EPFL
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SuNMIL
Supramolecular NanoMaterials and Interfaces Laboratory

Heterophase Grain Boundaries
Lesson 11

MSE 304

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Reading for this Class

→ Chapter 14 Howe's book

Chen–Hillard diffuse interface model

↳ original paper (uploaded)

Key Topics in the Previous Class

Coherent interfaces → DCL

coincidence lattice

$\vec{S}_1, \vec{S}_2$ $\quad \vec{b} = f(\vec{S}_1, \vec{S}_2)$

$\vec{b} \cdot \vec{n} = \vec{S}_1 - \vec{S}_1$ ledge dislocation

$\vec{b} \cdot \vec{n} = 0$ misfit dislocation $\} \; \vec{b}$

special interfaces → stacking faults

→ twin boundaries

Heterophase Grain Boundaries

solid-solid Material M, phase α, $\{h,k,l\}$, θ, $\vec{u}$

Coherent [5 -200 mJ/m^2]

two crystals that have: same phase same Bravais lattice, same crystal parameters, same facet

Semi-coherent [200-800 mJ/m^2]

2 phase (same material or different material) same Bravais lattice but different unit cell parameters

α, β, (h,k,l), θ (can be 0°), $\vec{u}$

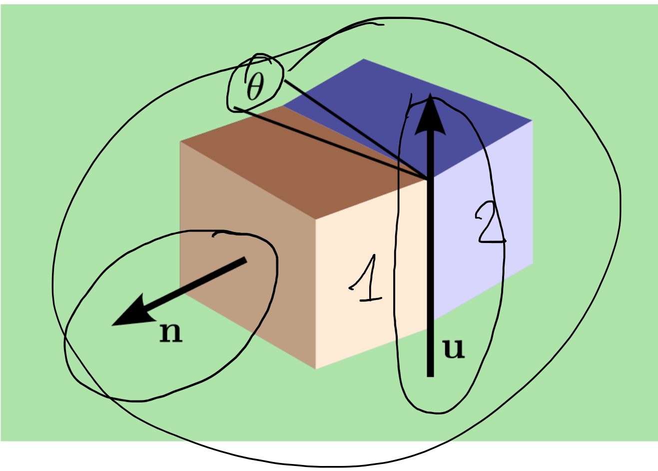
δ a_α a_β

Incoherent [800-2500 mJ/m^2]

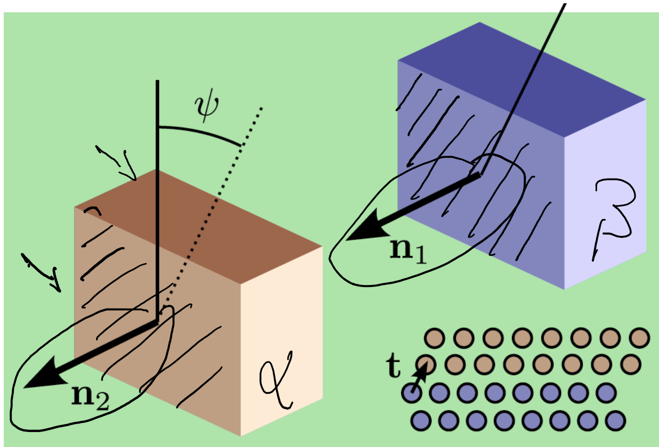
everything else

Heterophase Grain Boundaries: Nomenclature

For simple interfaces we have used this approach



For complex interfaces we to use:



5 degrees of freedom

Planes (hkl)

$(111)_\alpha \| (101)_\beta$; $[11]_\alpha \| [102]_\beta$

Directions [uvw]

$$(hkl)_\alpha \| (hkl)_\beta ; [uvw]_\alpha \| [uvw]_\beta$$

α : f.c.c. Fe_γ

β : b.c.c. Cu_α

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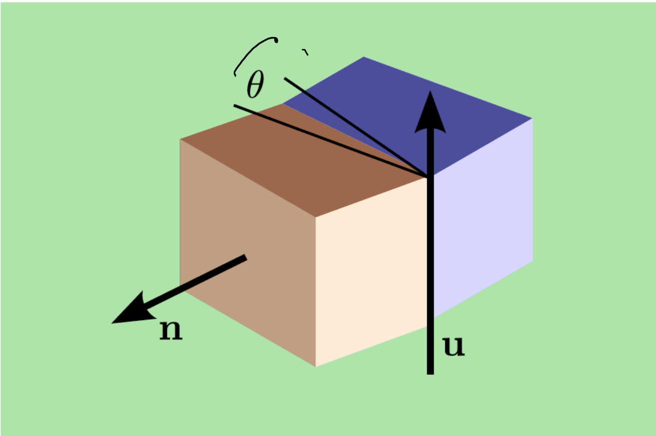
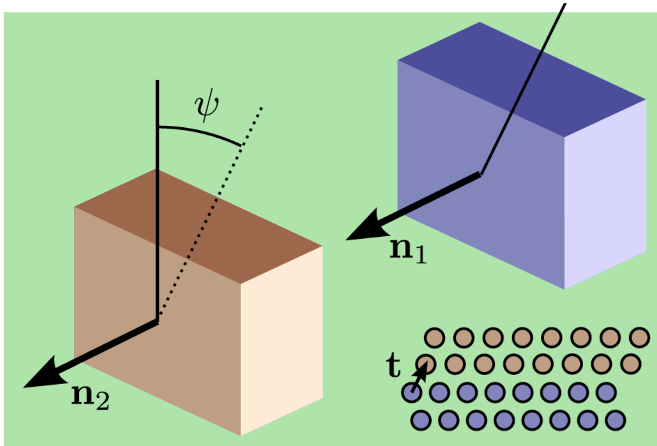
Heterophase Grain Boundaries: Nomenclature

