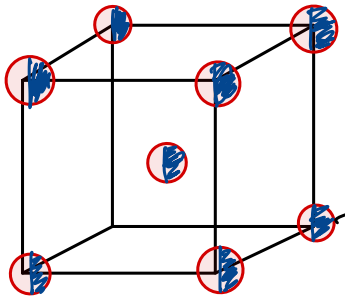
ORDER-DISORDER REACTIONS:

Example: ①

bcc

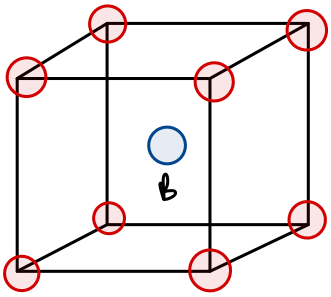


disordered phase on the bcc structure

A & B atoms are randomly distributed across the entire structure

⇒ NO LONG-RANG BCC ORDER

B2

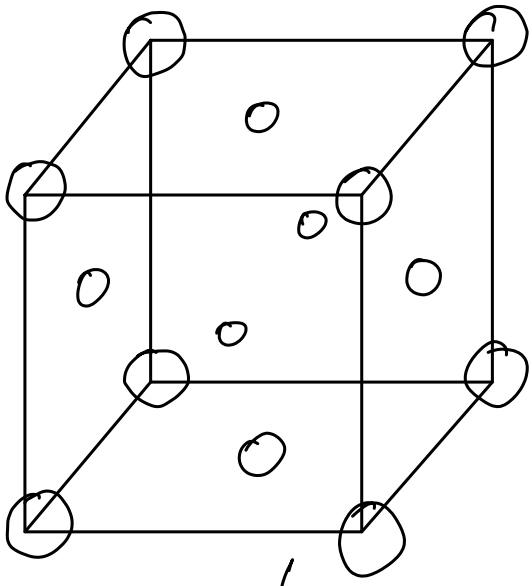


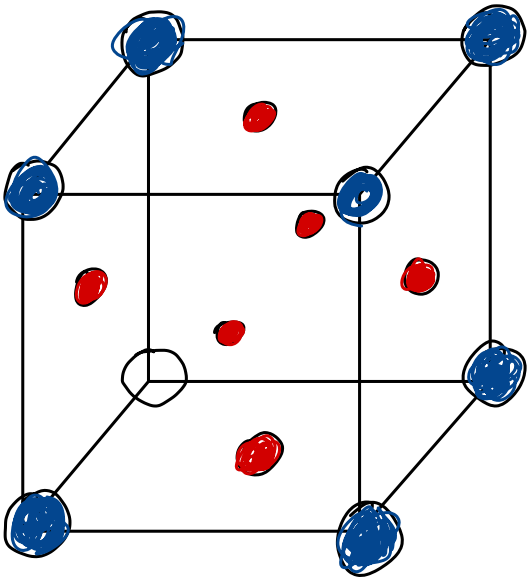
A atoms occupy one set of sites,

B atoms occupy the other.

Strukturbericht notation.

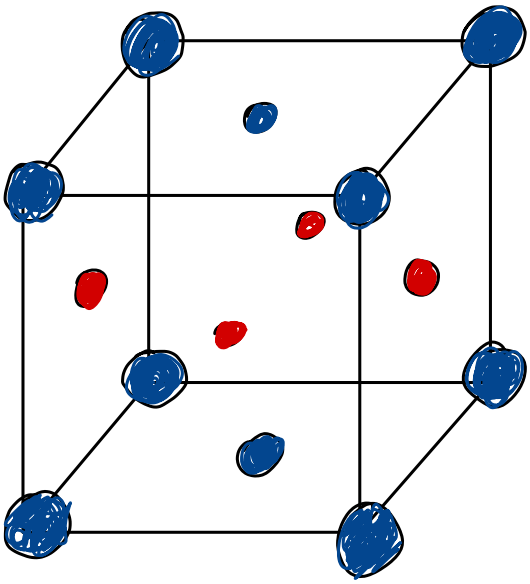
② fcc:





$L1_2$

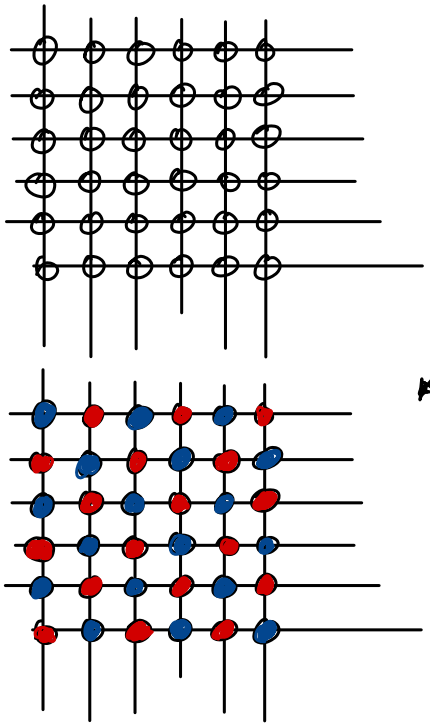
(A_3B)



$L1_0$

(AB)

2- Dimensional examples:



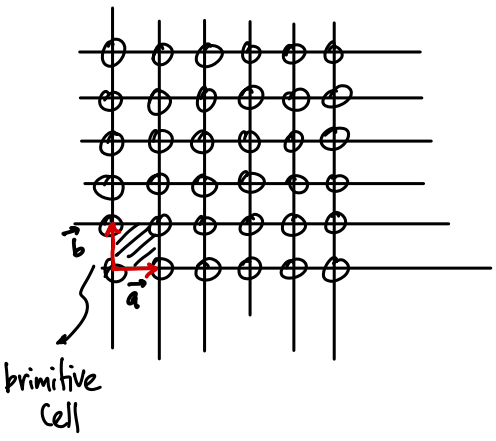
Consider a material system where A-B bonds are preferred.

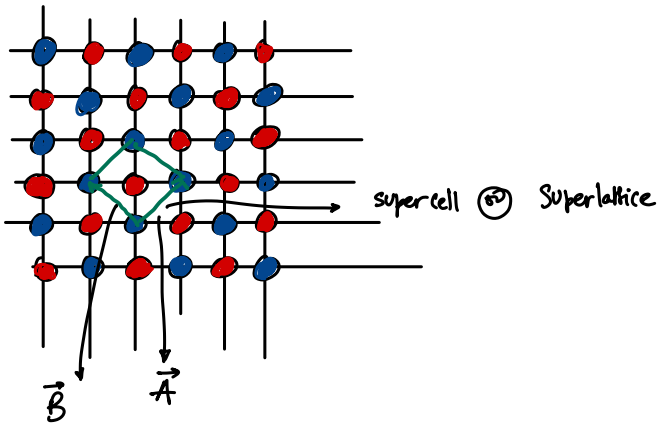
To describe these phase transitions we need descriptors that can uniquely identify each phase of interest.

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:



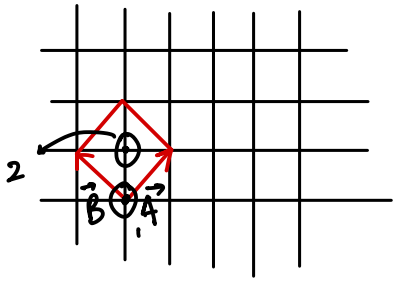


$$\vec{A} = \vec{a} + \vec{b}$$
$$\vec{B} = -\vec{a} + \vec{b}$$

$\Rightarrow$ 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".

