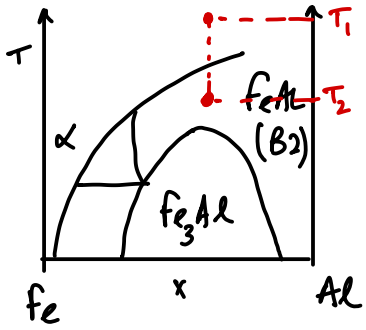
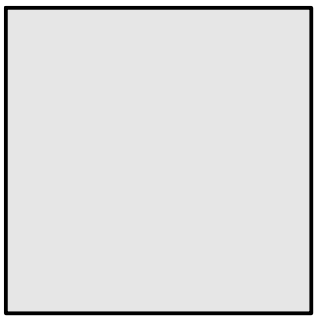
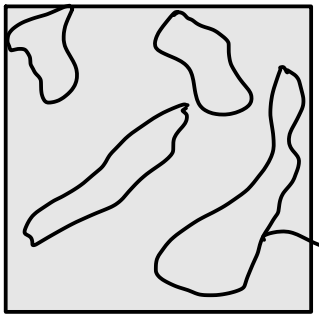
* PHENOMENOLOGICAL THEORY OF ALLEN-CAHN:



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



microstructure @ T_1

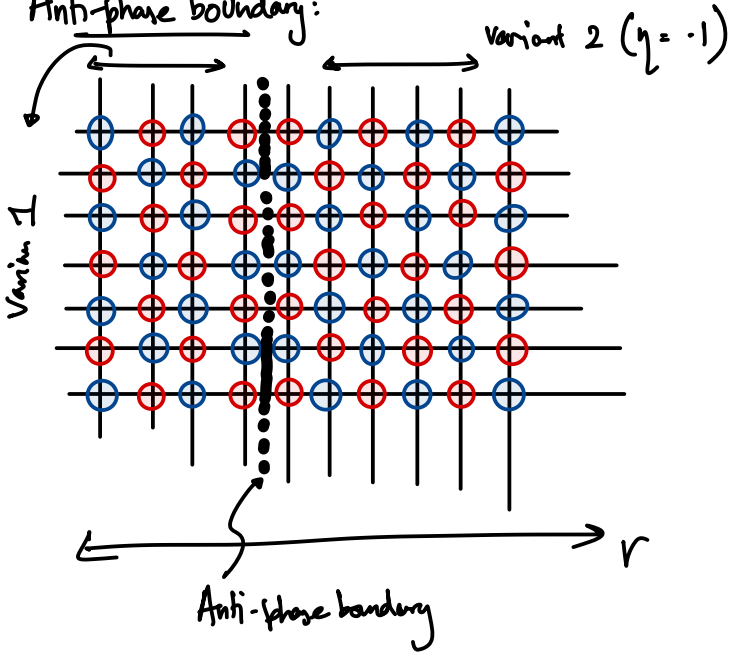


microstructure @ T_2

B2 phase everywhere but 2 different variants are formed.

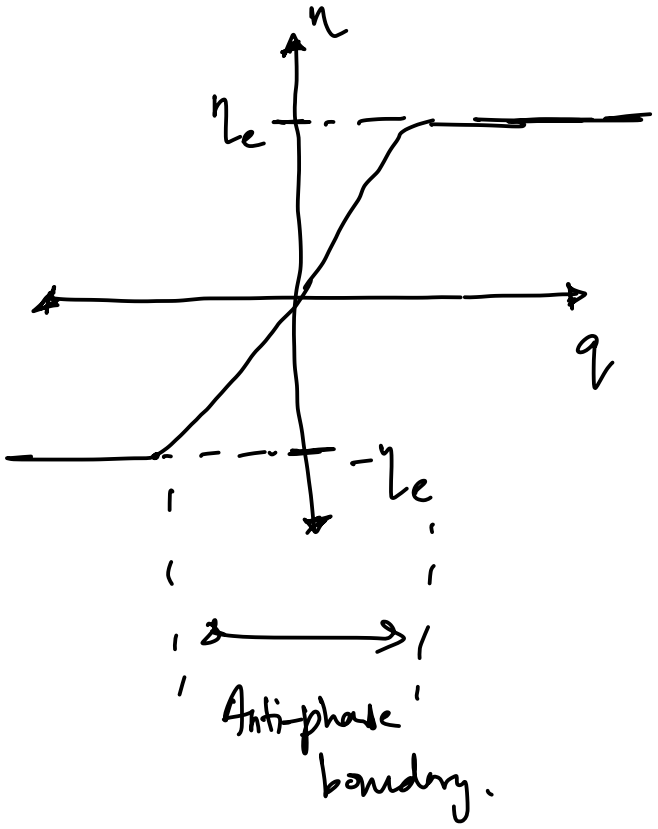
Anti-phase boundary.