For simple interfaces we have used this approach



For complex interfaces we to use:

α



Planes (hkl)

Directions [uvw]

$$\boxed{(hkl)_\alpha \| (hkl)_\beta;\ [uvw]_\alpha \| [uvw]_\beta}$$

$(111)_\alpha \,\|\, (311)_\alpha\ ;\ [111]_\alpha\ [311]_\alpha$

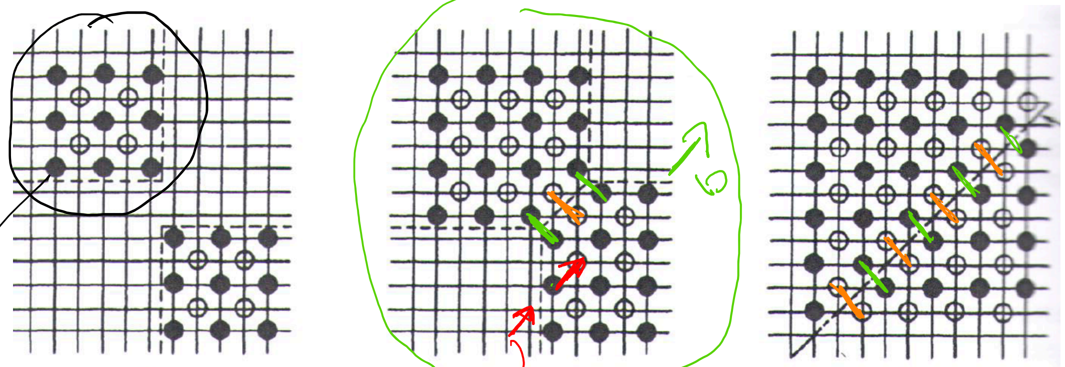
Special Grain Boundaries

semi coherent interface (coherent)

$\gamma = 2(a-b) - (a-a) - (b-b)$

Antiphase Domain Boundaries

CoPt

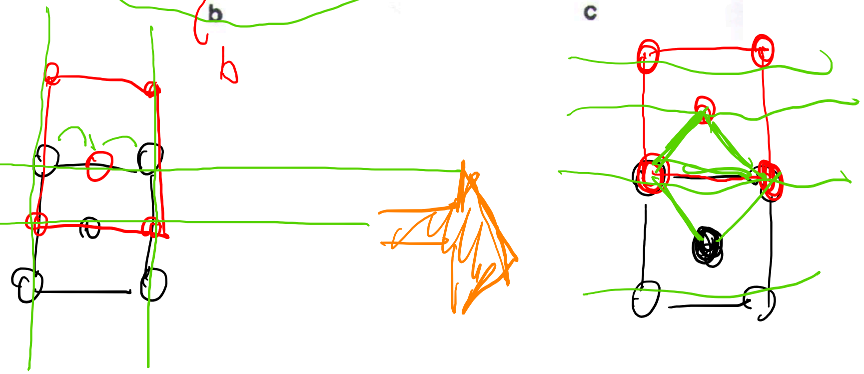


a b c

b

NaCl 2 f.c.c

(0, 0, 0) $\left(\frac{1}{3}, \frac{1}{3}, \frac{1}{3}\right)$



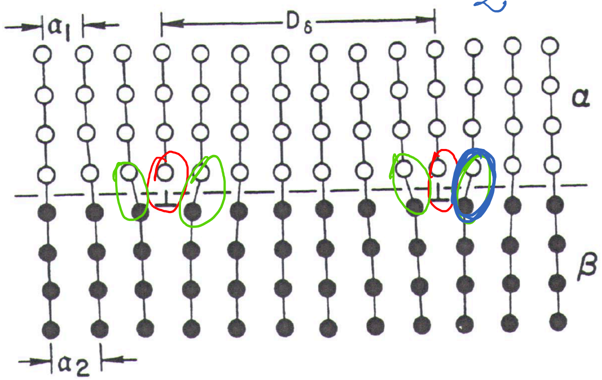
Energetics of Semi-coherent Grain Boundaries

