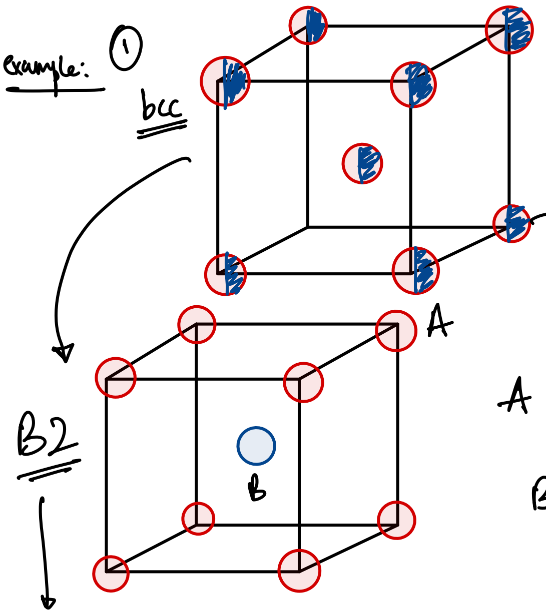
ORDER-DISORDER REACTIONS:

example: ①



disordered phase on the bcc structure

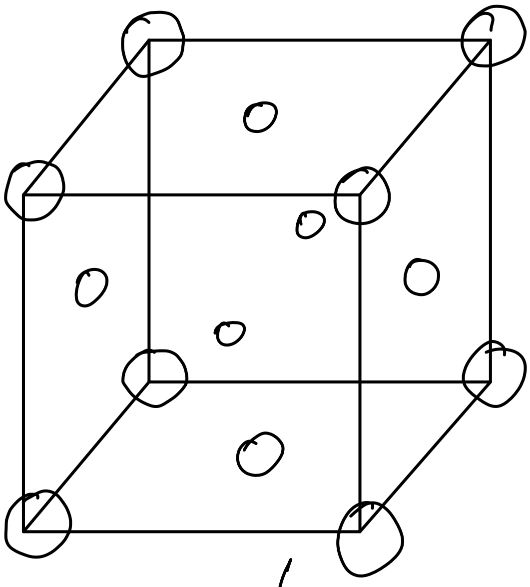
A & B atoms are randomly distributed across the entire structure

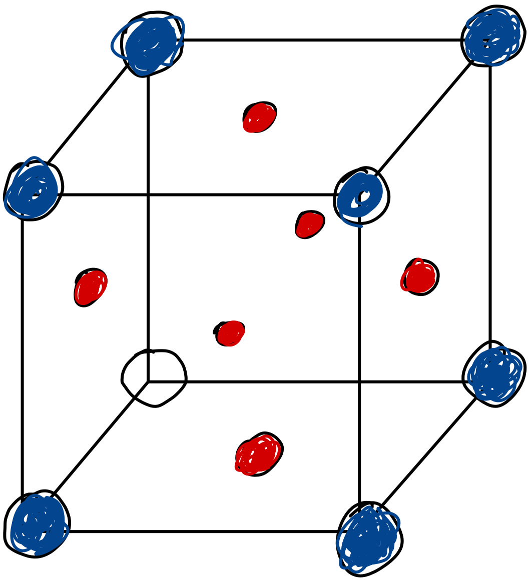
⇒ NO LONG-RANG BCC ORDER

A atoms occupy one set of sites,
B atoms occupy the other.

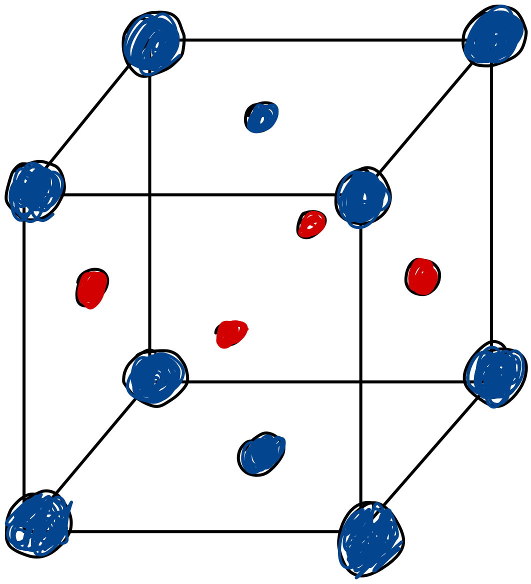
Strukturbericht notation.