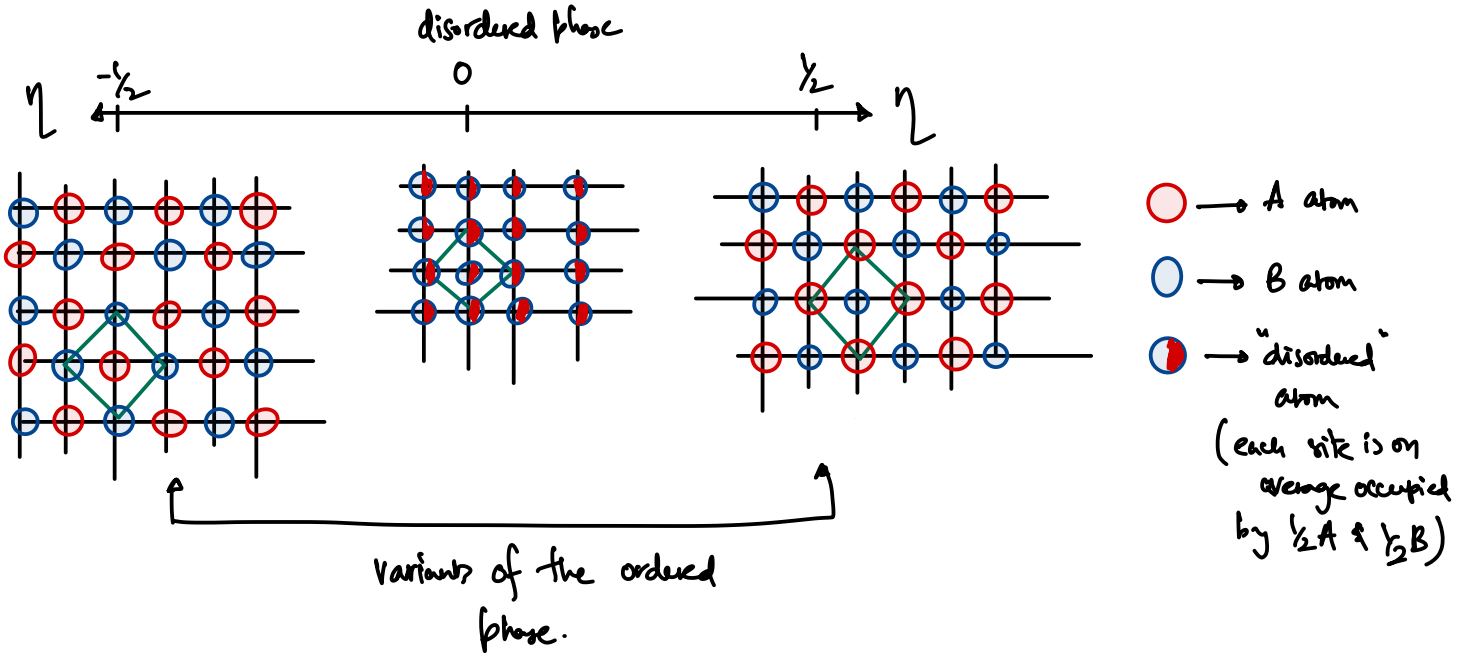
We have 2 sublattices in the above supercell.

Let the concentration of element A on sublattice 1 be X_1
and concn. in sublattice 2 be X_2

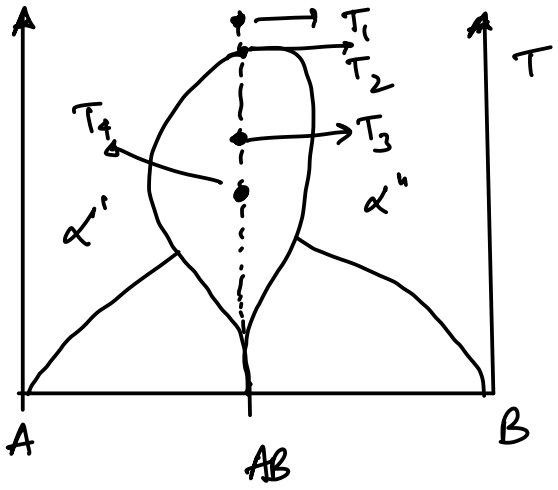
③ Order parameters can be derived as linear combinations of sublattice compositions:

$$X = \frac{X_1 + X_2}{2} = \text{Average composition of the alloy.}$$

$$\eta = \frac{X_1 - X_2}{2} = \text{order parameter to distinguish the ordered phase from the disordered phase}$$



* Phase Diagrams, Order Parameters & Free Energies:



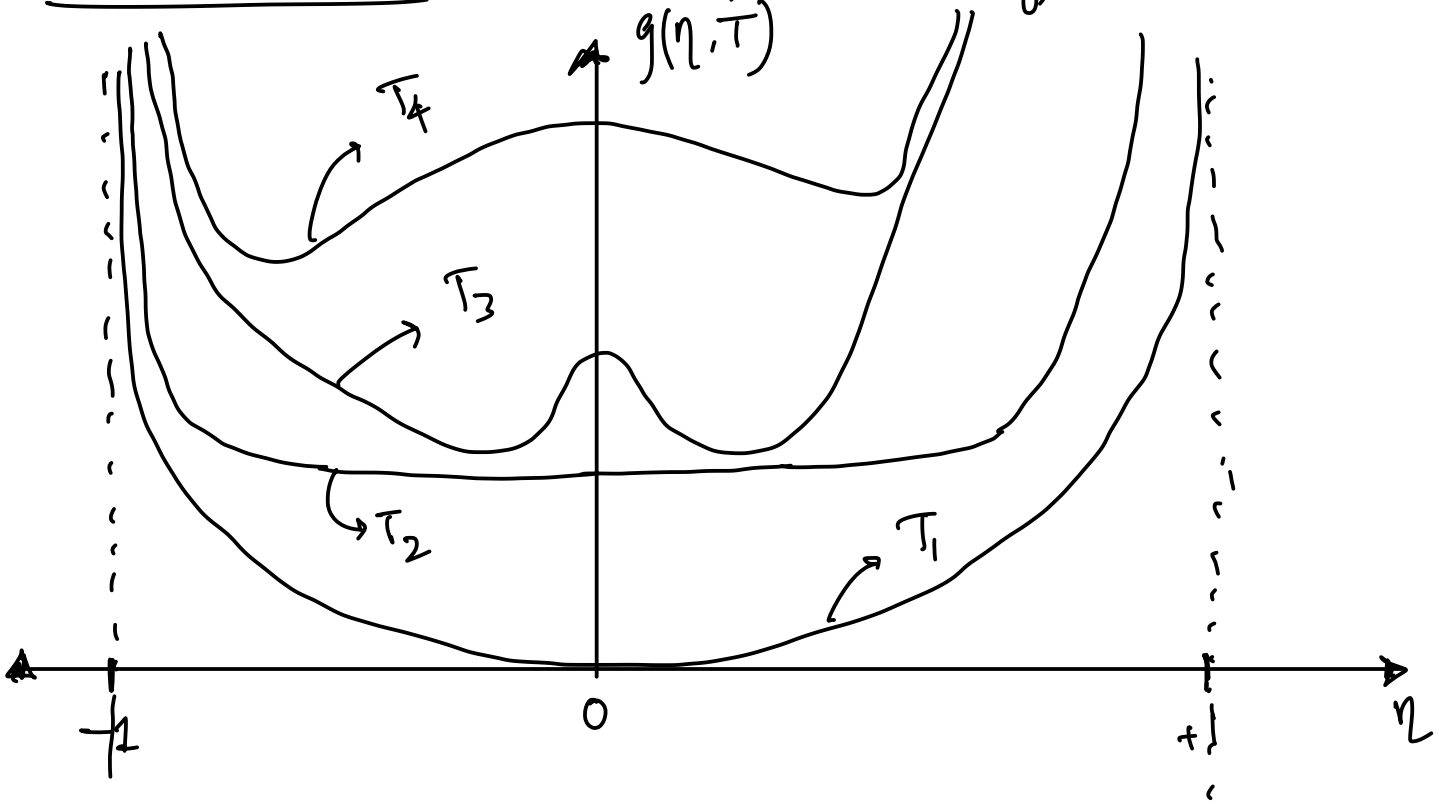
Consider the phase diagram

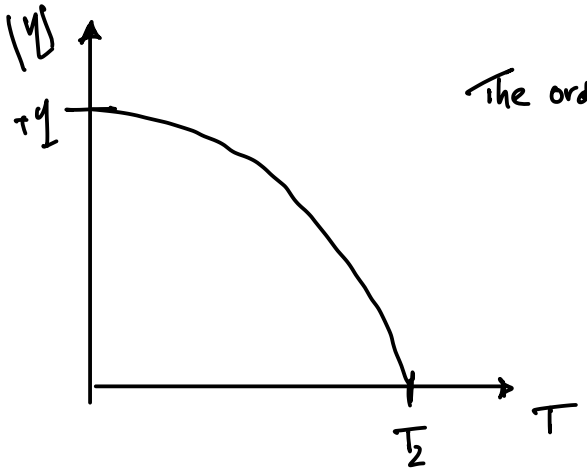
The ordered AB phase undergoes a 2nd order phase transition to the disordered phase at elevated temperatures.