$\varepsilon_m \cdot \frac{1}{D_\delta}$

$a' = \frac{a_1 + a_2}{2}$

$\gamma_{sc}^{ss} = \gamma_c^{ss} + \gamma_s^{ss}$

elastic strain



Turnbull $\gamma_{sc}^{ss} = \gamma_c^{ss} + \gamma_s^{ss}$

$$D_\delta = \frac{(a_1 + a_2)^2}{4(a_1 - a_2)}$$

$$\boxed{\delta = \frac{2(a_1 - a_2)}{a_1 + a_2} = \frac{a_1 - a_2}{a'}}$$

$$\boxed{D_\delta = \frac{a'}{\delta} = \frac{b}{\delta}}$$

net of misfit dislocations

$$\gamma_s^{ss} = \frac{\mu a'}{4\pi^2}\left\{1 + \Lambda - \left(1 + \Lambda^2\right)^{1/2} - \Lambda \ln\left[2\Lambda\left(1 + \Lambda^2\right)^{1/2} - 2\Lambda^2\right]\right\}$$

μ, μ_α, μ_β shear moduli

$$\Lambda = 2\pi\delta\left(\frac{C_8}{\mu}\right)$$

ν_α, ν_β → Poisson ratios

$$\frac{1}{C_8} = \frac{1 - \upsilon_\alpha}{\mu_\alpha} + \frac{1 - \upsilon_\beta}{\mu_\beta}$$

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Eterophase Interphases

$(hkl)_\alpha \| (hkl)_\beta$; $[uvw]_\alpha \| [uvw]_\beta$

2 materials

2 phases

→ 2 materials in 2 phases

$$\gamma_{1-2}^{SS} = \gamma_1 + \gamma_2 - W_{12}$$

$$\mathbf{A} = \begin{bmatrix} e_{11} & e_{12} \\ 0 & 1 \end{bmatrix}.$$

$$X_2 = \underset{\uparrow}{A} \cdot \vec{X}_1 \qquad |A| = 1 \rightarrow \vec{R}$$

A defined in the O-lattice formalism

Eterointerphases

$(hkl)_\alpha || (hkl)_\beta$; $[uvw]_\alpha || [uvw]_\beta$

$$\mathbf{A} = \begin{bmatrix} e_{11} & e_{12} \\ 0 & 1 \end{bmatrix}.$$

$\tan \vartheta = \frac{e_{11}}{e_{12}}$

coincidence lattice

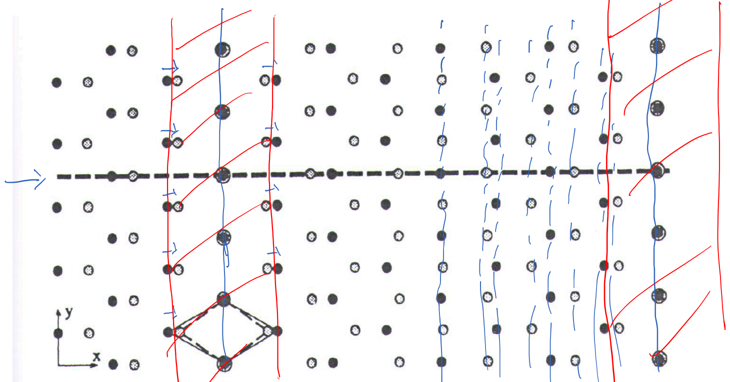

Figure 14.38. Schematic diagram representing the rhombic surface unit cells of a {111} f.c.c. plane (filled circles) and a {110} b.c.c. plane (open circles) when $\tau = a_{f.c.c.}/a_{b.c.c.} = 1.15$. From [143].

