
  - clustering or spinodal decomposition occurs



Random Solutions



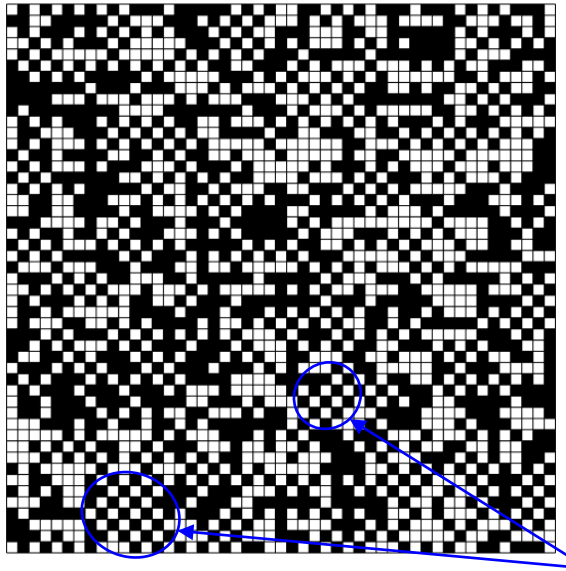


Computer generated arrangements of $N = 2304$ atoms and for $z = 4$ at $x_B = 0.5$

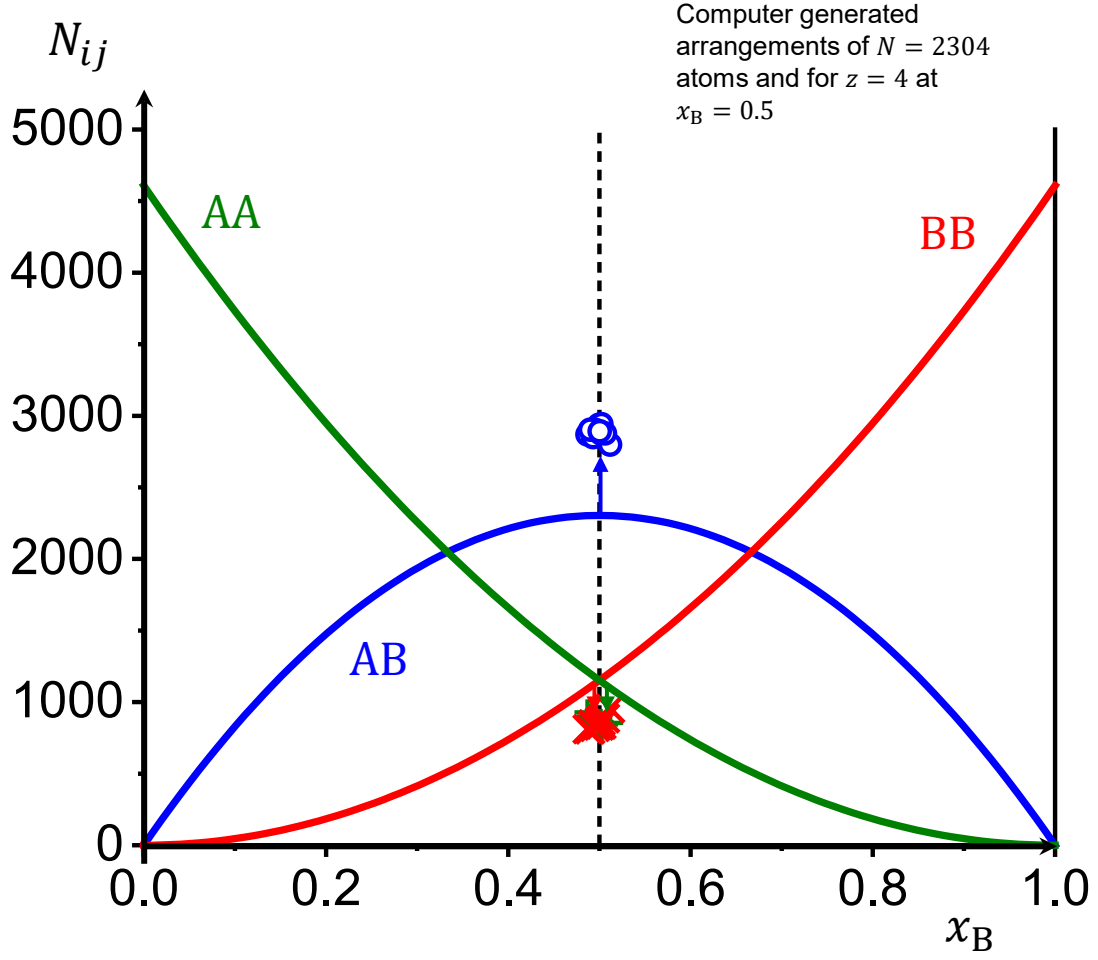
$\varepsilon = 0$

Deviations from Random Solutions

- Regions of local order increase the number of AB bonds while the number of AA and BB bonds decreases in comparison to the random solution.



regions of order



Computer generated arrangements of $N = 2304$ atoms and for $z = 4$ at $x_B = 0.5$

$\varepsilon < 0$

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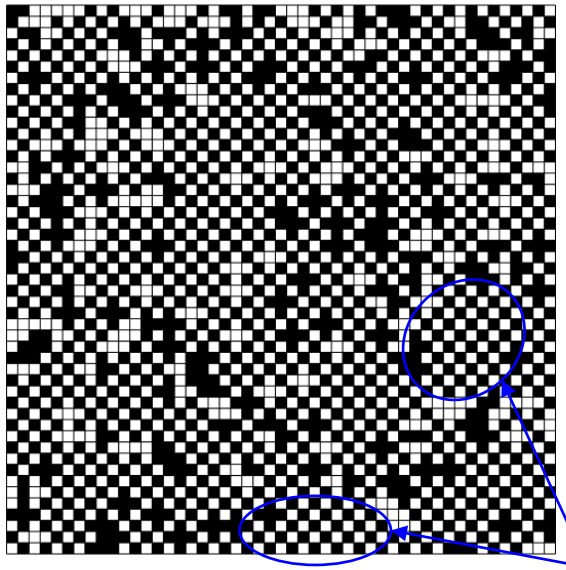
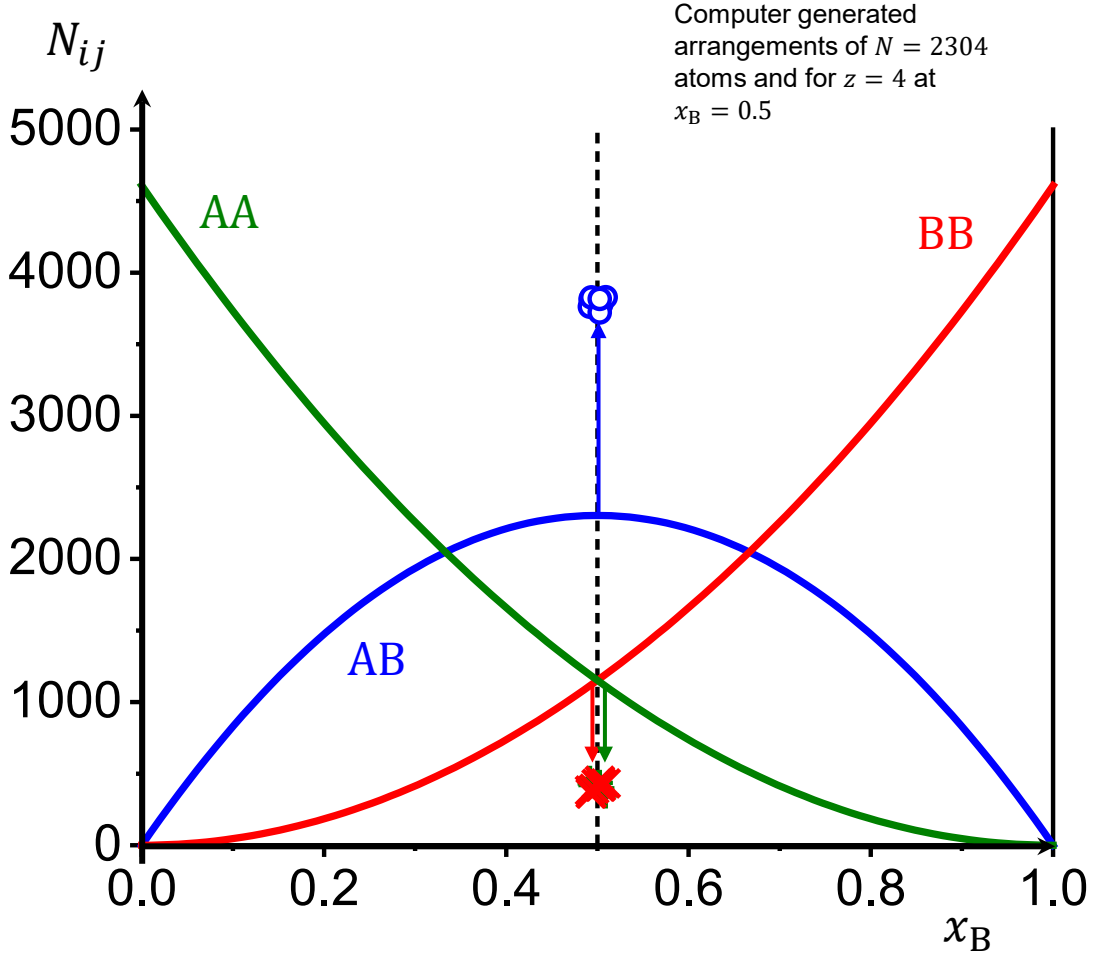