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

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

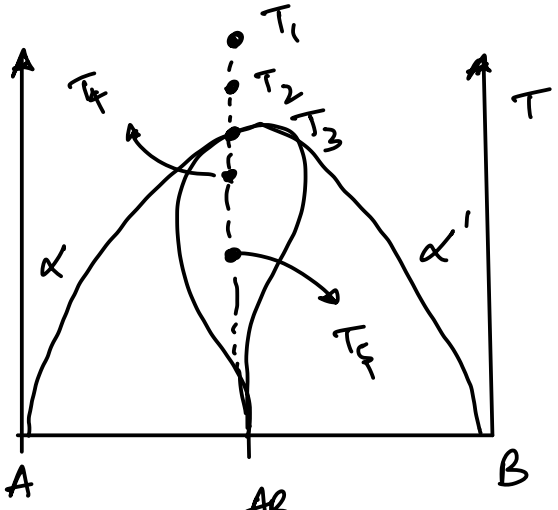
examples of such phase transitions: B2 $\leftrightarrow$ bcc, checkerboard ordering, $L1_0 \leftrightarrow$ fcc, ...

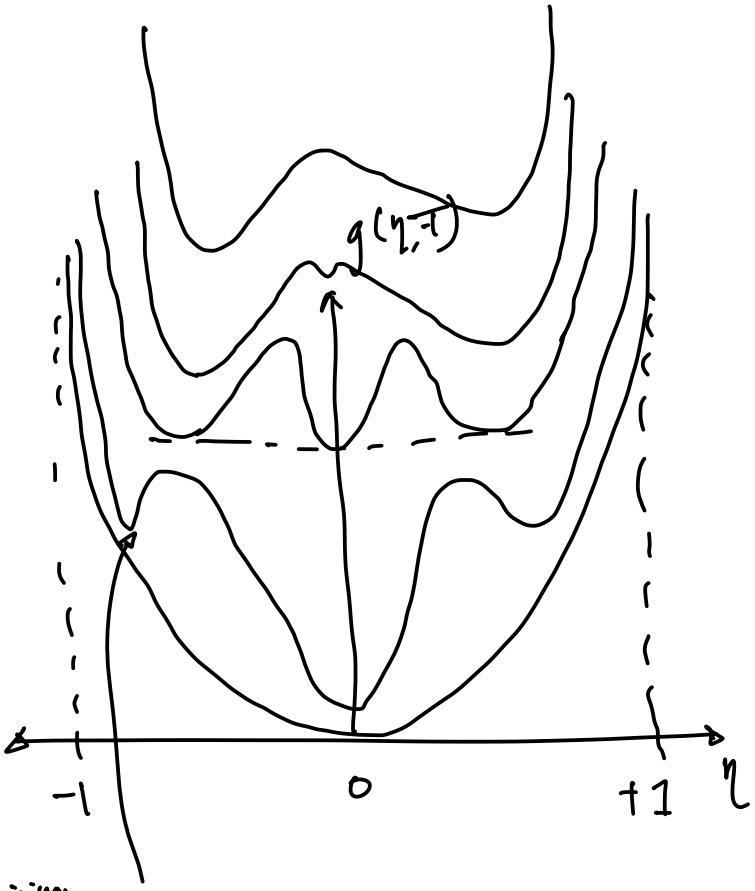




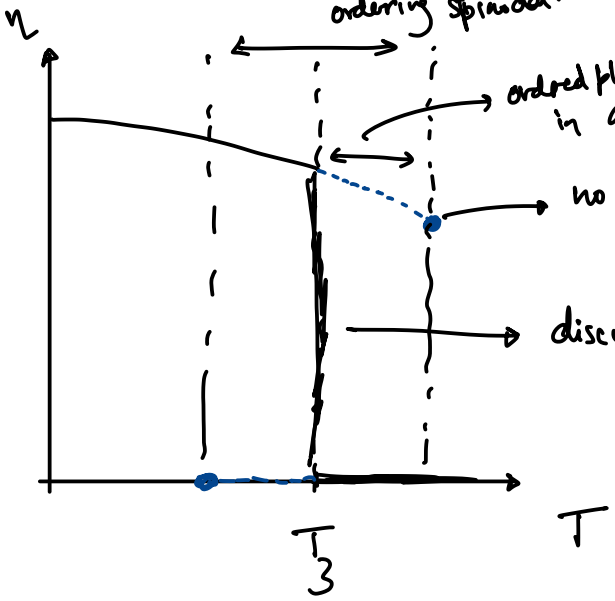
The order parameter smoothly transitions from 1 to 0

* 1st order phase transition:





local minima



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 transitions) 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.