High Index Interfaces

$(hkl)_\alpha || (hkl)_\beta$; $[uvw]_\alpha || [uvw]_\beta$

$$\mathbf{A} = \begin{bmatrix} e_{11} & e_{12} \\ 0 & 1 \end{bmatrix}.$$

misfit

O-lattice

low energy plane

ledge

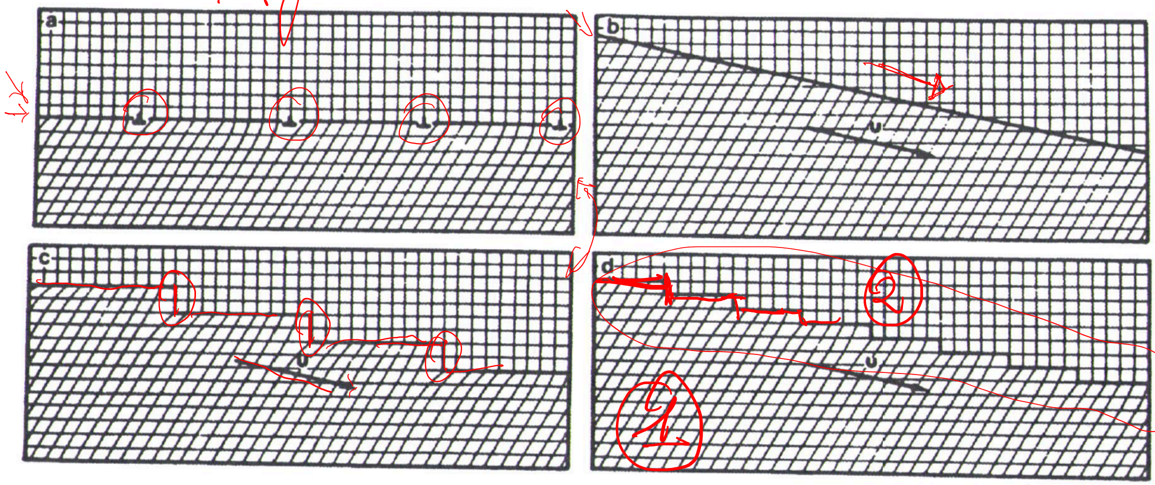

Figure 14.39. Possible interfaces for a transformation described by a shear e_{12} coupled with an expansion e_{11} in the shear plane. (a) The expansion is accommodated by a set of perfect lattice (misfit) dislocations. (b) The interface lies along an invariant line **u** and no dislocations are necessary. (c) The invariant line is resolved onto every other close-packed plane as in the f.c.c.–h.c.p. transformation where each ledge is an α/6<112> partial dislocation. (d) The invariant line is resolved onto every close-packed plane as in an f.c.c.–b.c.c. transformation where each ledge contains an α/12<112> partial dislocation. Reprinted with permission from [153] by Elsevier Science Ltd., Oxford, England.

DCL

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High Index Interfaces

$(hkl)_\alpha || (hkl)_\beta$; $[uvw]_\alpha || [uvw]_\beta$

$$\mathbf{A} = \begin{bmatrix} e_{11} & e_{12} \\ 0 & 1 \end{bmatrix}.$$

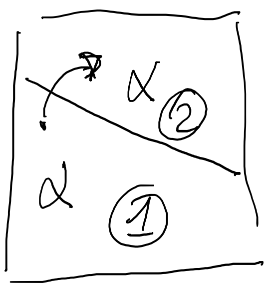
combination
of O-lattice
directions

$\perp$ misfit dislocations

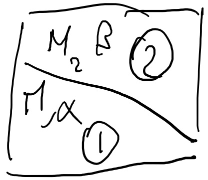
$\perp$ ledge dislocation

Coherent Interfaces: The Cahn Hillard Model

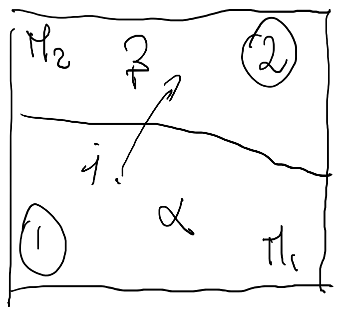
Atomically flat interfaces exist when at least 1 phase is solid and there is no driving force for ~~the~~ components of either phase to mix with the other phase



$$\mu_i^{\alpha}\Big|_{1} = \mu_i^{\alpha}\Big|_{2}$$



→ no solubility of the components of M_1 in M_2



$$\mu^{\alpha}_{i,M_1} \neq \mu^{\beta}_{i,M_2}$$

$\Delta\mu$ → chemical driving for

Coherent Interfaces: The Cahn Hillard Model

$\nabla_i c = \frac{\partial c}{\partial x_i}$

Taylor expansion

i, j direction

$$f(c, \nabla c, \nabla^2 c, \ldots) = f_0 + \sum_i L_i \nabla_i c + \sum_{i,j} k_{ij}^{(1)} \frac{\partial^2 c}{\partial x_i \partial x_j} + \frac{1}{2} \sum_{i,j} k_{ij}^{(2)} \frac{\partial c}{\partial x_i} \frac{\partial c}{\partial x_j} + \cdots$$

$G = N_v f = \sum_i N_i \mu_i$

local chemical potential

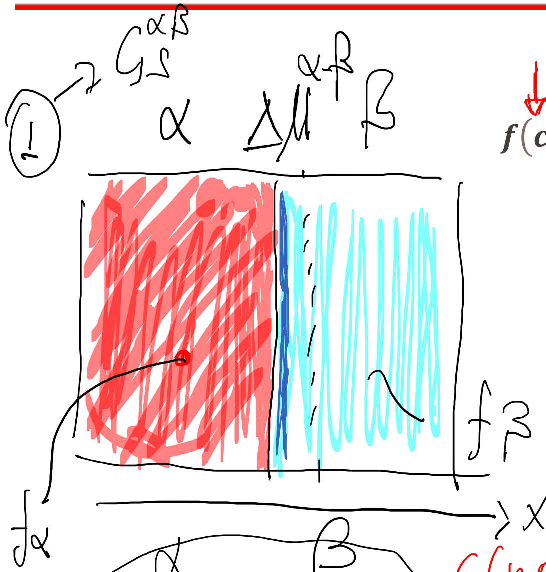
L in thermo

$$L_i = \frac{\partial f}{\partial \left(\partial c / \partial x_i \right)}$$

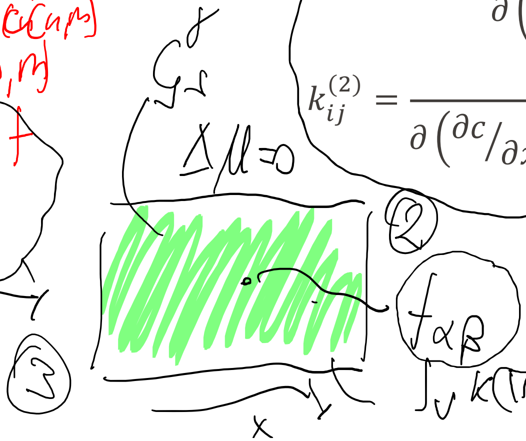
$$k_{ij}^{(1)} = \frac{\partial f}{\partial \left(\frac{\partial^2 c}{\partial x_i \partial x_j} \right)}$$

$$k_{ij}^{(2)} = \frac{\partial^2 f}{\partial \left(\partial c / \partial x_i \right) \partial \left(\partial c / \partial x_j \right)}$$

local free energy (typically molar free energy)