Anti-phase boundary:

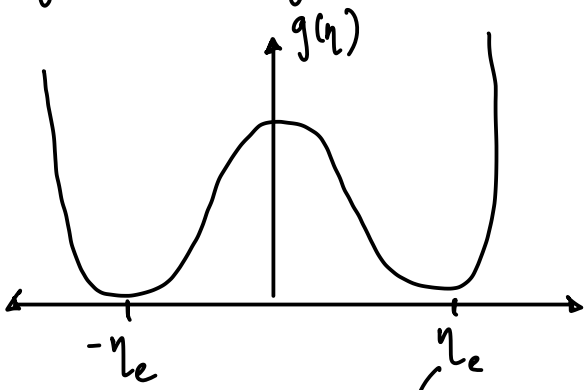


At the APB ⇒ A-A and B-B bonds are energetically unfavorable.

APB's cost the system energy.



System can minimize its energy by getting rid of APB



↳ value of the order parameter @ eq^m

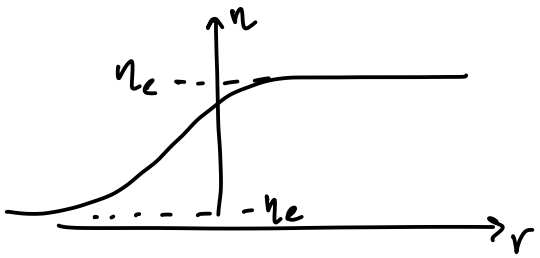
Similar to the case of Spinodal decomposition:

$$G\left[\eta(\vec{r})\right] = \int_V \left[g(\eta(\vec{r})) + k(\nabla\eta)^2\right] d\vec{r}$$

$G[\eta(\vec{r})]$: functional

$k(\nabla\eta)^2$: gradient energy.

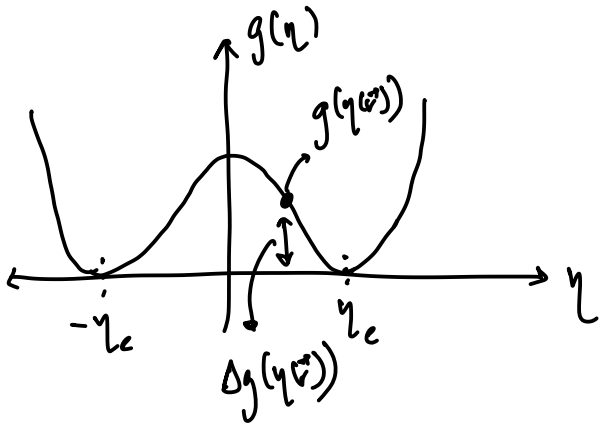
* Consider a planar APB that is @ eqm.



$$G^{excess} = \Delta G = G - G^{perfect}$$

$$G^{perfect} = \int_V g(\eta_e)\, d\vec{r}$$

$$\Delta G = \int_V \Big[\underbrace{\big(g(\eta(\vec{r})) - g(\eta_e)\big)}_{\Delta g(\eta(\vec{r}))} + k(\nabla\eta)^2 \Big]\, d\vec{r}$$



To find the $\eta(\vec{r})$ that corresponds to an APB @ eqm. we have to variationally minimize ΔG wrt $\eta(\vec{r})$:

$$\boxed{\frac{\delta \Delta G}{\delta \eta} = 0}$$

→ Identical mathematics to minimizing $\mathcal{L}$ for the spinodal decomposition.

The only difference is the lack of a Lagrange multiplier conserving $\eta(\vec{r})$

$$\Rightarrow \boxed{\frac{\partial \Delta g(\eta(\vec{r}))}{\partial \eta} - 2k\nabla^2\eta = 0}$$

In 1D: $\boxed{\frac{\partial \Delta g}{\partial \eta} = 2k\frac{\partial^2 \eta}{\partial r^2}}$ Integrate this equation to compute $\eta(\vec{r})$

$$\int_{-\eta_e}^{\eta} \frac{\partial \Delta g}{\partial \eta}\, d\eta = \int_{-\eta_e}^{\eta} 2k\frac{\partial^2 \eta}{\partial r^2}\, d\eta = \int_{-\eta_e}^{\eta} 2k\frac{\partial^2 \eta}{\partial r^2}\frac{\partial \eta}{\partial r}\, dr$$