② fcc:



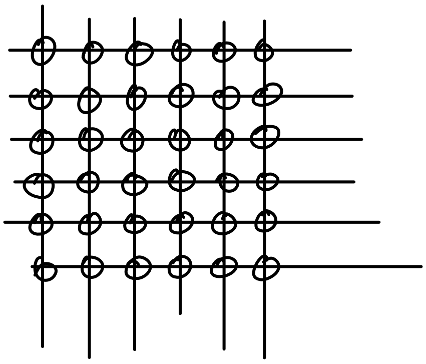


$L1_2$
(A_3B)

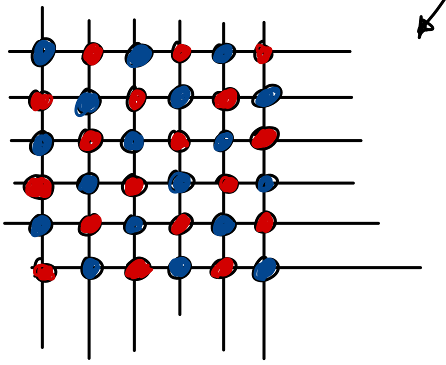


$L1_0$
(AB)

2- Dimensional examples:



Consider a material system where A-B bonds are preferred.

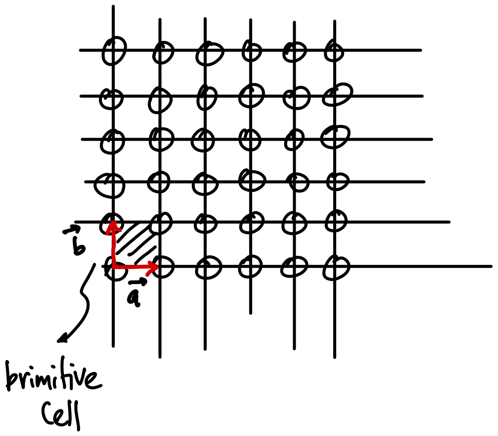


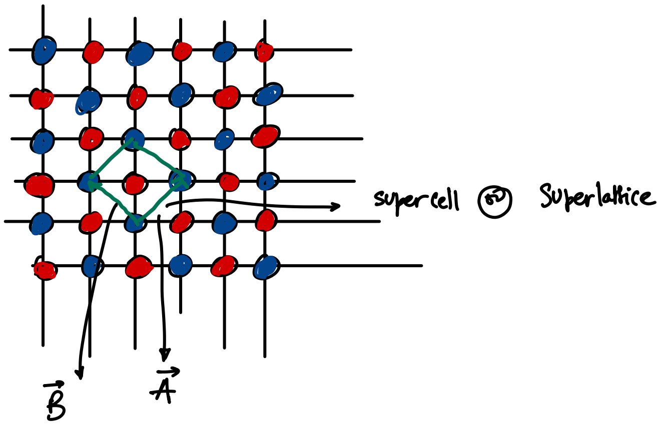
To describe these phase transitions we need descriptors that can uniquely identify each phase of interest.

DESCRIPTORS OF ORDERING:

- We would like to find "order parameters" that can distinguish the disordered phase from the ordered phase.
- In experiment you could use characterization techniques like XRD, TEM etc. to quantify the degree of ordering ⇒ what about in theory?