$\int_V k(\nabla c)^2 dV > 0$



$\int_V k(\nabla c)^2 dV \neq 0$

$\int f_\alpha dV_\alpha + \int_{V_\beta} f_\beta dV_\beta \ll \int_V f_{\alpha\beta} dV$

Coherent Interfaces: The Cahn Hillard Model

liquids, glasses

for anisotropic materials

or cubic materials

bcc
fcc
hcp

center of inversion

$$f(c, \nabla c, \nabla^2 c, \ldots) = f_0 + \sum_i L_i \nabla_i c + \sum_{i,j} k_{ij}^{(1)} \frac{\partial^2 c}{\partial x_i \partial x_j} + \frac{1}{2} \sum_{i,j} k_{ij}^{(2)} \frac{\partial c}{\partial x_i} \frac{\partial c}{\partial x_j} + \cdots$$

III

$x_i \rightarrow -x_i$ $\quad$ $x_i \rightarrow x_i$

$$L_i = \frac{\partial f}{\partial \left({\partial c}/{\partial x_i} \right)}$$

$L_i = 0$

[also all odd terms]

$$k_{ij}^{(1)} = \frac{\partial f}{\partial \left(\frac{\partial^2 c}{\partial x_i \partial x_j} \right)}$$

$$k_{ij}^{(2)} = \frac{\partial^2 f}{\partial \left({\partial c}/{\partial x_i} \right) \partial \left({\partial c}/{\partial x_j} \right)}$$

$k_{ij}^{(1)} = k^1 = \frac{\partial f}{\partial (\nabla^2 c)}$ $for\ i = j$; $\quad$ $k_{ij}^{(1)} = 0\ otherwise$

$i \neq j$

$k_{ij}^{(2)} = k^2 = \frac{\partial^2 f}{\partial (|\nabla c|^2)^{1/2}}$ $for\ i = j$; $\quad$ $k_{ij}^{(2)} = 0\ otherwise$

only with diagonal terms

$$f(c, \nabla c, \nabla^2 c, \ldots) = f_0 + \sum_i k^1 \frac{\partial^2 c}{\partial^2 x_i} + \sum_i k^2 \left(\frac{\partial c}{\partial x_i} \right)^2 + \cdots = \boxed{f_0 + k^1 \nabla^2 c + k^2 (\nabla c)^2 + \cdots}$$

Coherent Interfaces: The Cahn Hillard Model

$$F = \int \mu dN = \boxed{N_V \int_V f dV} = N_V \int_V \left(f_0 + k^1 \nabla^2 c + k^2 (\nabla c)^2\right) dV$$

F

in class

Divergence Theorem:

$$\int_V k^1 \nabla^2 c dV = -\int_V \frac{dk^1}{dc} (\nabla c)^2 dV + \int_S k^1 \vec{\nabla} c * \vec{n} dS$$

$\vec{\nabla} c \cdot \vec{n} = 0$ because the S is arbitrary

$= 0$

$$F = N_V \int_V \left(f_0 + k^1 \nabla^2 c + k^2 (\nabla c)^2\right) dV = N_V \int_V \left(f_0 - \frac{dk^1}{dc} (\nabla c)^2 + k^2 (\nabla c)^2\right) dV = \boxed{N_V \int_V \left(f_0 + k (\nabla c)^2\right) dV}$$

$$\boxed{k = k^2 - \frac{dk^1}{dc} = \frac{\partial^2 f}{\partial \left(|\nabla c|^2\right)^{1/2}} - \frac{d}{dc}\left(\frac{\partial f}{\partial (\nabla^2 c)}\right)}$$

Coherent Interfaces: The Cahn Hillard Model

- Take x_A moles of compound A, and $x_B = 1 - x_A$ moles of compound B, and **physically** mix them
- Assume only the entropy of solution matters (**ideal solution**)

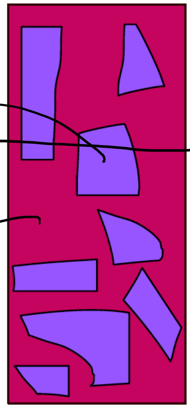
$$\mu_{A,B} = \mu^{\ominus}_{A,B} + RT \ln x_{A,B}$$

- Add an enthalpy of mixing term $\Omega x_A x_B$ (**regular solution**)