LHS: $\int_{-\eta_e}^{\eta} \frac{\partial \Delta g}{\partial \eta} d\eta = \Delta g(\eta(\vec{r})) - \Delta g(\eta_e) = \Delta g(\eta(\vec{r}))$ [recall $\Delta g = g(\eta) - g(\eta_e)$]

RHS: $\int_{-\infty}^{r} 2k \frac{\partial^2 \eta}{\partial r^2} \frac{\partial \eta}{\partial r} dr$

Let $\frac{\partial \eta}{\partial r} = u \Rightarrow du = \frac{\partial^2 \eta}{\partial r^2} dr$

RHS: $\int_{\partial\eta/\partial r|_{-\infty}}^{\partial\eta/\partial r|_r} 2k u\, du = \left(k u^2\right)_{u=0}^{u=\frac{\partial \eta}{\partial r}} = k\left(\frac{\partial \eta}{\partial r}\right)^2$

$\left(\frac{\partial \eta}{\partial r}\right)_{-\infty}$

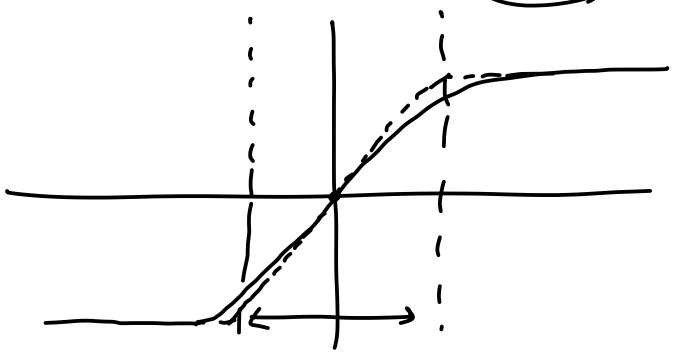
$$\boxed{\Delta g(\eta) = k\left(\frac{\partial \eta}{\partial r}\right)^2}$$

Integrate by separation of variables:

$$\boxed{\frac{d\eta}{\sqrt{\Delta g(\eta)}} = k\,dr}$$

Due to the symmetry of Δg about $\eta = 0$ the solution has to have a sigmoid shape:

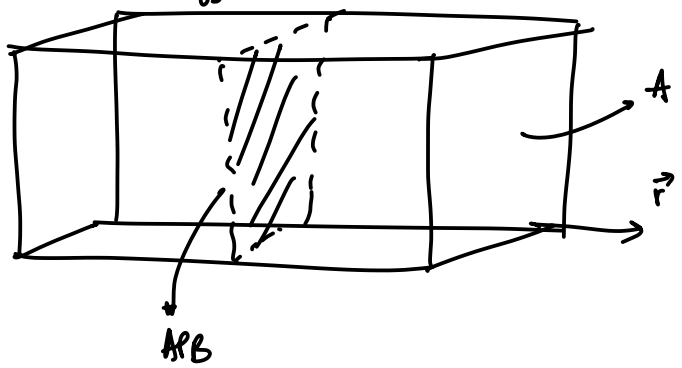
for instance: $\eta(r) \sim \tanh(\alpha r)$ (α: constant related to $\Delta g(\eta)$)



$$l \simeq 2\eta_e \left[\frac{k}{\Delta g_{max}}\right]^{1/2}$$

$$\boxed{\begin{array}{l} k \uparrow \; l \uparrow \\ \Delta g_{max} \downarrow \; l \uparrow \end{array}}$$

* Excess free energy per unit area:



$$\Delta G^{excess} = \int_A \int_r \left\{ \Delta g_0(\eta(r)) + K\left(\frac{\partial \eta}{\partial r}\right)^2 \right\} dr\, dA$$

$$\Delta G^{excess} = \int_A \int_r \left[K\left(\frac{\partial \eta}{\partial r}\right)^2 + K\left(\frac{\partial \eta}{\partial r}\right)^2 \right] dr\, dA = A \int_{-\infty}^{\infty} \left[2K\left(\frac{\partial \eta}{\partial r}\right)^2 \right] dr$$

$$\boxed{\frac{\Delta G^{excess}}{A} = \int_{-\infty}^{\infty} \left[2K\left(\frac{\partial \eta}{\partial r}\right)^2 \right] dr}$$

* 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.

  η → non-conserved. ⇒ no conservation equation.