* Orderings are typically formed on lattices that have a larger periodicity than the disordered phase:



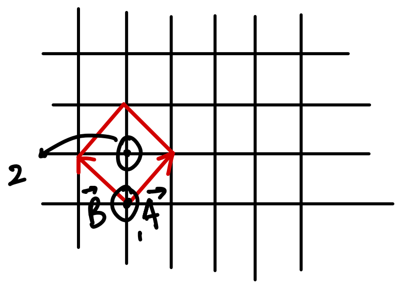


$$\boxed{\begin{aligned}\vec{A} &= \vec{a}+\vec{b}\\ \vec{B} &= -\vec{a}+\vec{b}\end{aligned}} \Rightarrow$$

Supercell Vectors can be written as linear combinations of primitive cell vectors.

To compute order parameters for a particular ordering:

① Identify the supercell that defines the periodicity of the ordering:



② Each site in the supercell corresponds to a "sublattice".

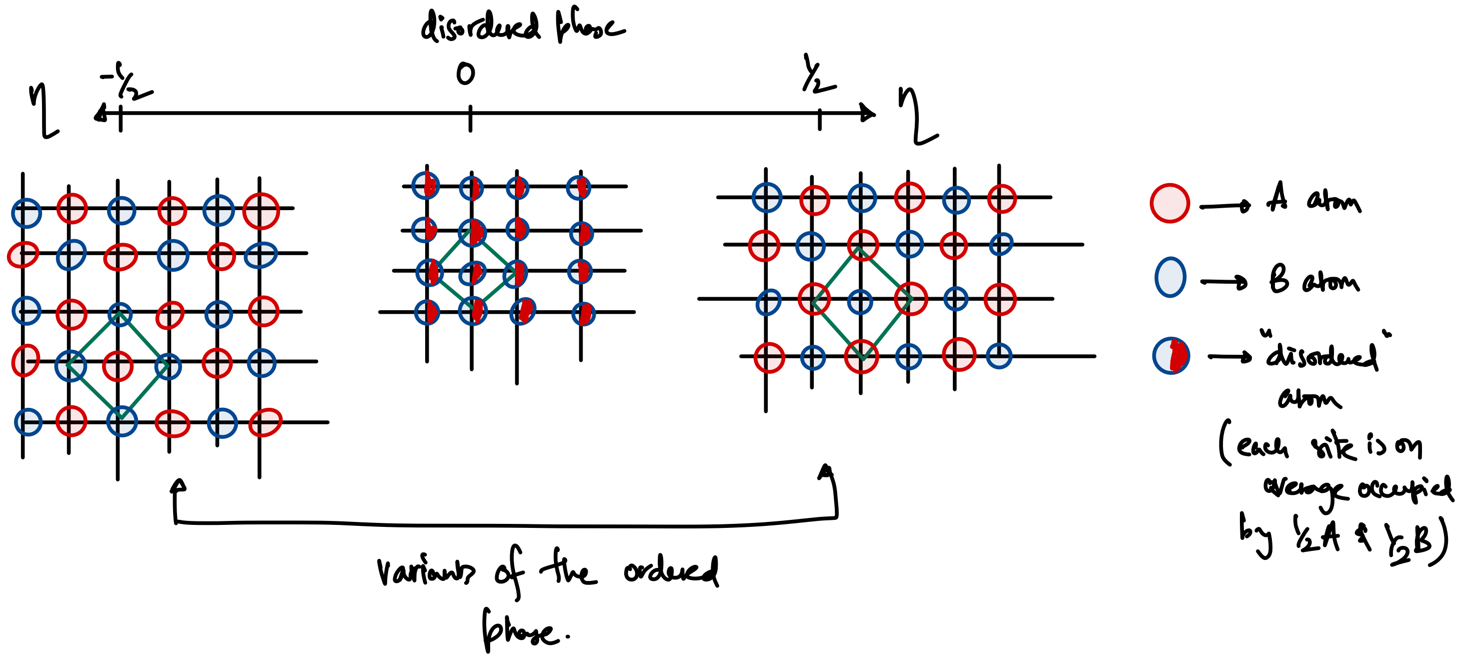
We have 2 sublattices in the above supercell.