regions of order

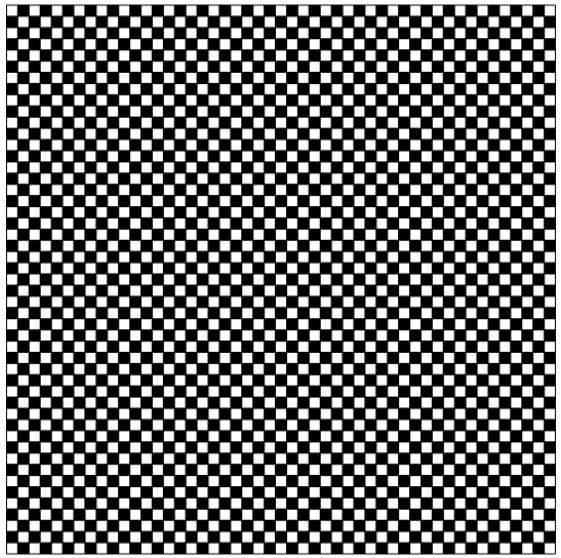


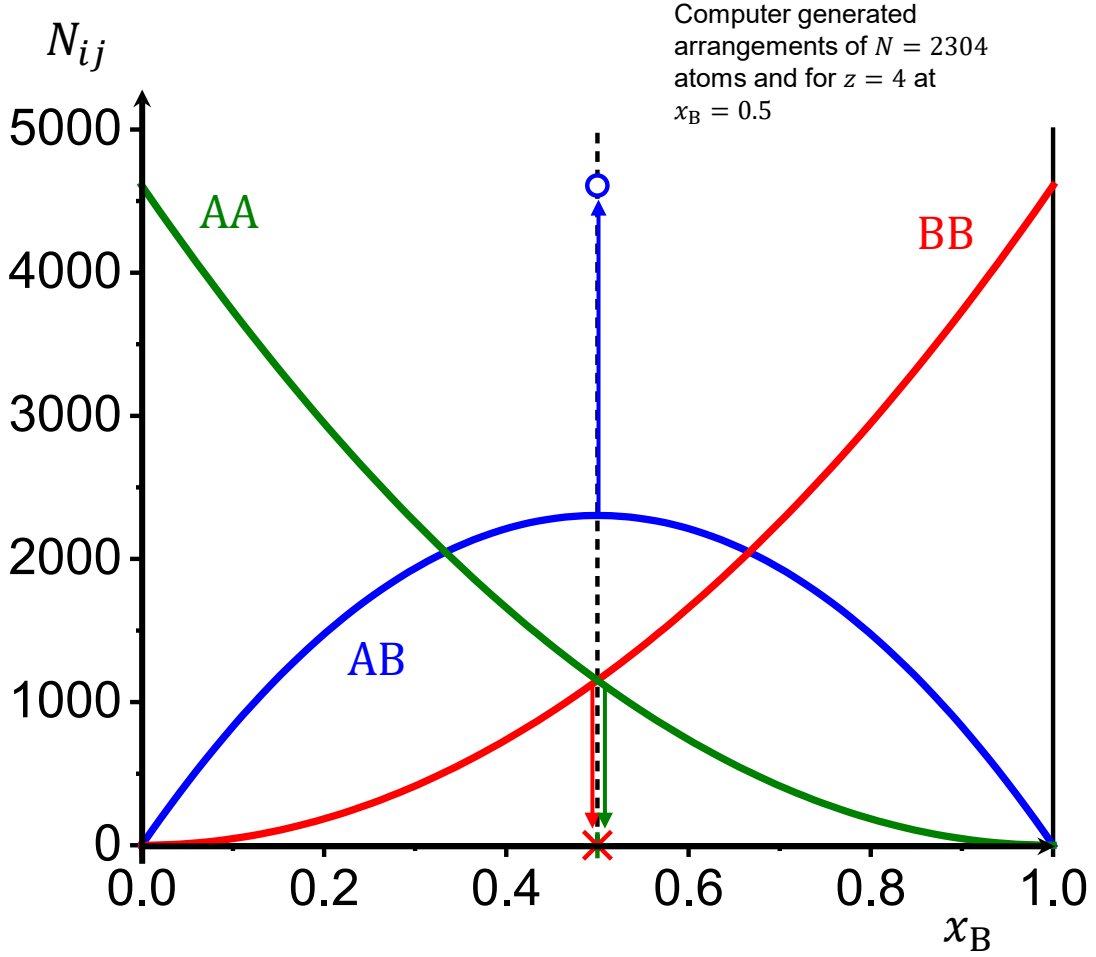
Computer generated arrangements of $N = 2304$ atoms and for $z = 4$ at $x_B = 0.5$

$\varepsilon < 0$

Deviations from Random Solutions

- In the fully ordered state, only AB bonds are present.





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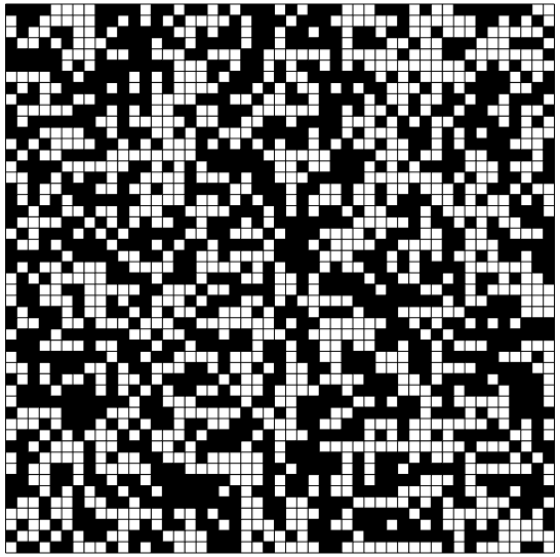
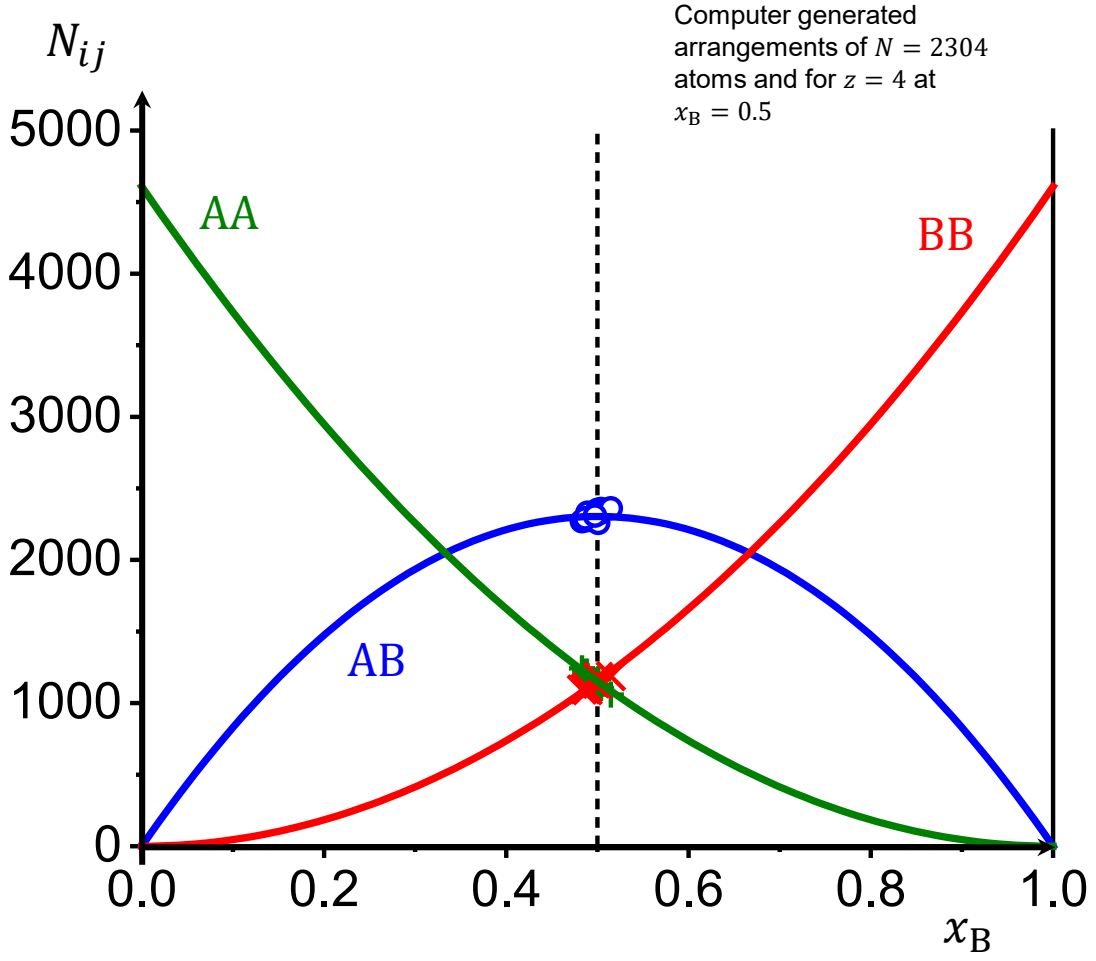
$\varepsilon < 0$

Random Solutions

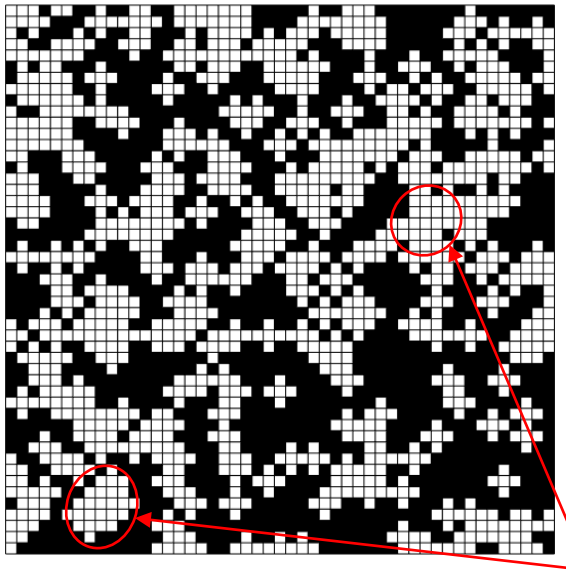




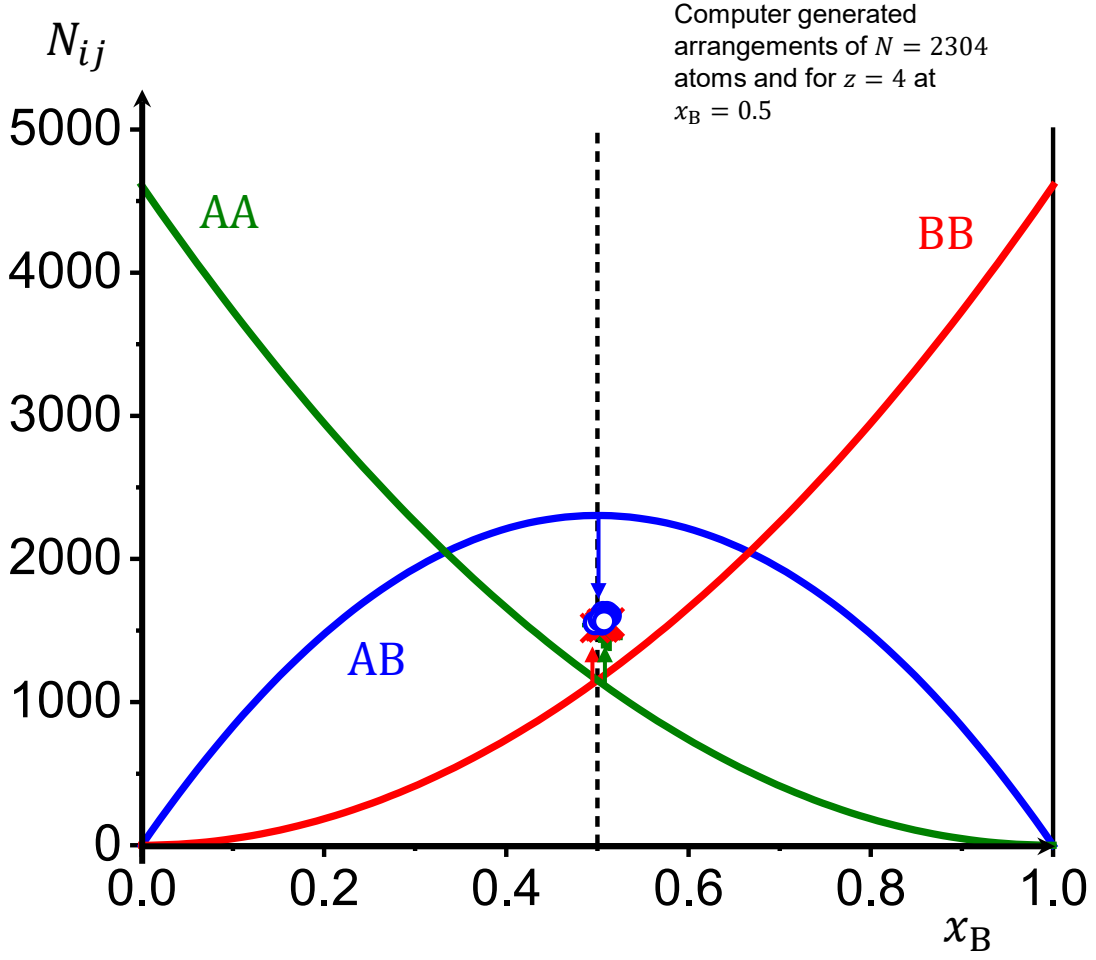
$\varepsilon = 0$

Deviations from Random Solutions

- Clustering of B leads to an increase of AA and BB bonds while the number of AB bonds decreases in comparison to the random solution.