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

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

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

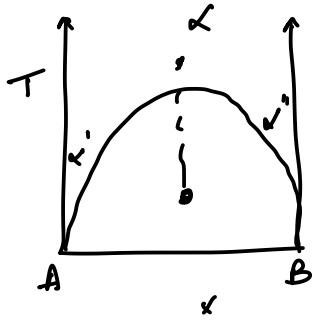
taking the variational derivative of $\Delta G = \int \{ \Delta g + K \nabla^2 \eta \} dr \Rightarrow \frac{\delta \Delta G}{\delta \eta} = \frac{\partial \Delta g}{\partial \eta} - 2K(\nabla^2 \eta)$

$$\boxed{\frac{\partial \eta}{\partial t} = -\alpha\left(\frac{\partial \Delta g_0}{\partial \eta}\right) + M \nabla^2 \eta}$$

* ROLE OF STRAIN ENERGY:

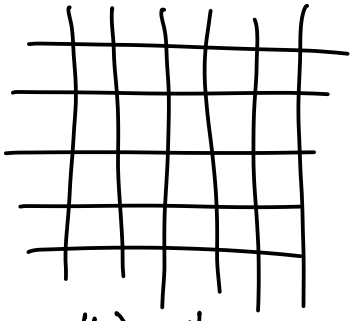
→ Most phase transformations in solids are accompanied by a change in the crystal structure.

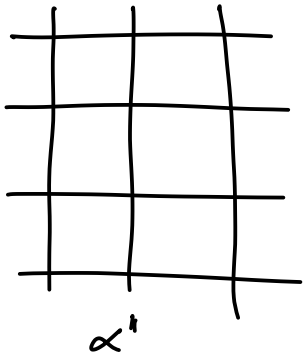
(eg)



say A & B have a cubic structure

in general the lattice parameter of A and B will be different.

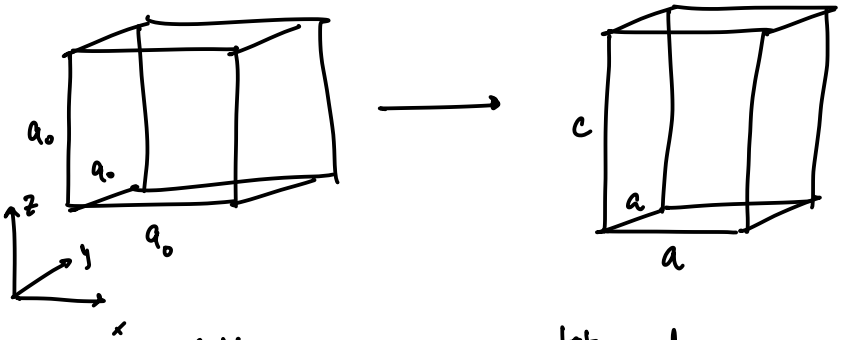




for α' & α'' to coexist (coherently). α' we will need to strain both or one of them.

MEASURING STRAIN:

- measure of deformation → has to be measured relative to a reference state.

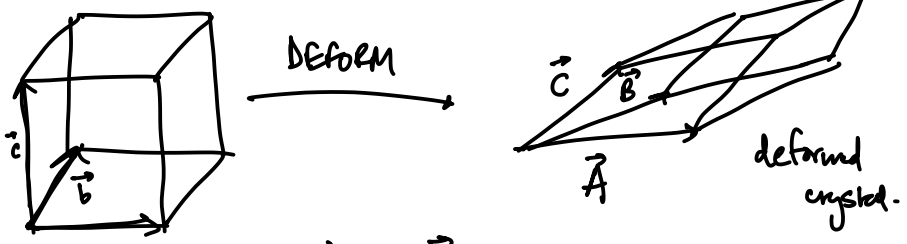


cubic ⟶ tetragonal.

if the changes in lengths are small: (infinitesimal strain)

$$\varepsilon_{xx} = \frac{a - a_0}{a_0} \qquad \varepsilon_{yy} = \frac{a - a_0}{a_0} \qquad \varepsilon_{zz} = \frac{c - a_0}{a_0}$$

What if the changes are much larger?



reference crystal.