Let the concentration of element A on sublattice 1 be x_1 and concn. in sublattice 2 be x_2

③ Order parameters can be derived as linear combinations of sublattice compositions:

$$X = \frac{x_1 + x_2}{2} = \text{Average composition of the alloy.}$$

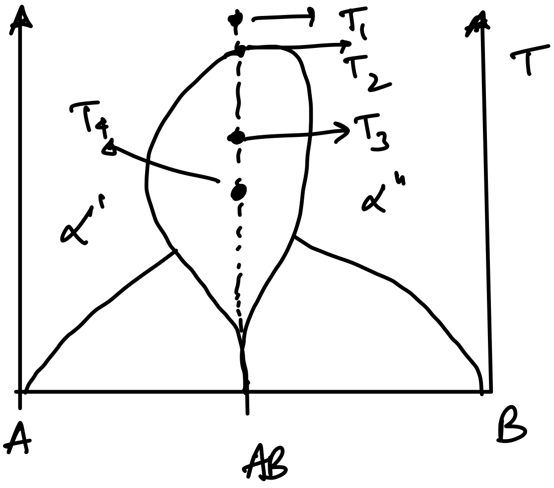
$$\eta = \frac{x_1 - x_2}{2} = \text{order parameter to distinguish the ordered phase from the disordered phase}$$



(each site is on average occupied by ½A & ½B)

variants of the ordered phase.

* PHASE DIAGRAMS, ORDER PARAMETERS & FREE ENERGIES:



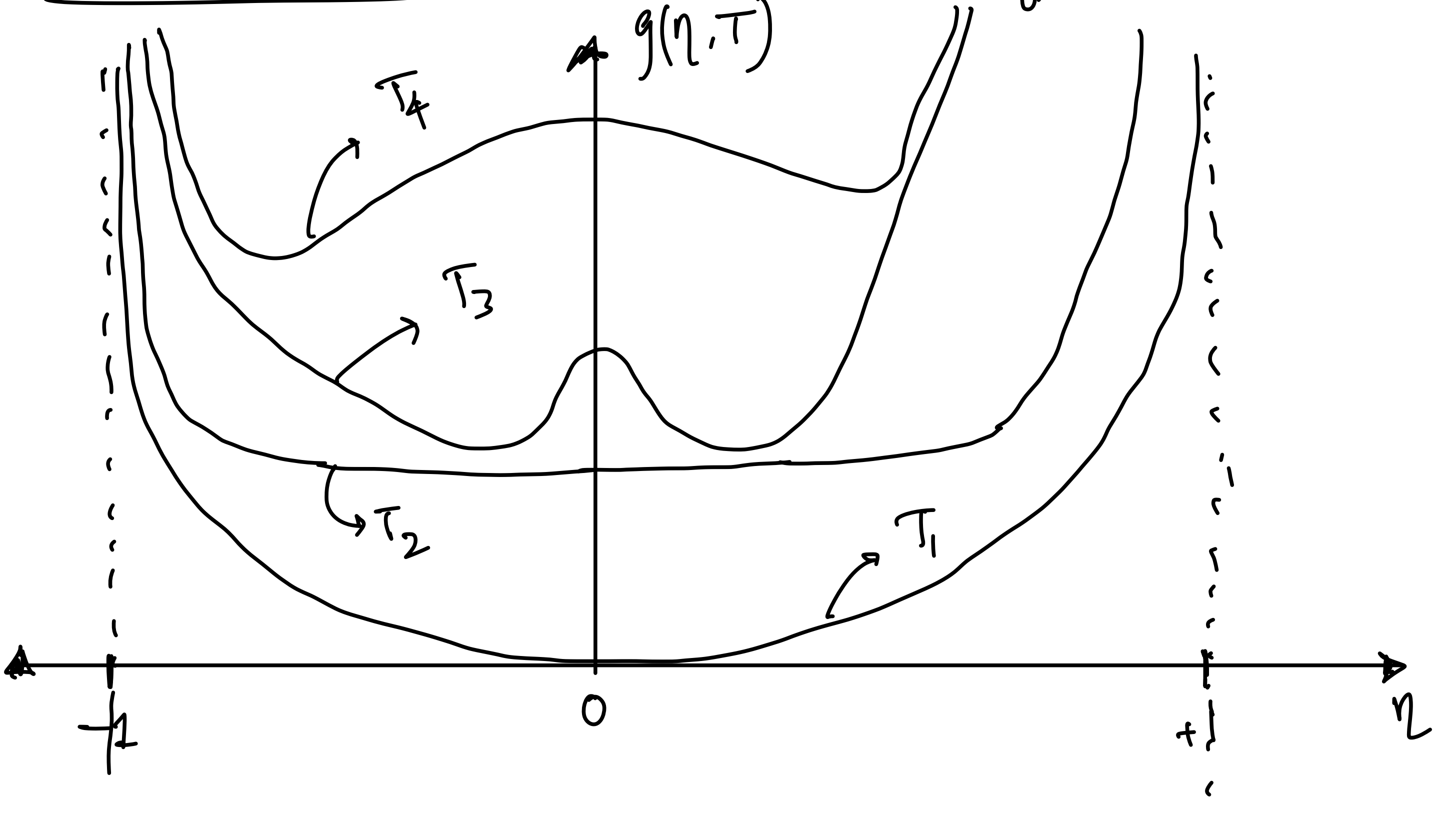
Consider the phase diagram

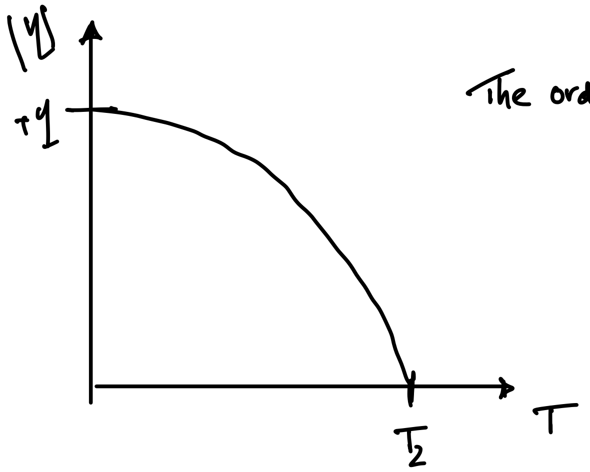
The ordered AB phase undergoes a 2nd order phase transition to the disordered phase at elevated temperature.

For simplicity: say a single order parameter (η) can distinguish the ordered phase from the disordered phase. $\Rightarrow \eta$

$$\eta = \begin{cases} 0, & \text{disordered phase} \\ \pm 1, & \text{ordered phase.} \end{cases}$$

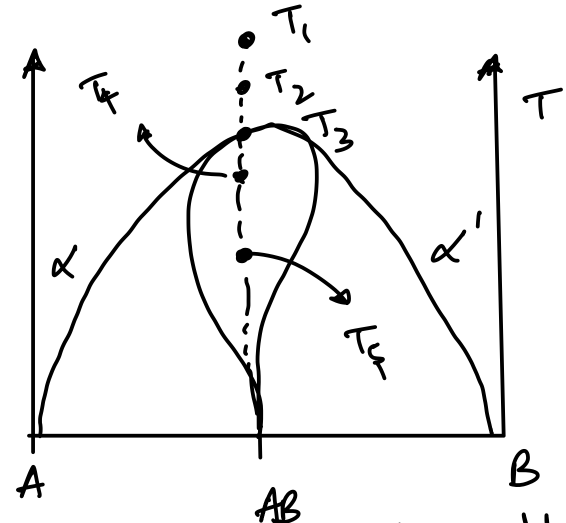
examples of such phase transitions: B2 ↔ bcc, checkerboard ordering, $L1_0$ ↔ fcc, ...