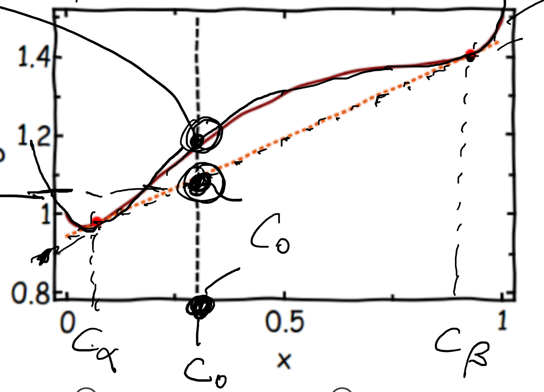
G^{γ}_{sr}

$f(c)$

$G^{\alpha\to\beta}_{sr}$ $\quad C_\beta$



α



$X_A C_\alpha + (1-X_A) C_\beta = C_0$

$$\mu^{\ominus}_A = 1 \qquad \mu^{\ominus}_B = 1.5$$
$$RT = 1 \qquad \Omega = 2.5$$

$$G = x_A\left(\mu^{\ominus}_A + RT\ln x_A\right) + (1-x_A)\left(\mu^{\ominus}_B + RT\ln(1-x_A)\right) + \Omega x_A(1-x_A)$$

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Coherent Interfaces: The Cahn Hillard Model

$dV = d(A \cdot x) = x\,dA + \boxed{A\,dx}$

$dA = 0$

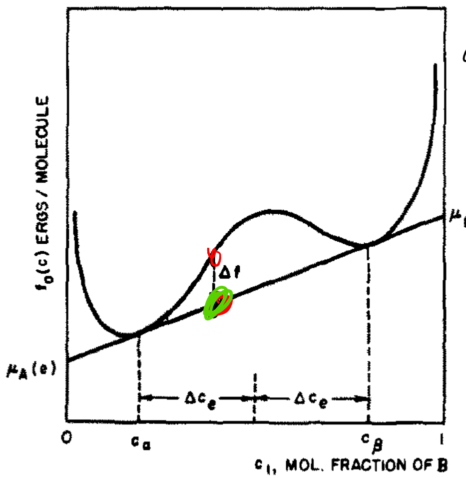

FIG. 1. $f_0(c)$ for $T < T_c$.

A

$$F = N_V \int_V \left(f_0 + k(\nabla c)^2\right) dV = N_V A \int_{-\infty}^{+\infty} \left(f_0 + k\left(\frac{dc}{dx}\right)^2\right) dx$$

no ~~in~~ interface

$$\frac{F - F(e)}{A}$$

$$\gamma = N_V \int_{-\infty}^{+\infty} \left[f_0 + k\left(\frac{dc}{dx}\right)^2 - \{c\mu_\beta(e) + (1-c)\mu_\alpha(e)\}\right] dx$$

→ energy of the system @ equilibrium

$$\gamma = N_V \int_{-\infty}^{+\infty} \left[\Delta f(c) + k\left(\frac{dc}{dx}\right)^2\right] dx$$

$\Delta f(c) = f_0 - \{c\mu_\beta + (1-c)\mu_\alpha\}$

$f(c)$ continuous

and $\nabla \frac{\delta f}{\delta c}$ of kT ~~x~~ bond length

$$\boxed{\nabla = \frac{d}{dx}} + \cancel{\frac{d}{dy}} + \cancel{\frac{d}{dz}}$$

Coherent Interfaces: The Cahn Hillard Model

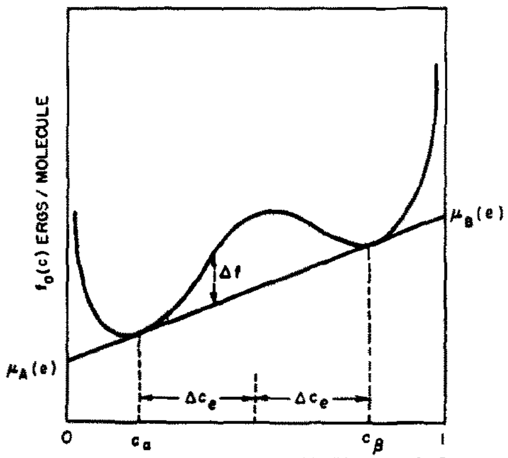

FIG. 1. $f_0(c)$ for $T<T_c$.

@ equilibrium

[min $\gamma(c)$]

minimize γ

$\frac{dc}{dx}$

$$\gamma = N_V \int_{-\infty}^{+\infty} \left[\Delta f(c) + k\left(\frac{dc}{dx}\right)^2 \right] dx$$

$k\left(\frac{dc}{dx}\right)^2$

Euler equation:

I is the integrand

$$I - \left(\frac{dc}{dx}\right)\left[\frac{\partial I}{\partial\left(\frac{dc}{dx}\right)}\right] = 0$$

$$\underbrace{\Delta f + k\left(\frac{dc}{dx}\right)^2}_{I} - \left(\frac{dc}{dx}\right)\cdot\left[2k\left(\frac{dc}{dx}\right)\right] = 0$$

$$\boxed{\Delta f(c) - k\left(\frac{dc}{dx}\right)^2 + \text{const} = 0}$$

$\lim_{x\to\infty} \Delta f = 0$

$\lim_{x\to\infty} \frac{dc}{dx} = 0$

const = 0

$\Delta f = k\left(\frac{dc}{dx}\right)^2$

$(dx)^2 \Delta f = k(dc)^2$

$dx = \left(\frac{k}{\Delta f}\right)^{1/2} dc$

$$\Delta f(c) = k\left(\frac{dc}{dx}\right)^2$$

$$dx = \left(\frac{k}{\Delta f(c)}\right)^{1/2} dc$$

$$\gamma = 2N_V \int_{-\infty}^{+\infty} \Delta f(c) dx$$

$k\left(\frac{dc}{dx}\right)^2$

const

$$\gamma = 2N_V \int_{c_\alpha}^{c_\beta} \left(k\Delta f(c)\right)^{1/2} dc$$

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Coherent Interfaces: The Cahn Hillard Model