clusters of B



Computer generated arrangements of $N = 2304$ atoms and for $z = 4$ at $x_B = 0.5$

$\varepsilon > 0$

Deviations from Random Solutions

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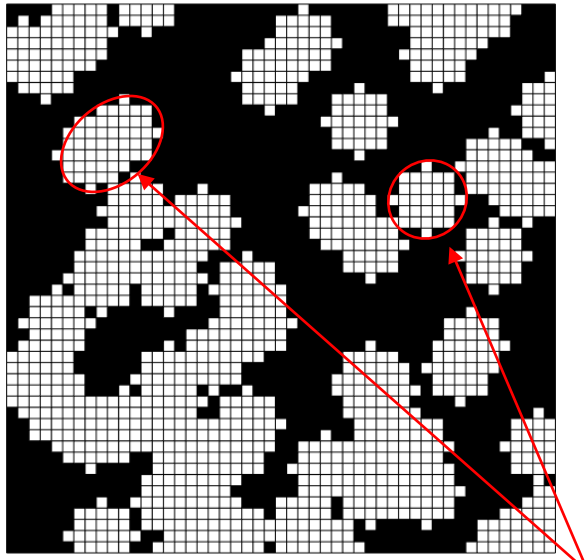
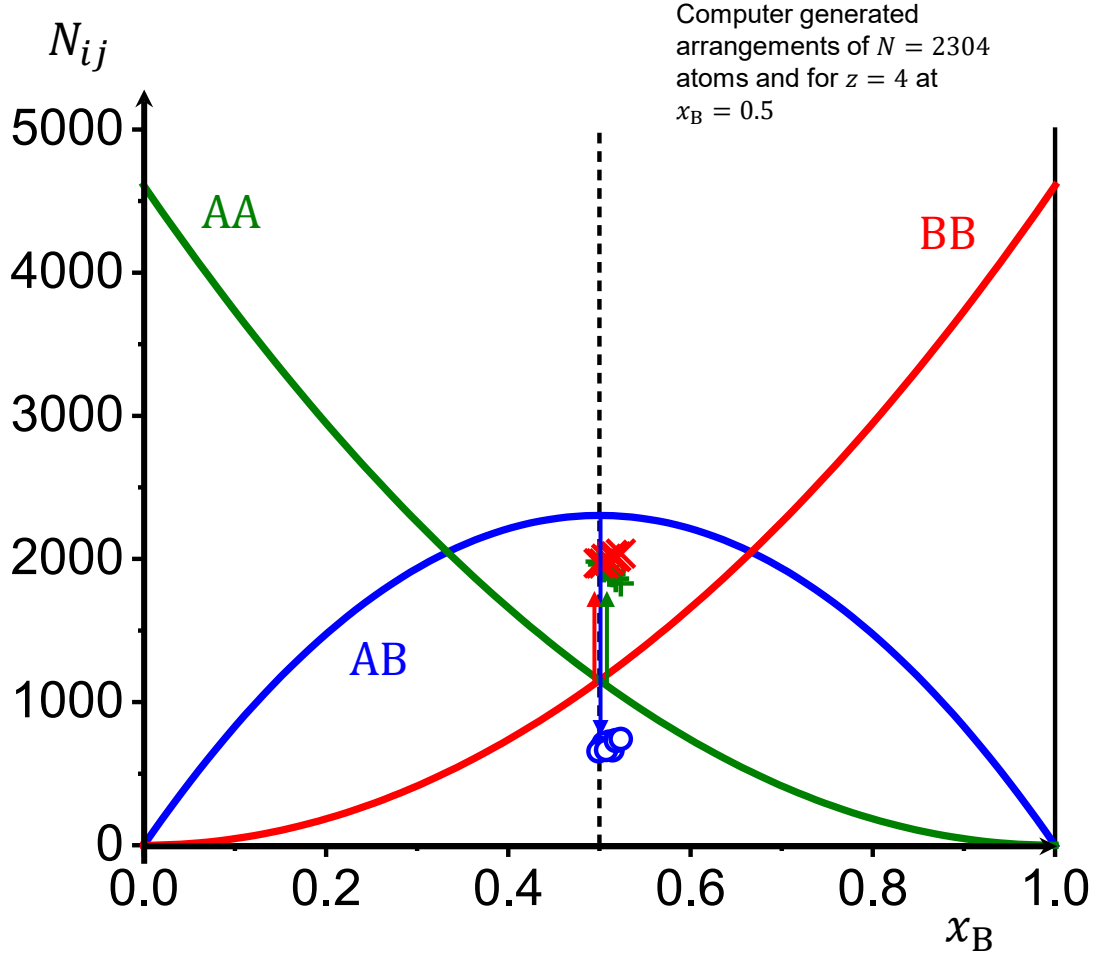


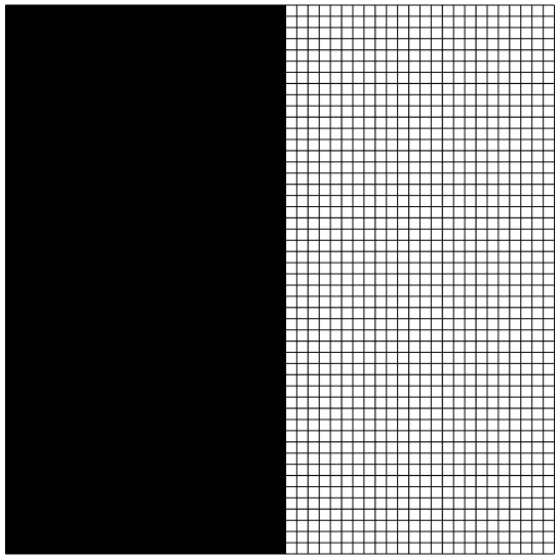


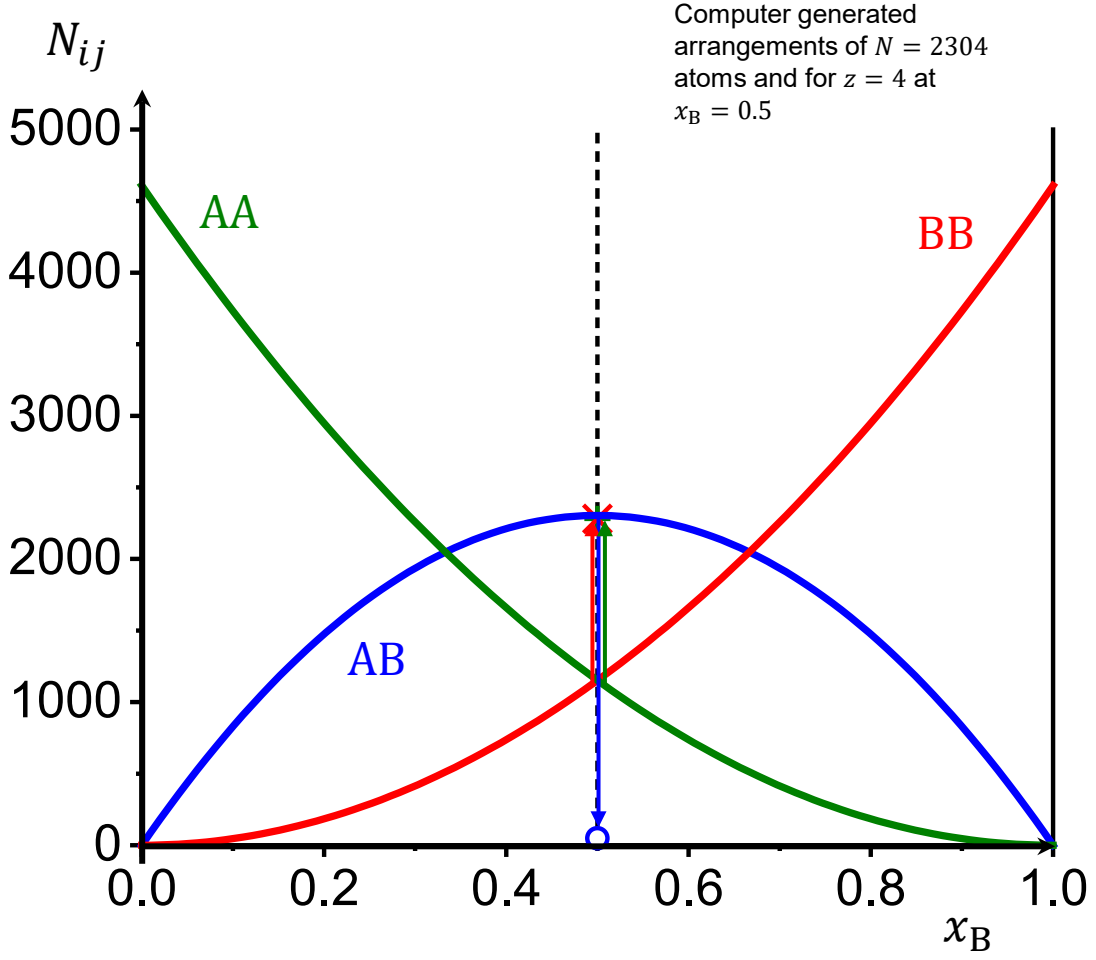
Computer generated arrangements of $N = 2304$ atoms and for $z = 4$ at $x_B = 0.5$

$\varepsilon > 0$

Deviations from Random Solutions

- Full separation of the two species leads to maximum amount of AA and BB bonds. The number of AB bonds depends on the interface area between the two species.