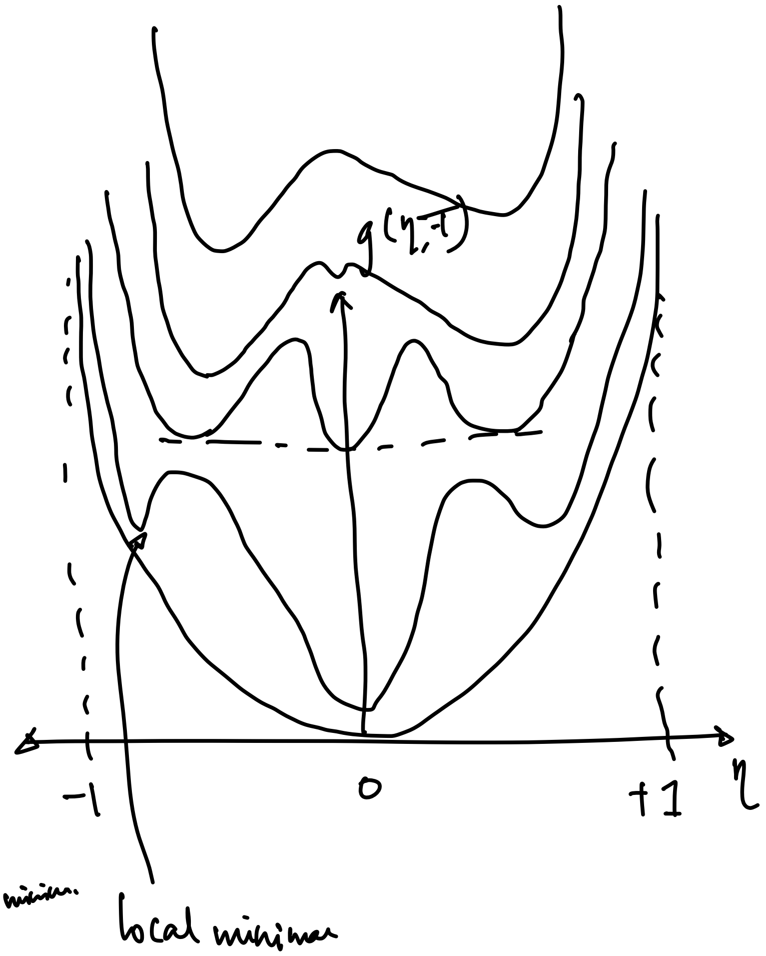


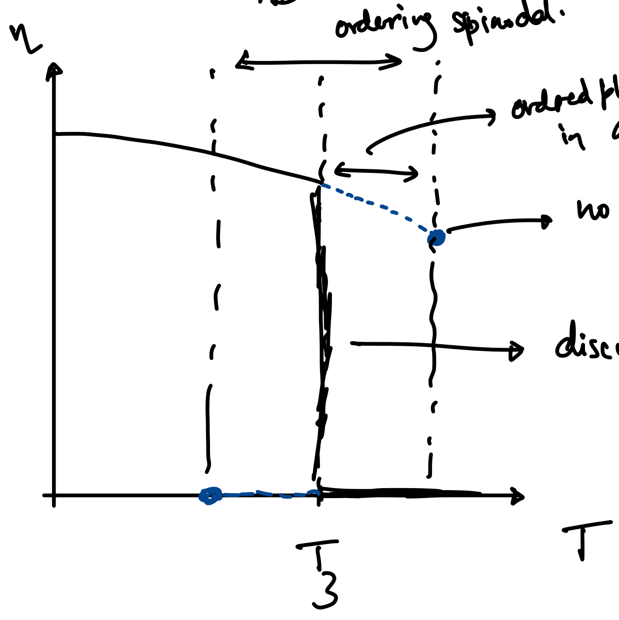


The order parameter smoothly transitions from 1 to 0

* 1st order phase transition:







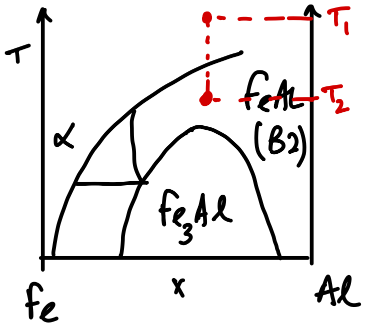
ordered phase is in a local minimum.