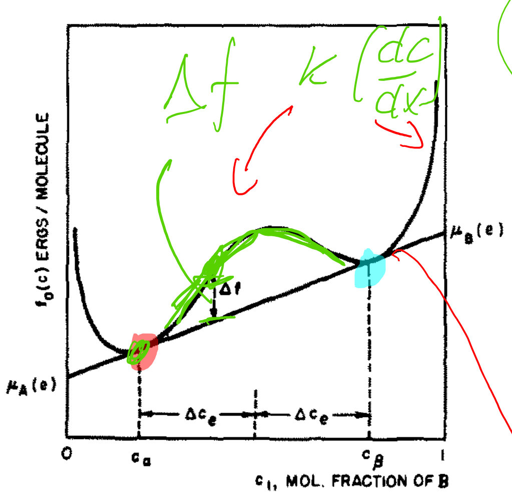
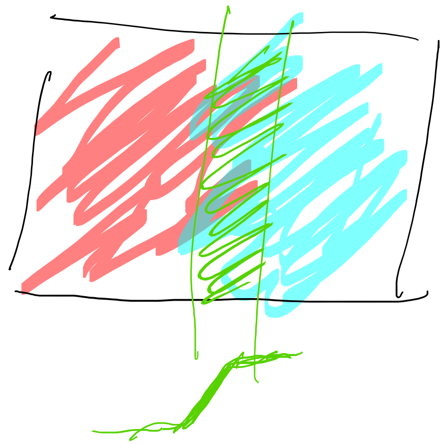


FIG. 1. $f_0(c)$ for $T < T_c$.

$$\boxed{\gamma = 2N_V \int_{c_\alpha}^{c_\beta} \left(k\Delta f(c)\right)^{1/2} dc}$$

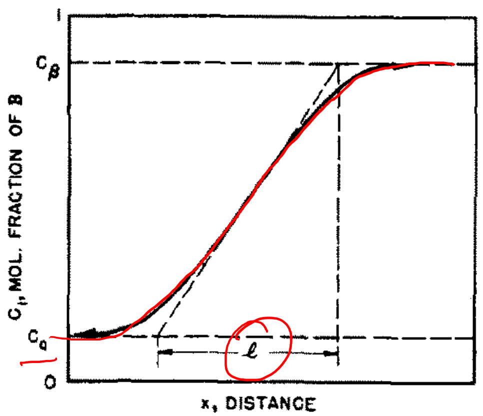
$$dx = \left(\frac{k}{\Delta f(c)}\right)^{1/2} dc$$

$$\frac{dc}{dx} = \left(\frac{k}{\Delta f(c)}\right)^{1/2}$$



$f = \phi(1-c^2)$

tanh



c_β

FIG. 2. Interface profile.

ℓ

Coherent Interfaces: The Cahn Hillard Model

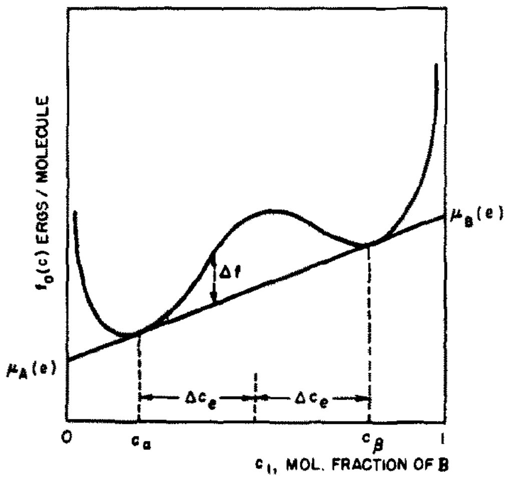
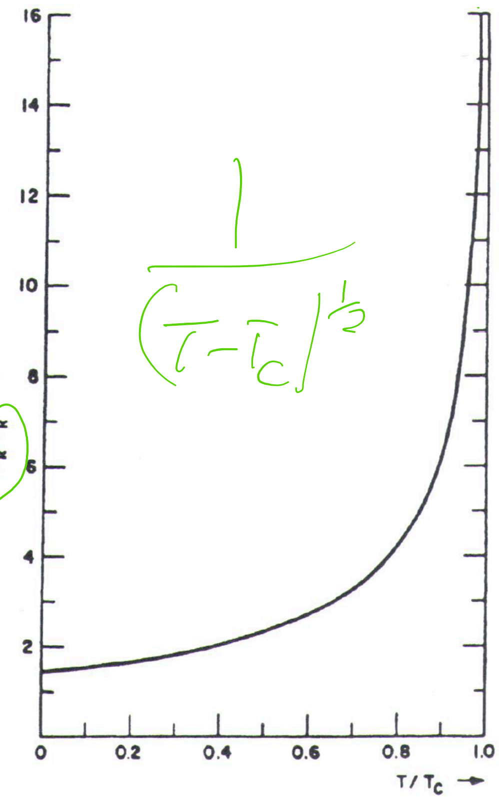