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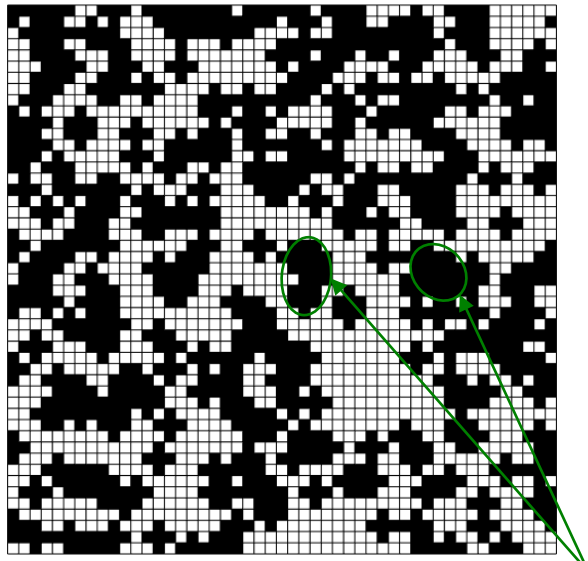
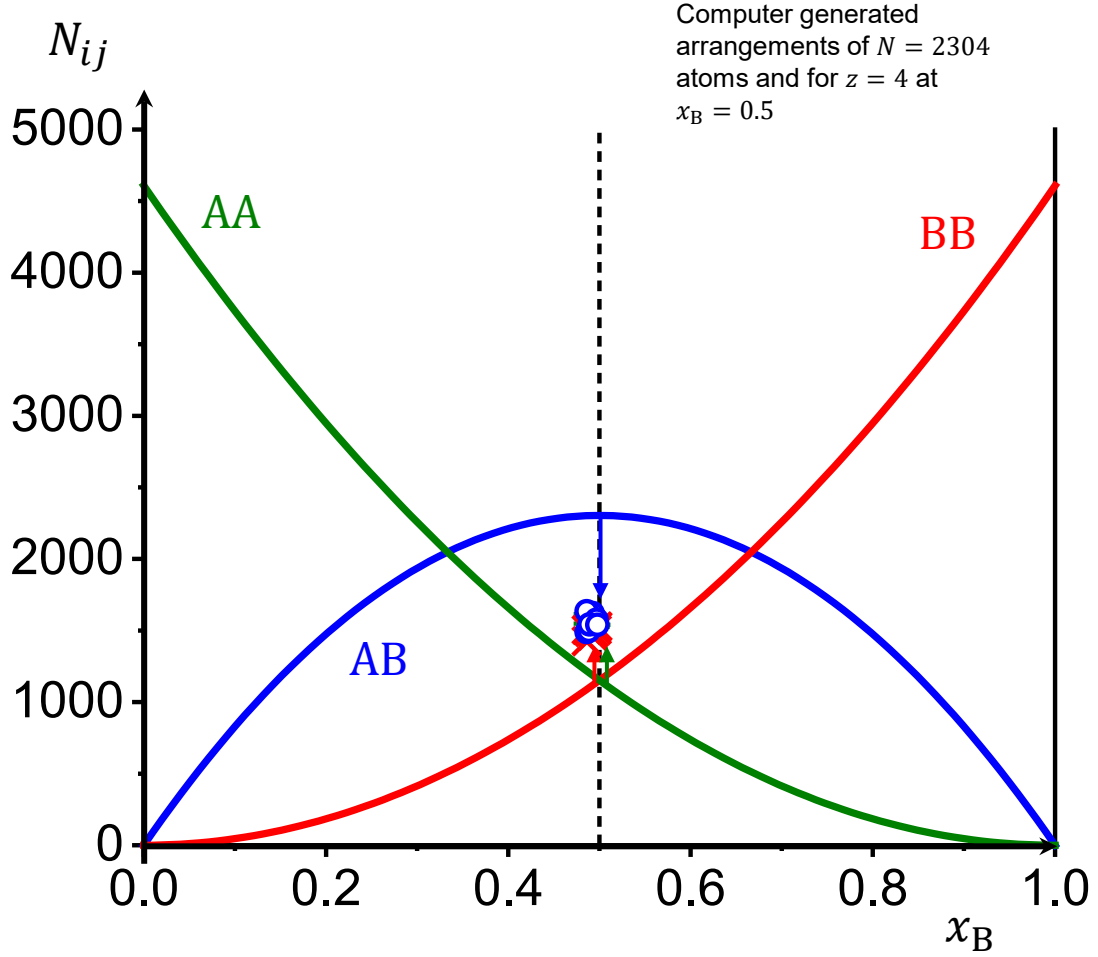
Deviations from Random Solutions

- Clustering of A leads to an increase of AA and BB bonds while the number of AB bonds decreases in comparison to the random solution.





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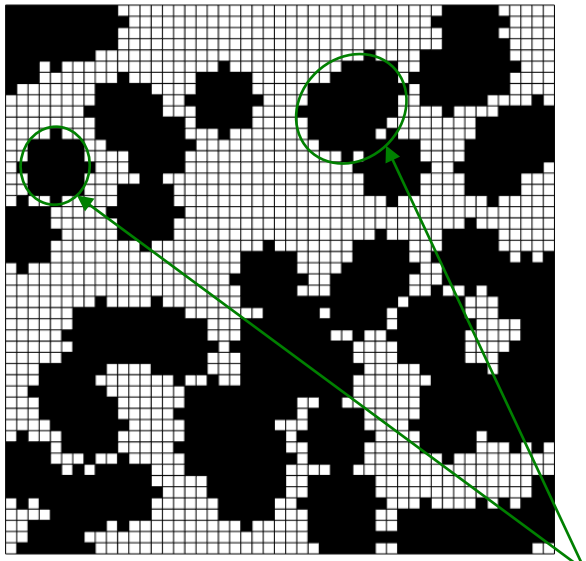

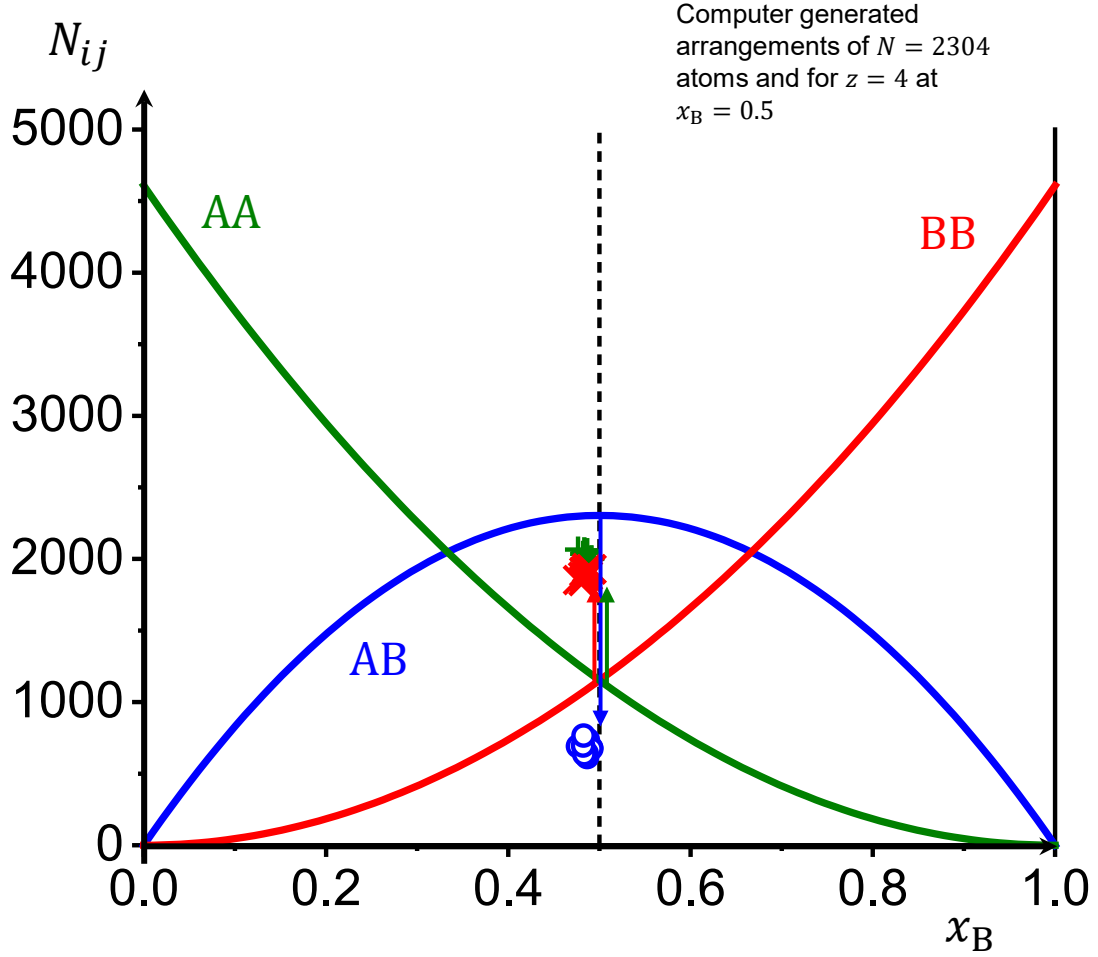

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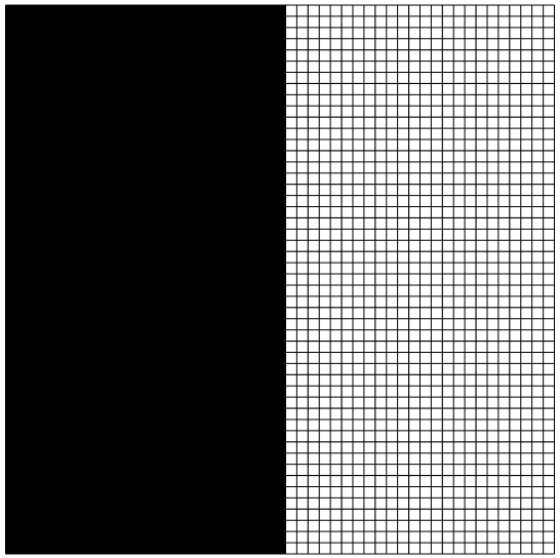
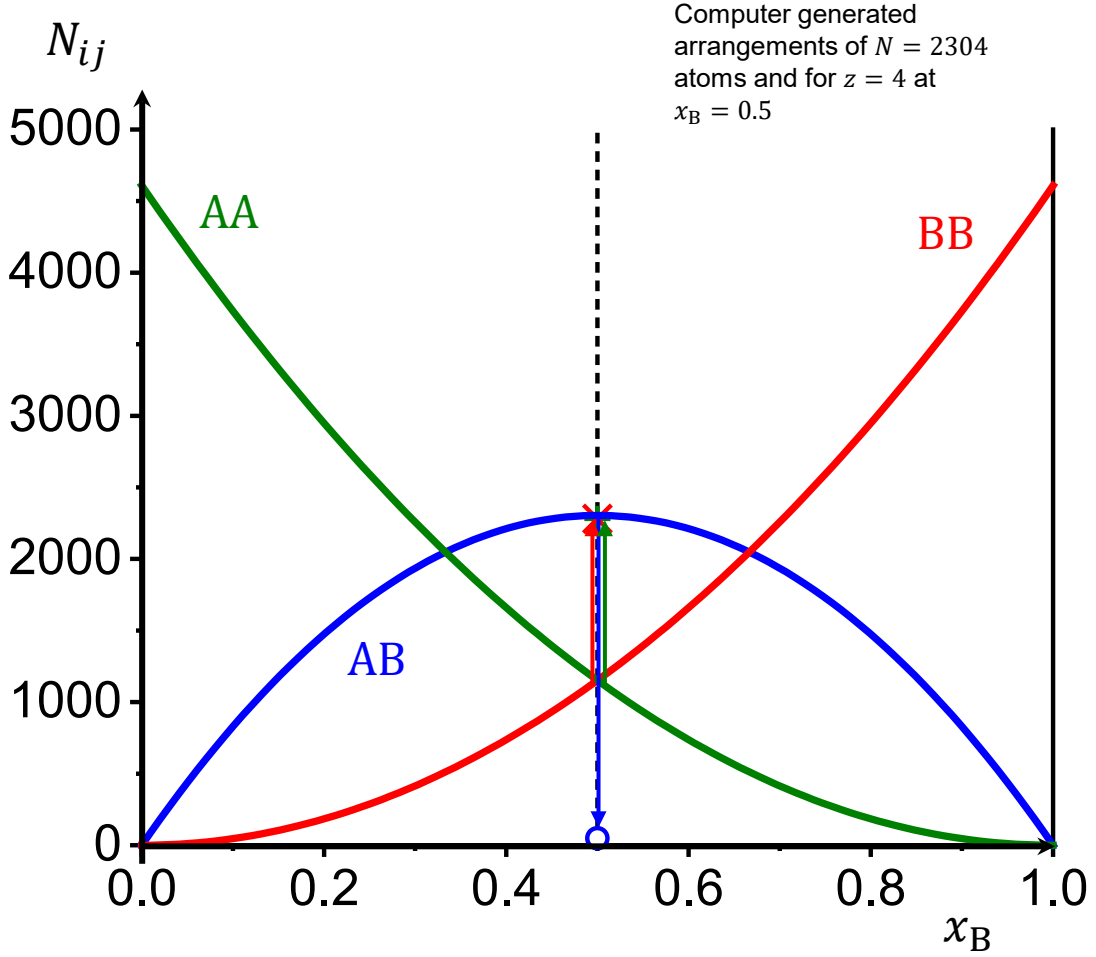
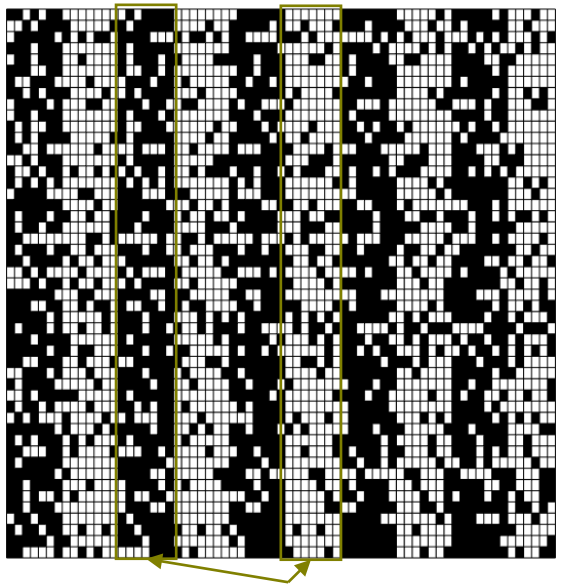