no longer a local minima for the ordered phase at temperatures higher than this

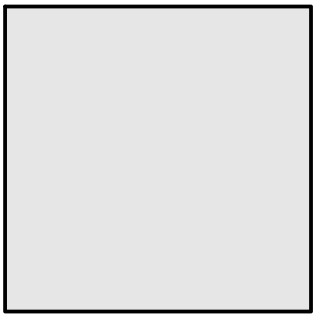
discontinuity in order parameter ⇒ 1st order

At temperatures below the order-disorder transition temperature (for 2nd order phase transition and below the ordering spinodal for 1st order we will have a negative curvature of the free energy w/respect to η ⇒ Similar mechanism and kinetics to Spinodal decomposition.

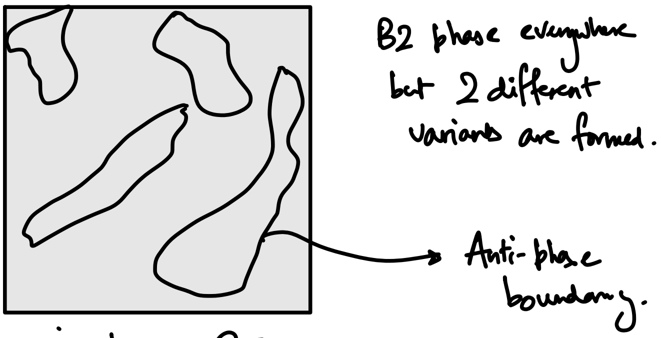
* PHENOMENOLOGICAL THEORY OF ALLEN-CAHN:



Allen-Cahn: studying the binary Fe-Al alloy with a composition ~ 25% Al



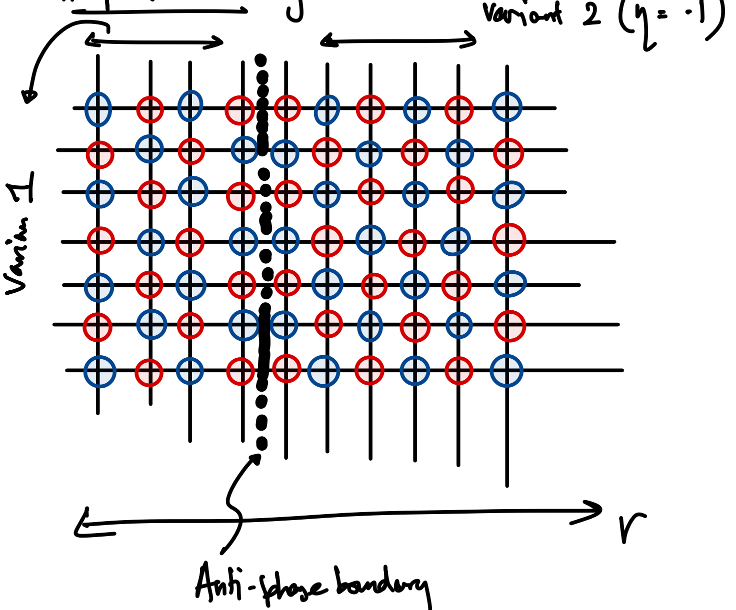
microstructure @T_1



microstructure @T_2

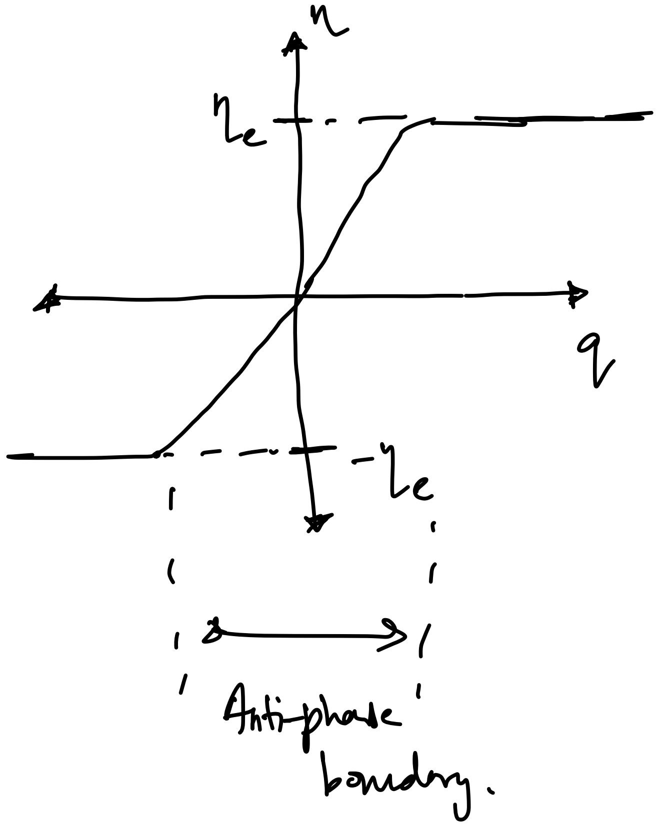
B2 phase everywhere but 2 different variants are formed.

Anti-phase boundary:

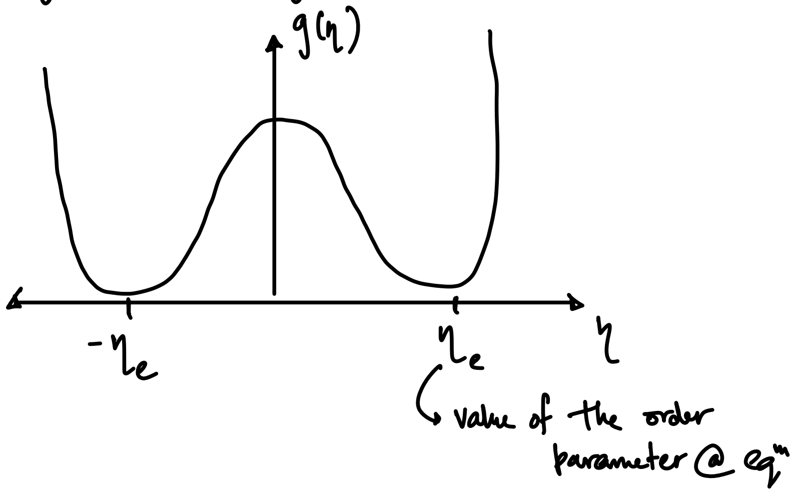


At the APB ⇒ A-A and B-B bonds are energetically unfavorable.

APB's cost the system energy.



System can minimize its energy by getting rid of APB



Similar to the case of spinodal decomposition:

$$\underset{\text{functional}}{G\left[\eta(\vec{r})\right]} = \int_V \left[g(\eta(\vec{r})) + \underbrace{\kappa(\nabla\eta)^2}_{\text{gradient energy}} \right] d\vec{r}$$

* EVOLUTION EQUATION:

- for Cahn-Hilliard → we obtained an evolution equation from ficks. first and 2nd laws
- we need an evolution equation for the order parameter field.

$\eta \rightarrow$ non-conserved. ⇒ no conservation equation.

- The evolution equation must result in an overall decrease in the total free energy with time.

$$\frac{\partial \eta}{\partial t} = -\alpha \frac{\delta \Delta G}{\delta \eta}$$

Allen-Cahn Mobility → related to how quickly APB's move.

taking the variational derivative of $\Delta G = \int \{ \Delta g + \kappa \nabla^2 \eta \} \, dr \Rightarrow \frac{\delta \Delta G}{\delta \eta} = \frac{\partial \Delta g}{\partial \eta} - 2\kappa (\nabla^2 \eta)$

$$\boxed{\frac{\partial \eta}{\partial t} = -\alpha \left(\frac{\partial \Delta g}{\partial \eta} \right) + M \nabla^2 \eta}$$