FIG. 1. $f_0(c)$ for $T < T_c$.

$$\gamma = 2N_V \int_{c_\alpha}^{c_\beta} \left(k\Delta f(c)\right)^{1/2} dc$$

$$\gamma = 2N_V \int_{c_\alpha}^{c_\beta} \left(k\Delta f(c)\right)^{1/2} dc$$

$$\frac{dc}{dx} = \left(\frac{k}{\Delta f(c)}\right)^{1/2}$$



$$\frac{1}{(T-T_c)^{\frac{1}{2}}}$$

T_c critical temperature
α and β mix

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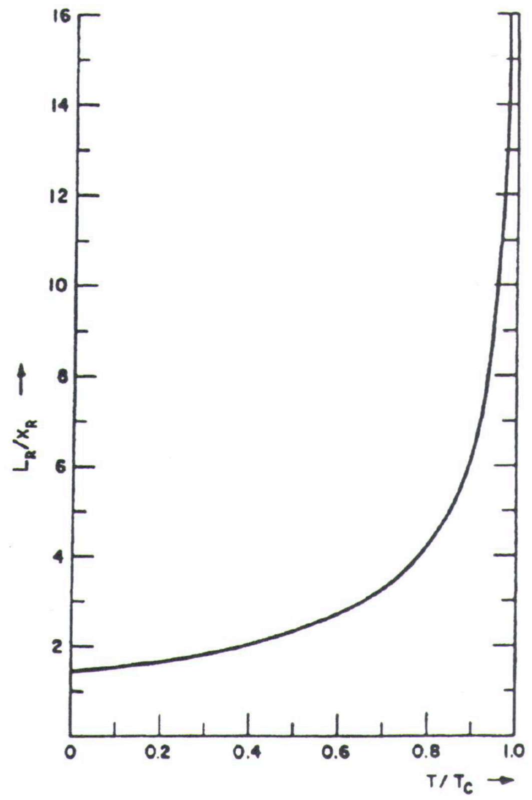
Coherent Interfaces: The Cahn Hillard Model

depends on temperature



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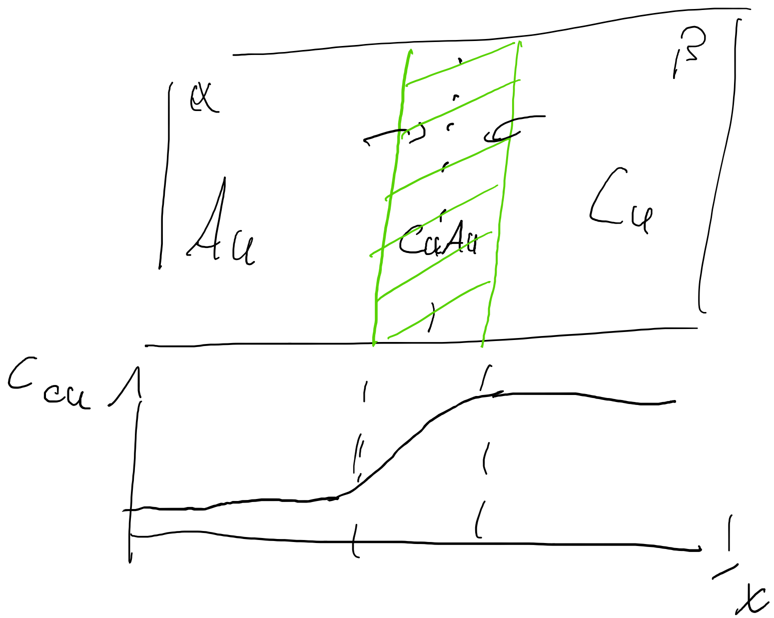
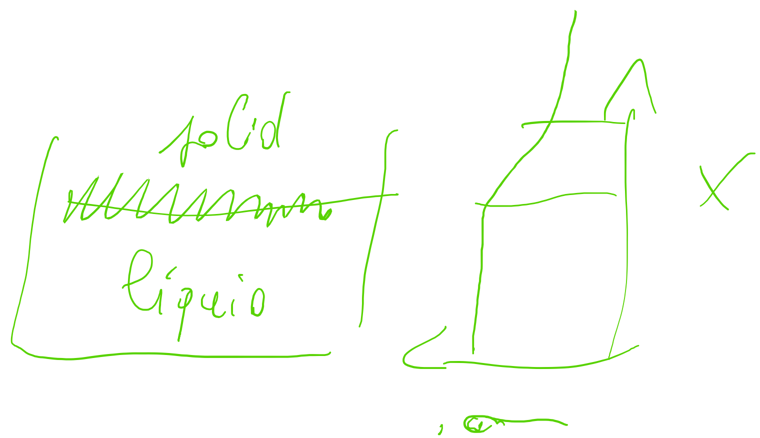
Coherent Interfaces: The Cahn Hillard Model





Conclusions

hetero interfaces

A ↳ not atomically flat