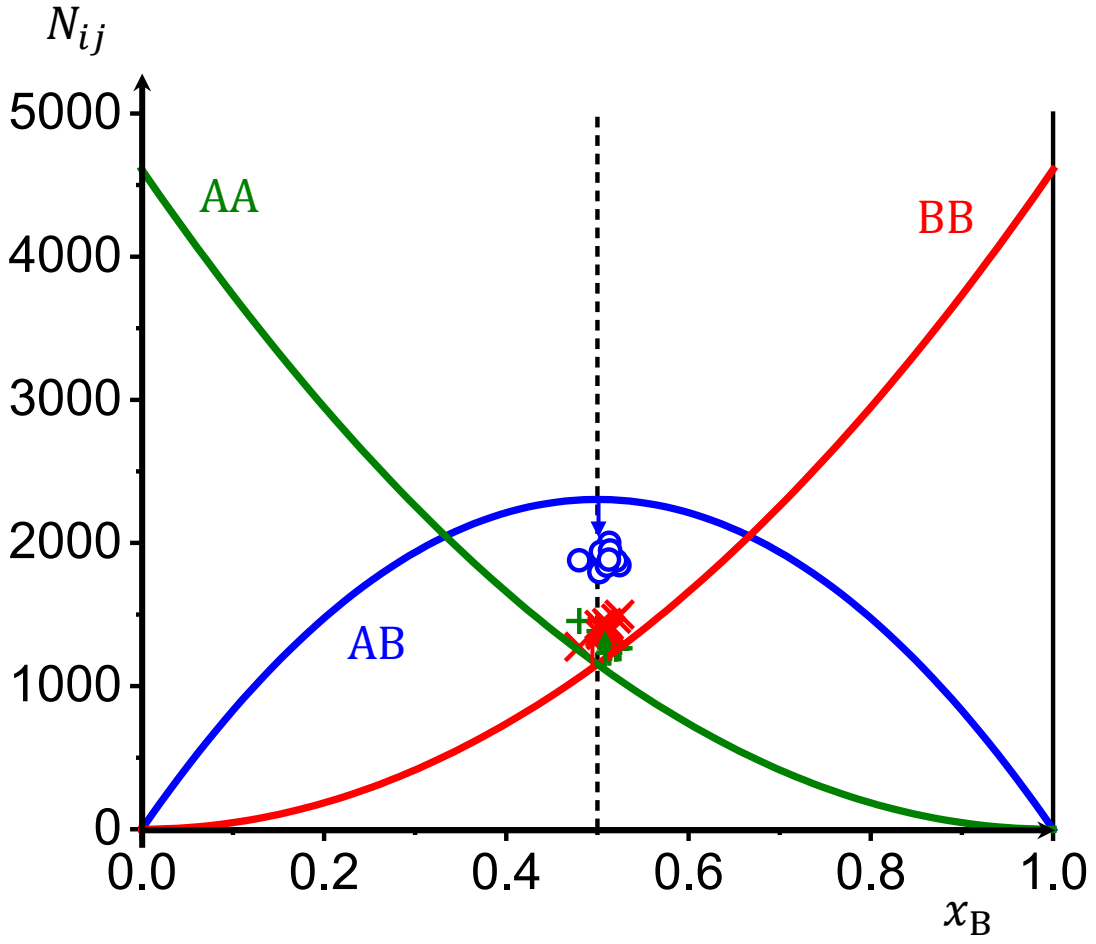
$\varepsilon > 0$

Deviations from Random Solutions

- In systems with tendency to form clusters, a similar distribution of bonds is achieved by a decomposition into two random solutions of different composition.



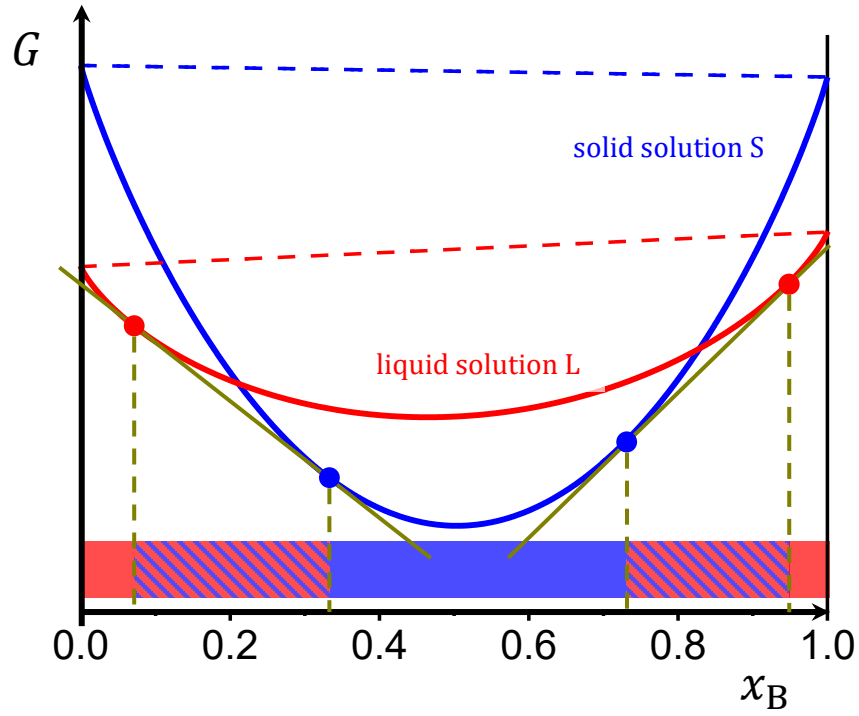
lamellae of different x_B



$\varepsilon > 0$

Impact of ΔH^{mix}: Extrema of the Liquidus Line

- For slightly negative ΔH^{mix}, two intersections of the G curves of solid solution and liquid might be obtained.
- A maximum of the liquidus line can be observed instead of a cigar-like two-phase region.



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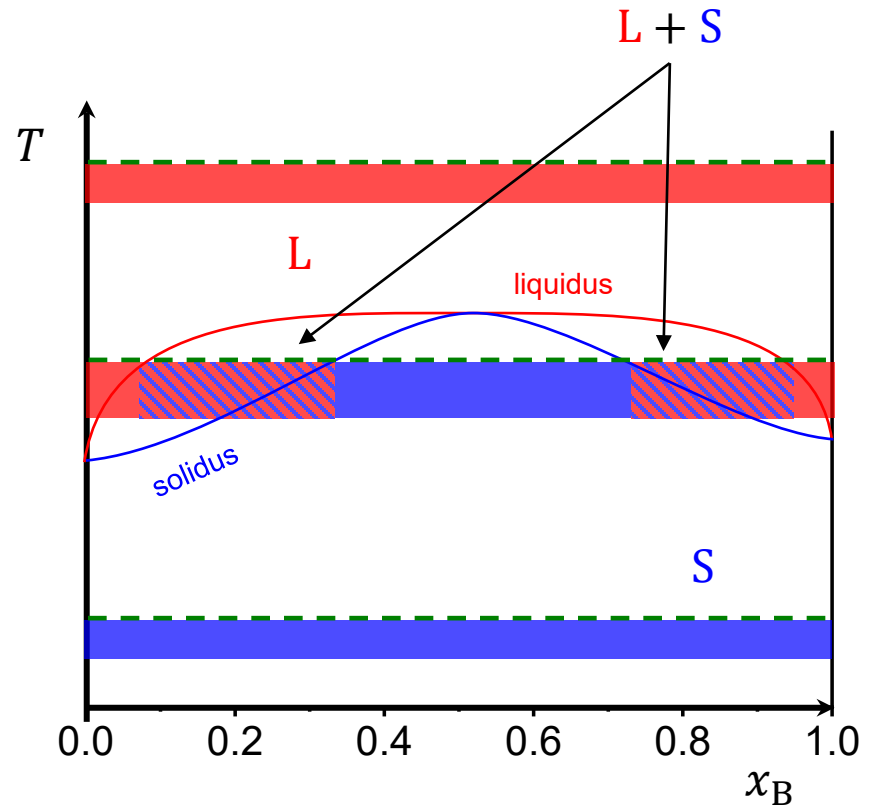

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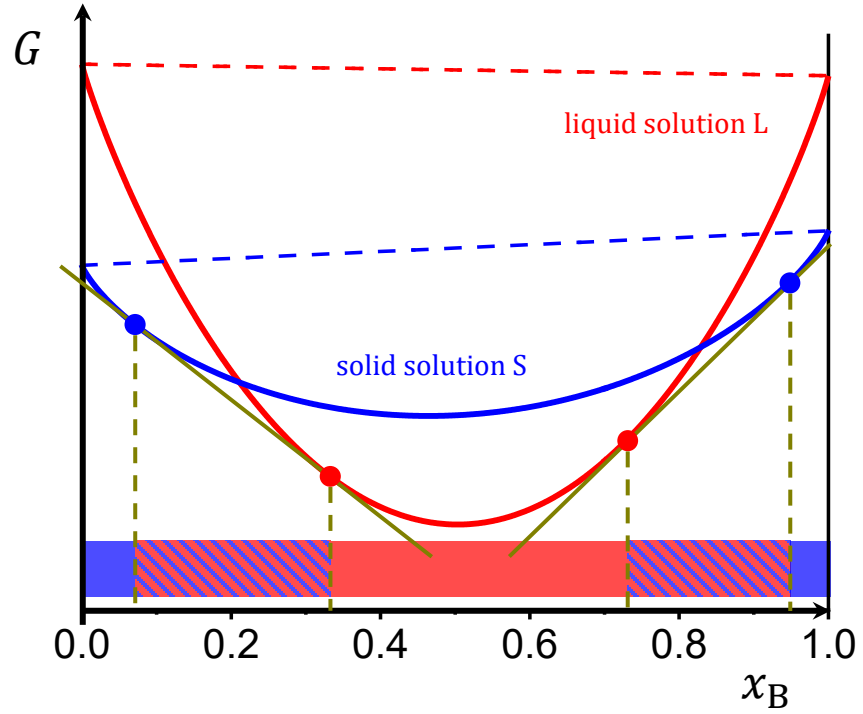

