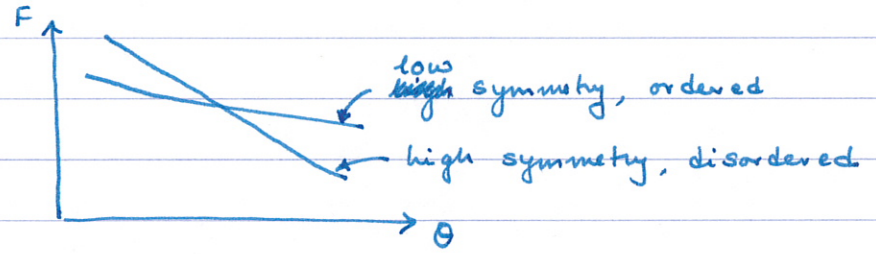
3. Phase transitions in solids

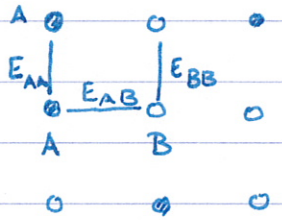
Recall from thermodynamics,

$$F = U - \Theta S$$

- F: free energy
- U: internal energy
  - energy of atomic bonds + vibrations
  - promotes order, low symmetry
- S: entropy
  - vibrational + configurational
  - promotes disorder, high symmetry



3.1 Binary alloys in square lattices



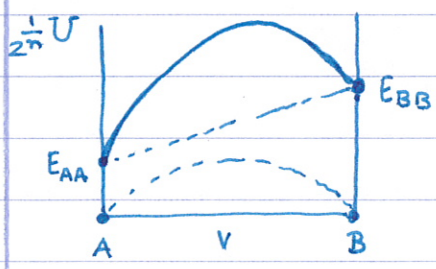
- n atoms, n_A of material A, n_B of B.
- Nearest neighbor interactions with bonds of strength (E_{AA}, E_{BB}, E_{AB}) (energy)
- $E_{AA} \leq 0$, $E_{BB} \leq 0$, $E_{AB} \leq 0$; $\boxed{E_{AB} > \frac{1}{2}(E_{AA} + E_{BB})}$

1. Internal energy of a random arrangement

$$U = \frac{4n}{2}\left[v\left(vE_{AA} + (1-v)E_{AB}\right) + (1-v)\left(vE_{AB} + (1-v)E_{BB}\right)\right]$$

$\frac{n_A}{n}$, vol. fraction of A atoms

$$= 2n\left[vE_{AA} + (1-v)E_{BB} + v(1-v)\underbrace{\{2E_{AB} - E_{AA} - E_{AA}\}}_{<0}\right]$$



… likes ordered/pure A or B states

2. Entropy

Assume energy differences are not too large, equidistributed configuration.

Probability of finding some state i (config) $= P_i = \left(\frac{n!}{n_A! n_B!}\right)^{-1}$

Recall Stirling formula $\log n! = n \log n - n$

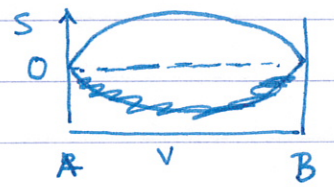
$$S = -k_B \sum_i P_i \log P_i$$

$$\log\left(\frac{n_A! n_B!}{n!}\right) \simeq n_A \log n_A + n_B \log n_B - n \log n \quad (n = n_A + n_B)$$

$$= n\left[\frac{n_A}{n} \log \frac{n_A}{n} + \frac{n_B}{n} \log \frac{n_B}{n}\right]$$

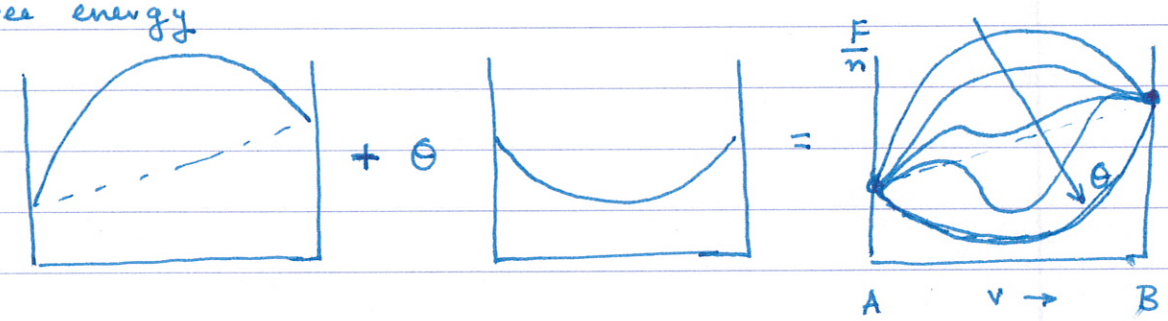
$$= n\left[v \log v + (1-v) \log (1-v)\right]$$

$$= -k_B n \left[v \log v + (1-v) \log (1-v)\right]$$



Note $-\theta S$ promotes disorder.

3. Free energy



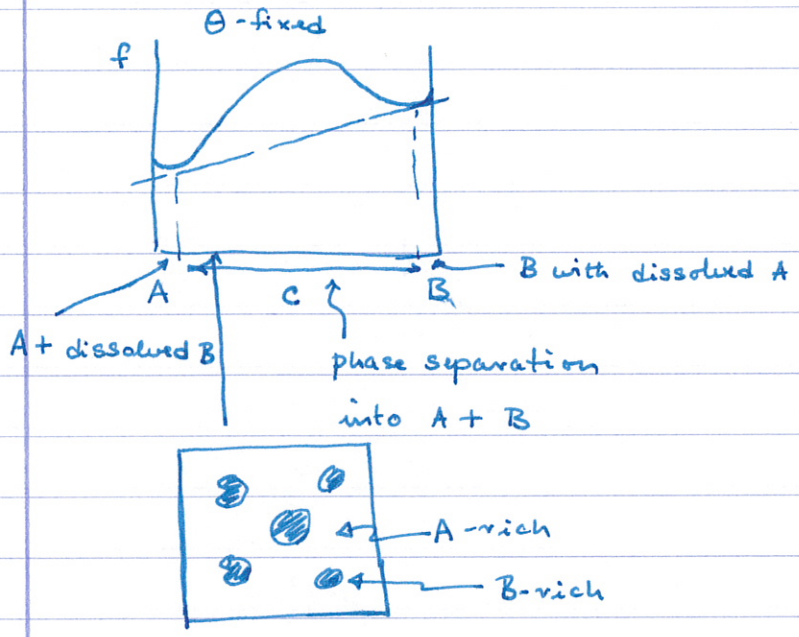
4. Phase diagrams.

Normalize with atomic volume to obtain free energy per unit volume $f(c)$, composition/unit volume

$$\min_{\langle c \rangle = \bar{c}} \int_\Omega f(c)\,dx = \text{volume } \Omega \min_{\langle c \rangle = \bar{c}} \langle f(c) \rangle$$

$$= \text{vol. } \Omega \; f^c(\bar{c})$$

↑ convexification of f.



Repeat at various temperatures to obtain phase diagram

Examples from Porter and Easterling.

Examples from materials

Comments. - Surface energy

- Kinetics

- Diffusion