$\vec{a} \longrightarrow \vec{A}$

$\vec{b} \longrightarrow \vec{B}$

$\vec{c} \longrightarrow \vec{C}$

The deformation can be represented with the DEFORMATION TENSOR (f)

$f \longrightarrow 3\times 3$ matrix

such that

$$f\vec{a} = \vec{A}$$
$$f\vec{b} = \vec{B}$$
$$f\vec{c} = \vec{C}$$

$\vec{a}, \vec{b}, \vec{c}$ can be collected within a matrix:

$$\mathcal{L} = [\vec{a}, \vec{b}, \vec{c}] = \begin{bmatrix} a_x & b_x & c_x \\ a_y & b_y & c_y \\ a_z & b_z & c_z \end{bmatrix}$$

Similarly

$$\mathcal{L}' = [\vec{A}, \vec{B}, \vec{C}]$$

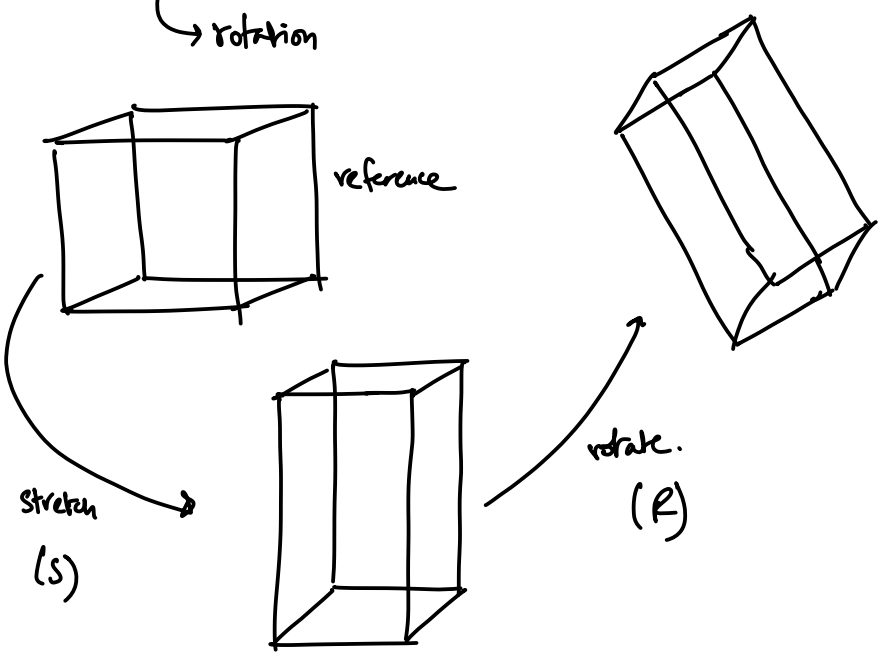
$$F[\vec{a}, \vec{b}, \vec{c}] = [\vec{A}, \vec{B}, \vec{C}]$$

(N) $\boxed{f\mathcal{L} = \mathcal{L}'}$

if we have $\mathcal{L}, \mathcal{L}' \longrightarrow f = \mathcal{L}'\mathcal{L}^{-1}$ (O) if we would like to impose a particular strain $f\mathcal{L} = \mathcal{L}'$

We can decompose f as

$F = R \cdot S$ → stretch.
↳ rotation



$R \longrightarrow$ rotation matrix $\longrightarrow$ unitary

$$\Rightarrow \bar{R}R = I$$

Consider:

$$f^T f = (RS)^T (RS) = S^T \underbrace{R^T R}_{I} S = S^T S$$

$f^T f \longrightarrow$ invariant to rigid rotations!

Can we use $f^T f$ as a metric of strain?

Say $f = I \Rightarrow f\mathcal{L} = \mathcal{L}' \Rightarrow \mathcal{L} = \mathcal{L}' \Rightarrow$ the crystal is not deformed $\Rightarrow$ Strain should be zero.

$$f^T f = I^T I = I \neq 0$$

One metric that is convenient:

$$E = \text{Green-Lagrange strain} = \frac{1}{2}(f^T f - I) = \frac{1}{2}(S^T S - I) \longrightarrow E \text{ is symmetric}$$

when the deformations are small:

$$E \approx \begin{bmatrix} \varepsilon_{xx} & \varepsilon_{xy} & \varepsilon_{xz} \\ \varepsilon_{xy} & \varepsilon_{yy} & \varepsilon_{yz} \\ \varepsilon_{xz} & \varepsilon_{yz} & \varepsilon_{zz} \end{bmatrix}$$

* FREE ENERGY & STRAIN:

The free energy of a phase will in general depend on the state of strain

$$H\left(\varepsilon_{xx}, \varepsilon_{yy}, \varepsilon_{zz}, \varepsilon_{yz}, \varepsilon_{yx}, \varepsilon_{xz}, c_i, \eta_j, T\right)$$

In general ε_{ij} should be replaced with E_{ij}, we will continue to use ε_{ij} for clarity.

Say the reference crystal has a volume V_0:

$$h = \frac{H}{V_0} = \text{free energy density.}$$

Taylor expand h around $\varepsilon_j = 0$