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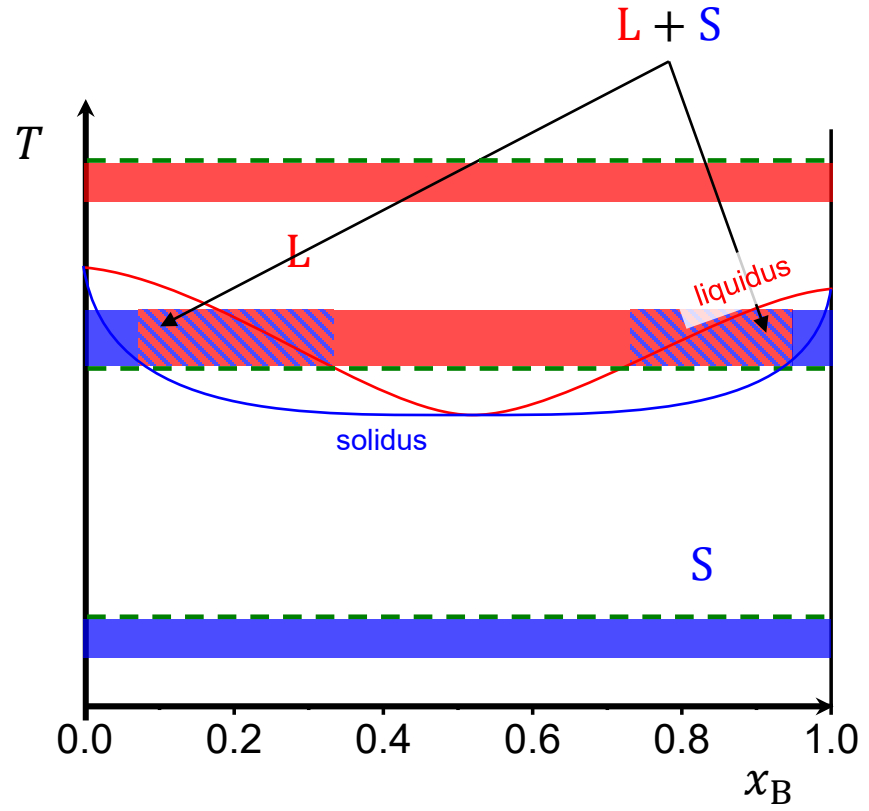
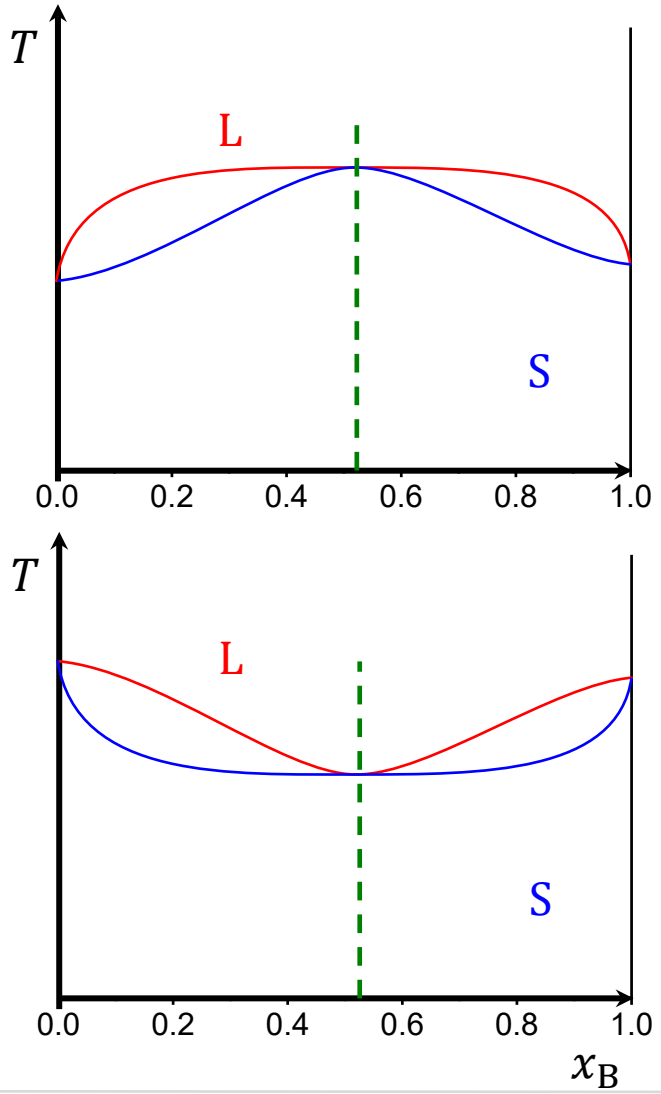


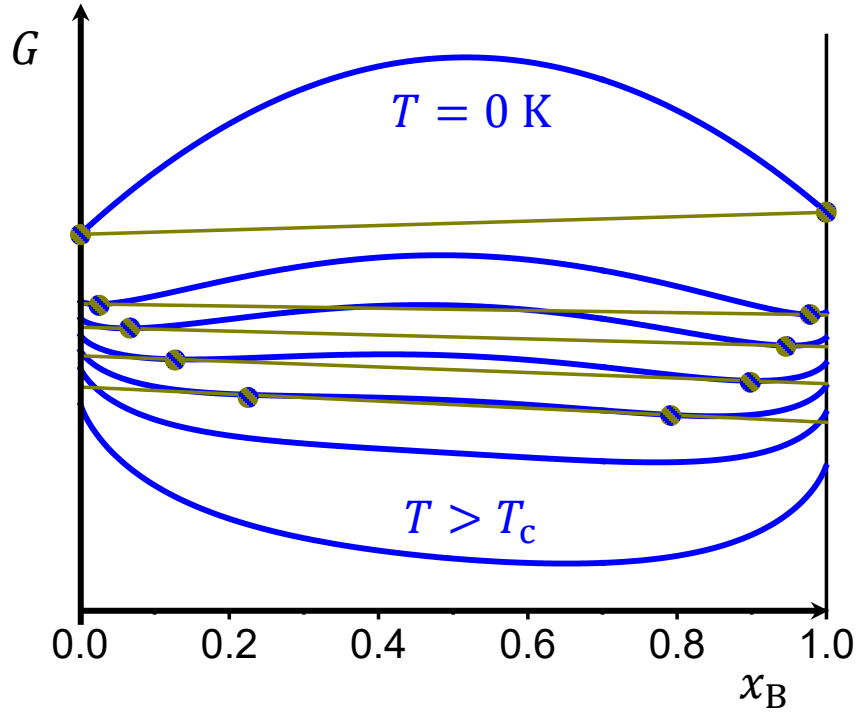
Congruent Solidification

- For both situations, congruently melting alloys are obtained at the extrema of the liquidus curves. These alloys solidify like elements ($F^* = 0$).
- All other alloys undergo a similar solidification process when trespassing the two-phase region as discussed in Ch. 4b.



Impact of ΔH^{mix}: Miscibility Gap

- For $\Delta H^{\mathrm{mix}} > 0$ in the solid, a miscibility gap occurs at low temperatures due to the temperature-dependent interplay of the $\Delta H^{\mathrm{mix}} = \mathrm{const.}$ and $-T\,\Delta S^{\mathrm{mix}}$.
- At high T, the strongly negative ΔS^{mix} dominates the G curve and the solid solution is stable in the entire composition range (if the liquid G curve does not intersect).
- At low $T < T_{\mathrm{c}}$, two stable solutions occur according to the common tangent.



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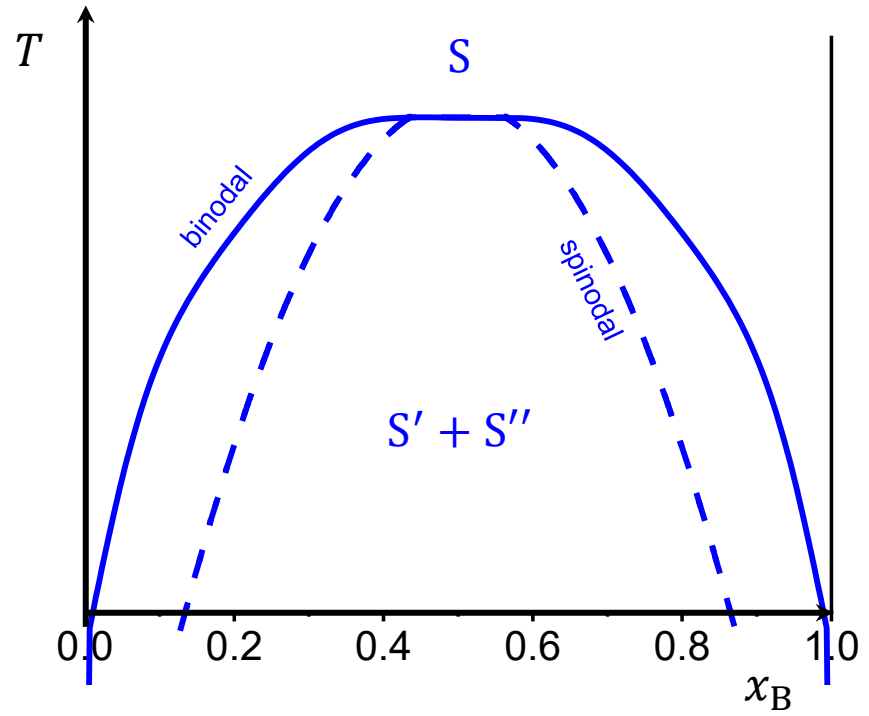
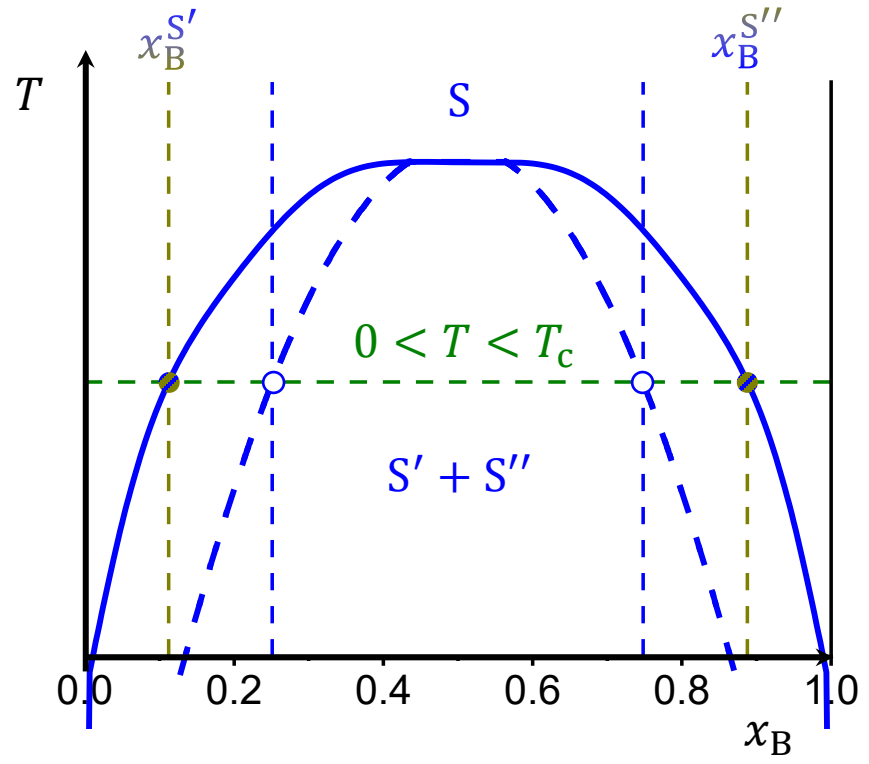


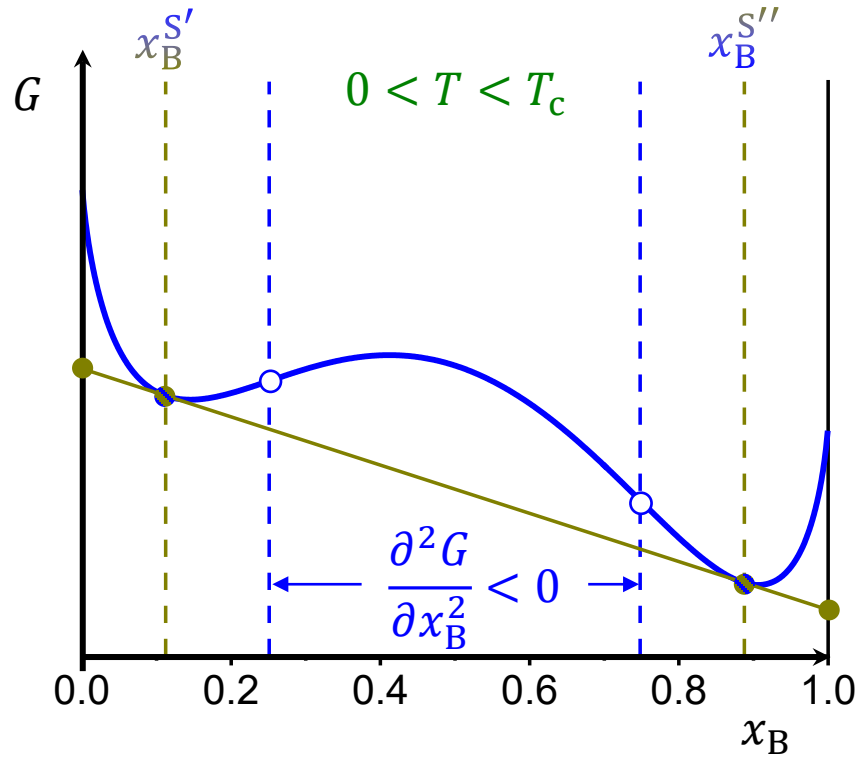
Binodal vs. Spinodal Line

- Thermodynamic equilibrium is obtained for the two points the common tangent touches the G curve. The temperature-dependent composition of the two stable solutions is referred to as binodal line.
- Within the region, a second region can be distinguished for which $\frac{\partial^2 G}{\partial x_B^2} < 0$. The according line is referred to as spinodal line.



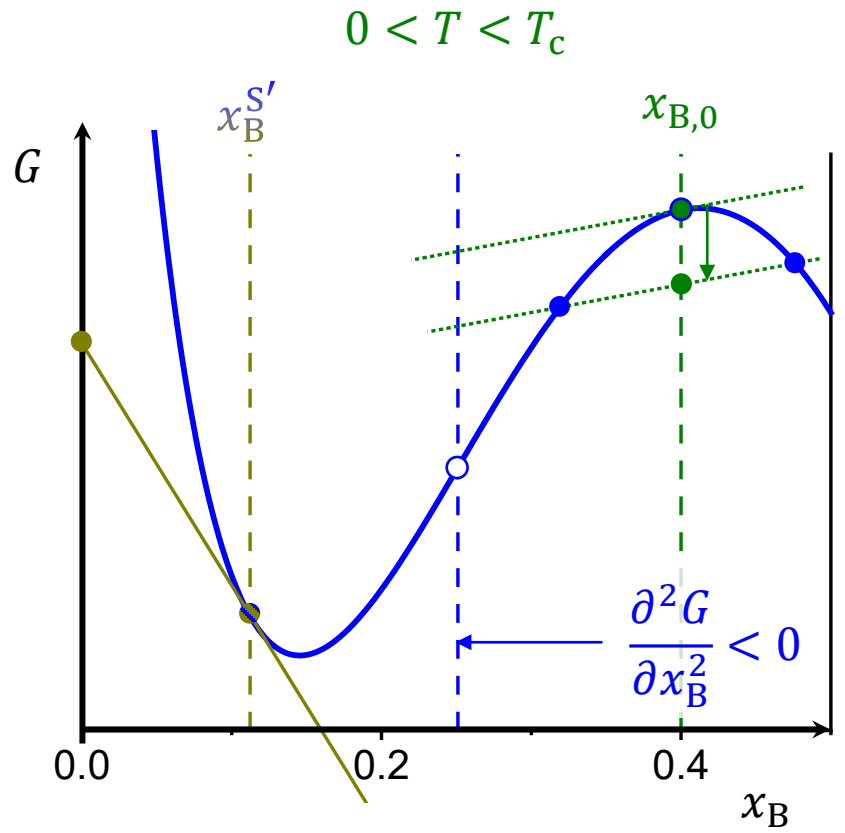
Binodal vs. Spinodal Line

- Within the spinodal line, the homogenous solid solution is unstable and decomposition occurs spontaneously without thermal activation (continuous phase transformation, compare to Ch. 3e).
- In the region between spinodal and binodal line, the homogeneous solid solution is metastable and the decomposition occurs by nucleation and growth (discontinuous phase transformation).



Decomposition (Spontaneous, Continuous)

- Consider an alloy of $x_{\mathrm{B},0}$ quenched to the spinodal region. Any decomposition will lead to a decrease of the total G of the system.
- Hence, the diffusion process to mediate the decomposition will occur spontaneously (even though being up-hill the concentration gradient).
- The concentration gradients are continuous throughout the process.



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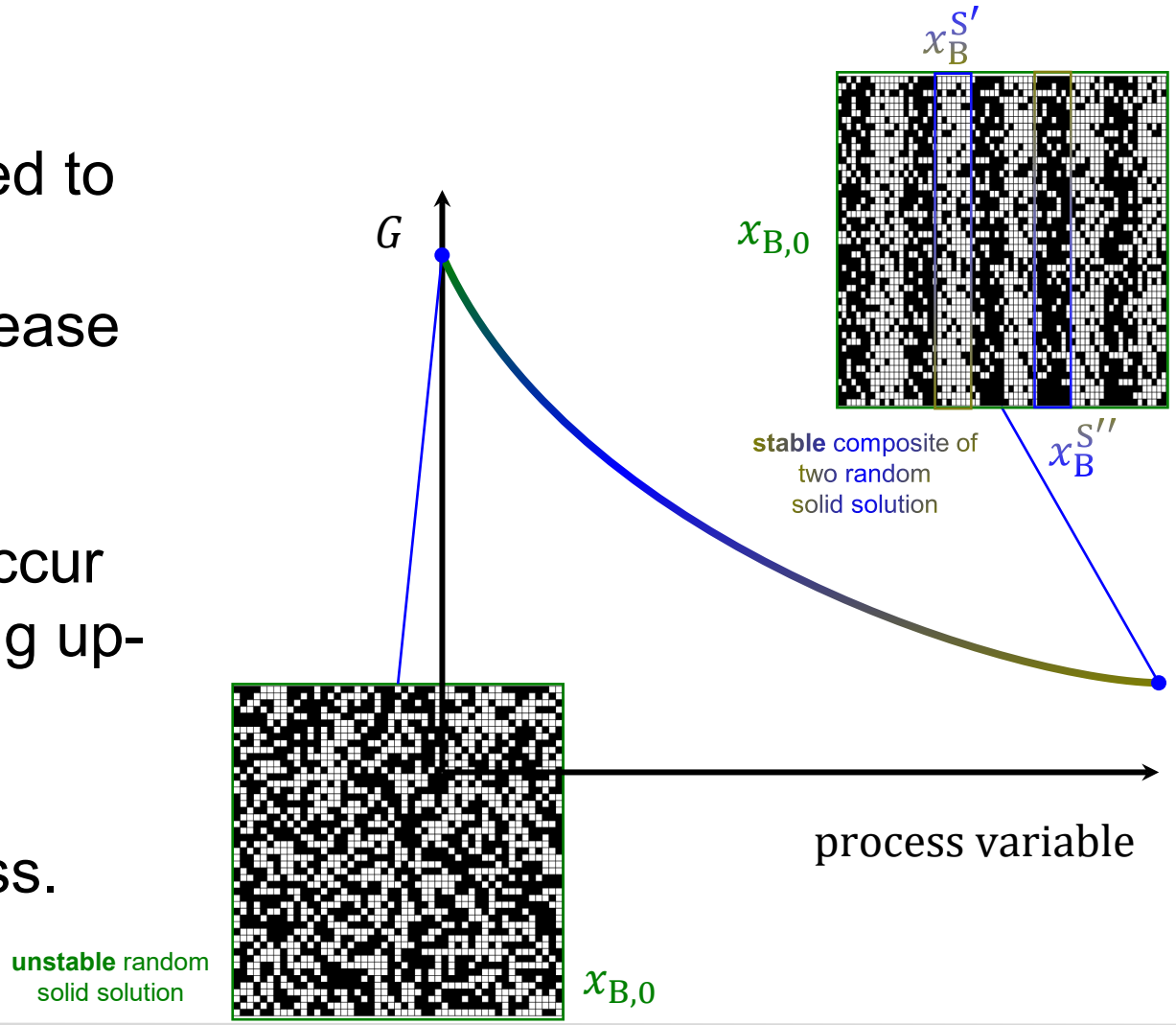

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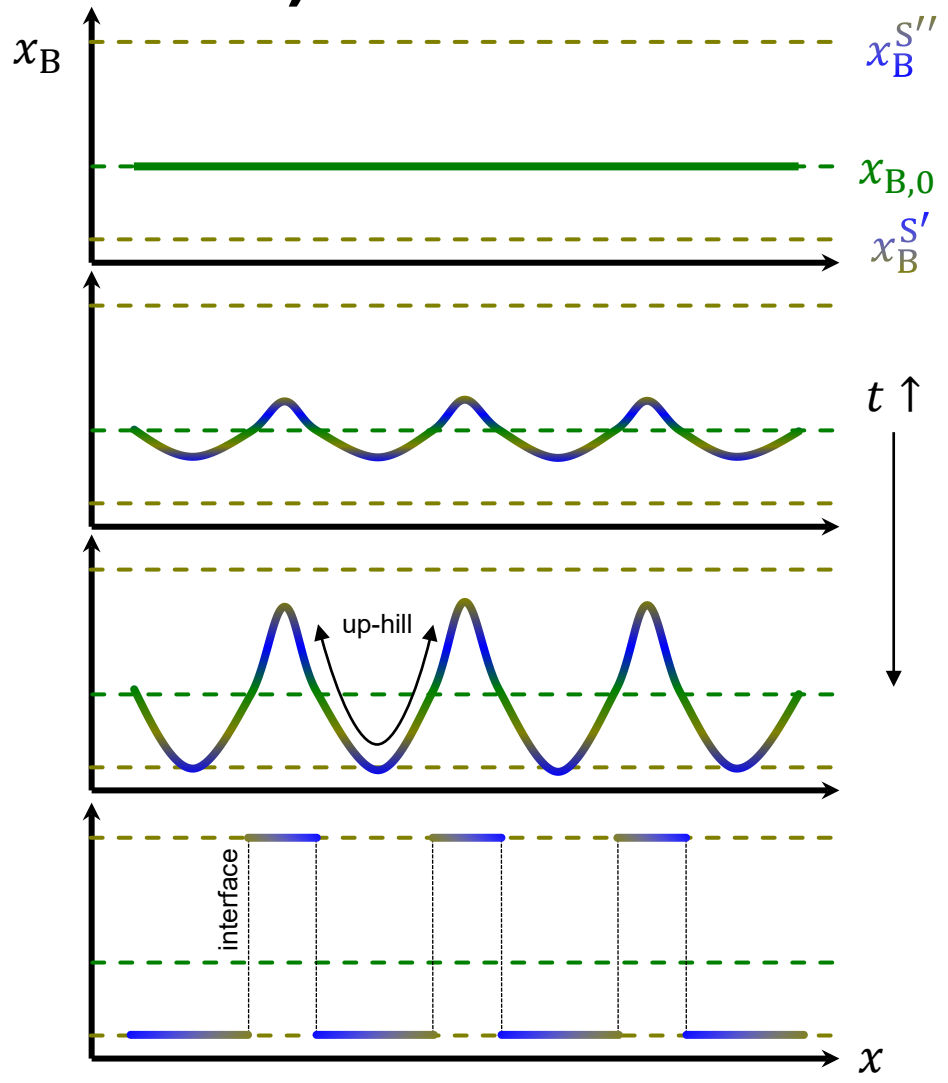
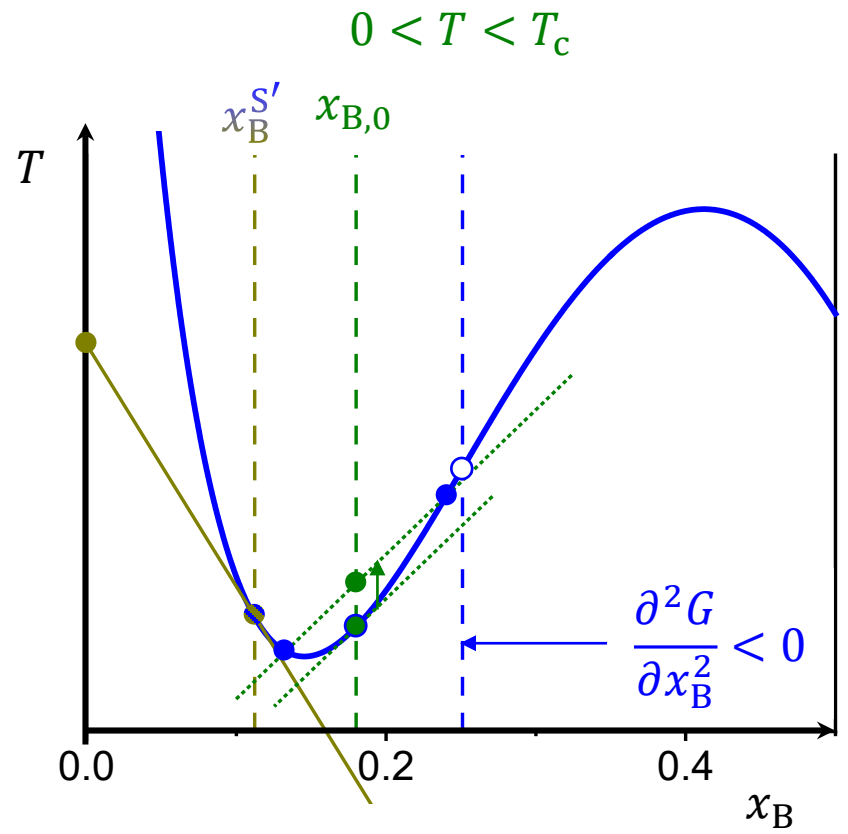


Decomposition (Nucl. and Gr., Discontinuous)

- Consider an alloy of $x_{B,0}$ quenched to between the spinodal and binodal line. Any decomposition will lead to an increase of the total G of the system.
- The decomposition occurs via the formation of a distinct interface between the two stable compositions $x_B^{S'}$ and $x_B^{S''}$ during nucleation. The region of $x_B^{S''}$ grows (via interface motion) until equilibrium is achieved.
- Hence, the decomposition requires an activation to overcome this initial energy barrier.



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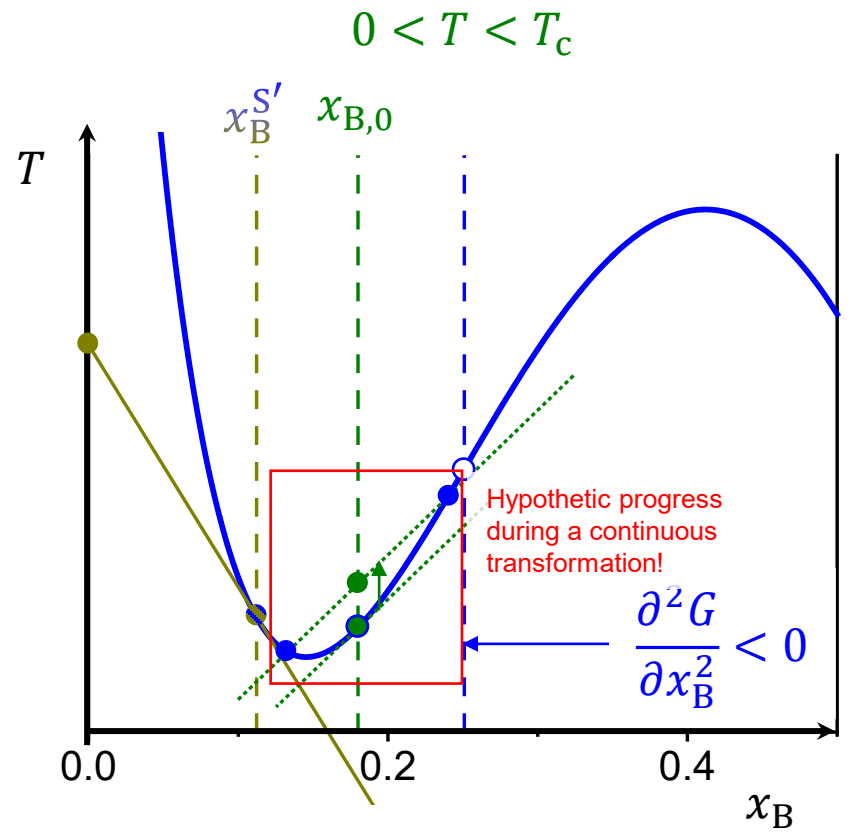

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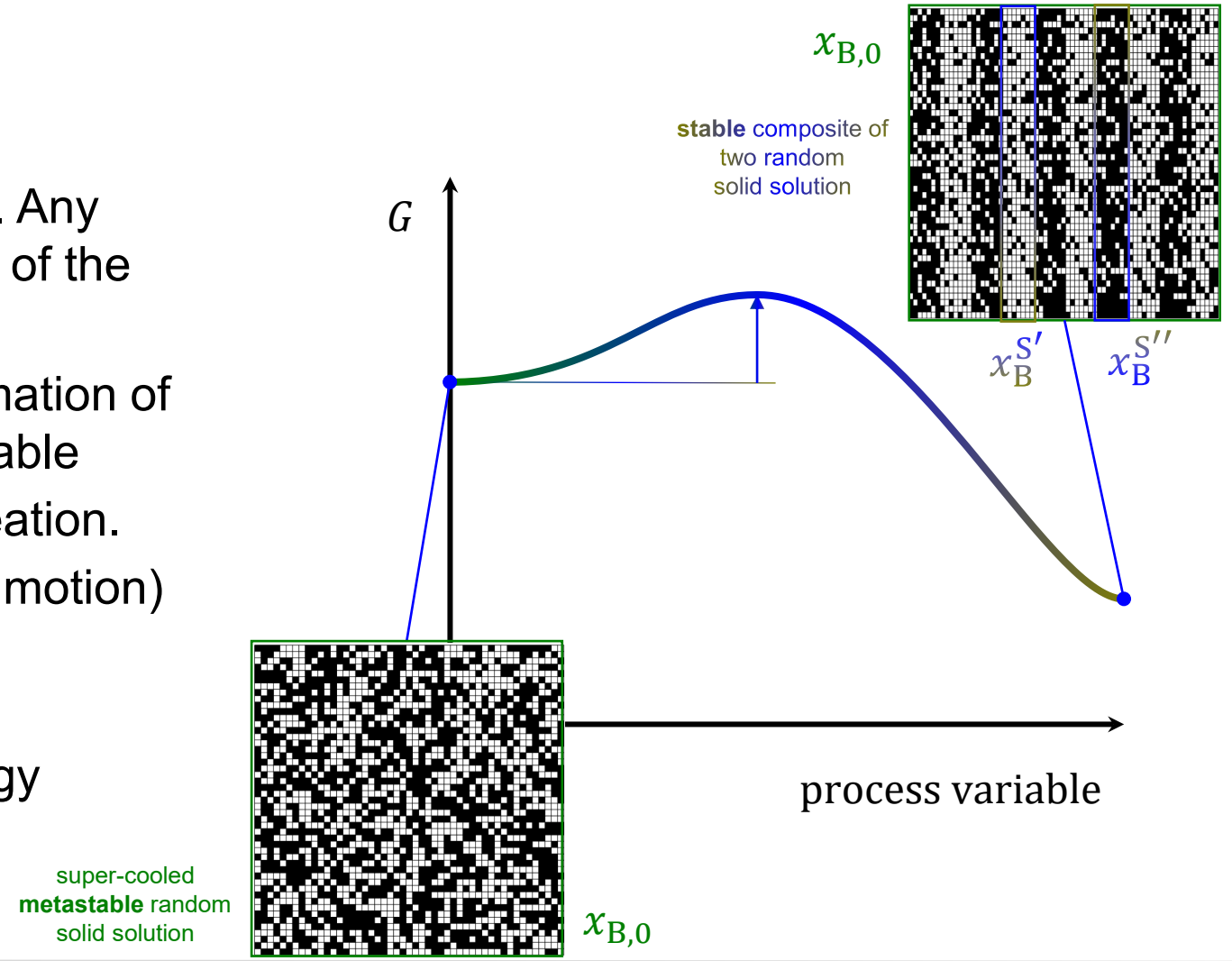

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