EPFL
École polytechnique fédérale de Lausanne

Institute of Materials - Institute of Bioengineering

sunmil.epfl.ch

SuNMIL
Supramolecular NanoMaterials and Interfaces Laboratory

Heterophase Grain Boundaries
Lesson 11

MSE 304

Francesco Stellacci

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Reading for this Class

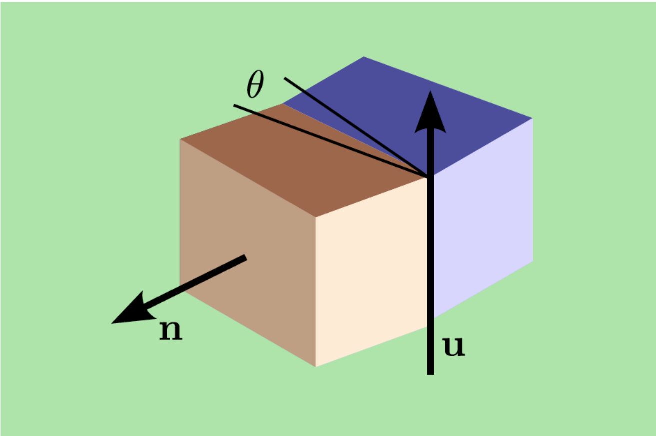
Key Topics in the Previous Class

Heterophase Grain Boundaries

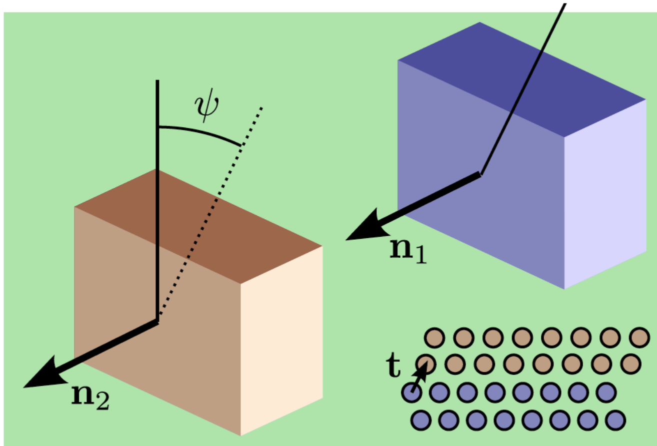
Coherent	**[5 -200 mJ/m^2]**
Semi-coherent	**[200-800 mJ/m^2]**
Incoherent	**[800-2500 mJ/m^2]**

Heterophase Grain Boundaries: Nomenclature

For simple interfaces we have used this approach



For complex interfaces we to use:



Planes (hkl)

Directions [uvw]

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

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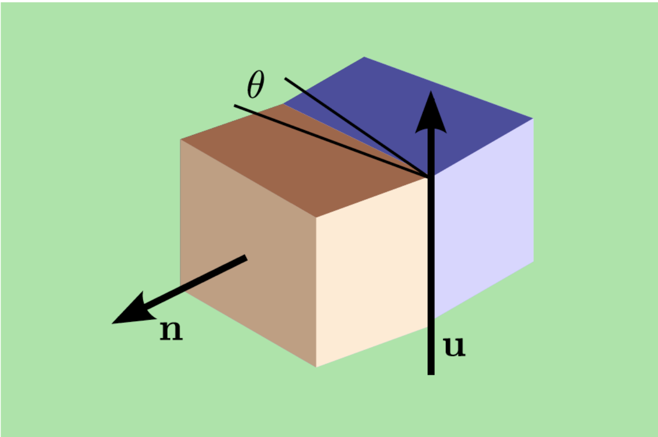
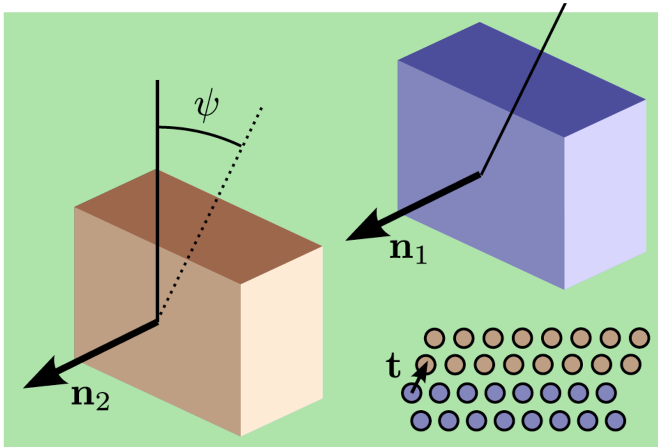
Heterophase Grain Boundaries: Nomenclature

For simple interfaces we have used this approach



For complex interfaces we to use:



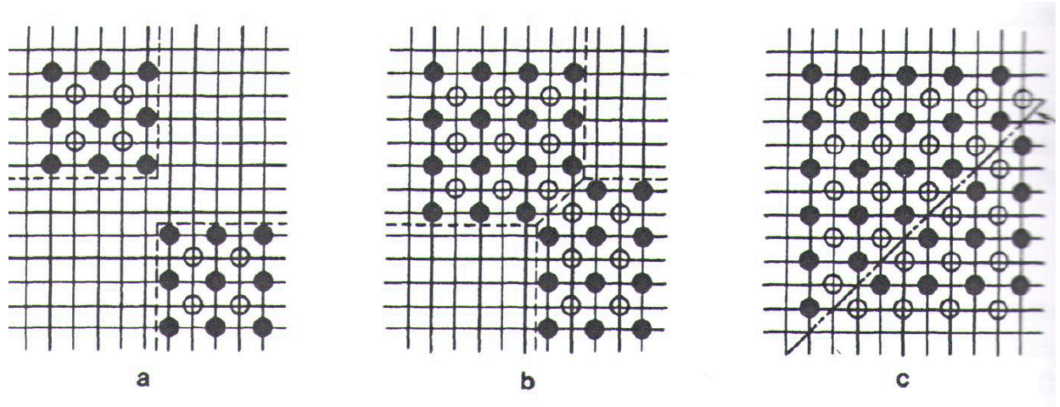
Planes (hkl)

Directions [uvw]

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

Special Grain Boundaries

Antiphase Domain Boundaries



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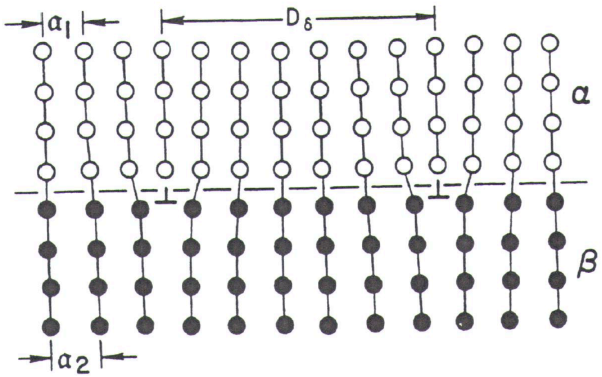
Energetics of Semi-coherent Grain Boundaries



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

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

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

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

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

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

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

Eterophase Interphases

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

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

Eterointerphases

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

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

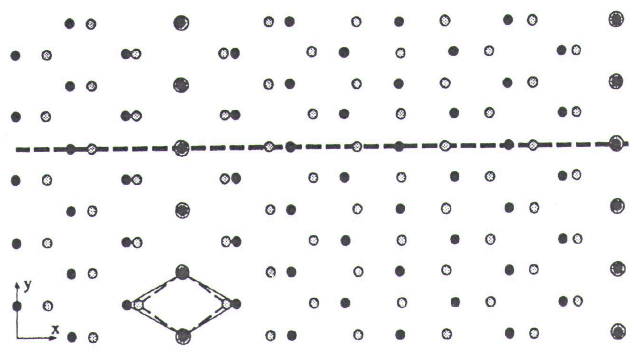


Figure 14.38. Schematic diagram representing the rhombic surface unit cells of a {111} f.c.c. plane (filled circles) and a {110} b.c.c. plane (open circles) when $\tau = a_{f.c.c.}/a_{b.c.c.} = 1.15$. From [143].

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High Index Interfaces

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

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

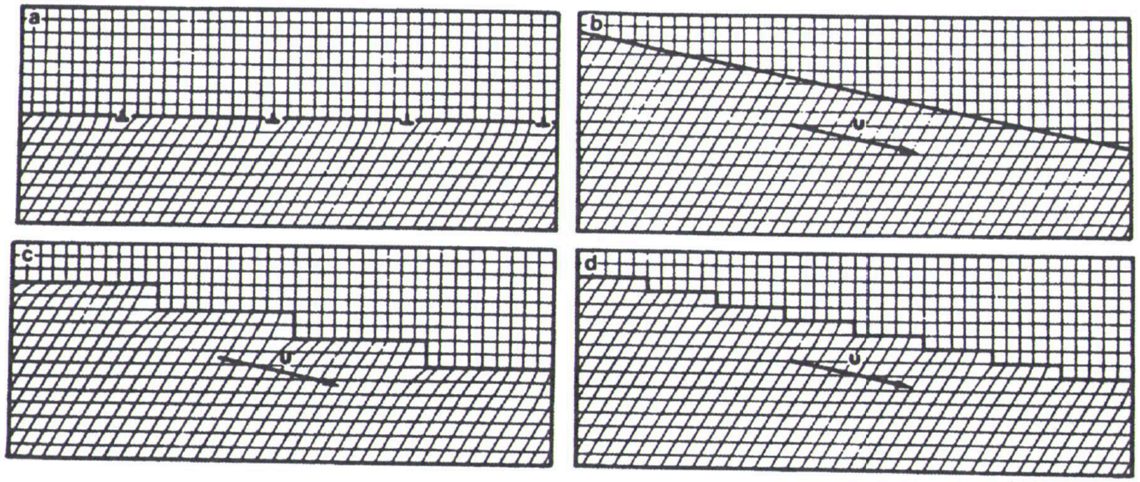

Figure 14.39. Possible interfaces for a transformation described by a shear e_{12} coupled with an expansion e_{11} in the shear plane. (a) The expansion is accommodated by a set of perfect lattice (misfit) dislocations. (b) The interface lies along an invariant line **u** and no dislocations are necessary. (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 $\alpha/6\langle 112\rangle$ 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 $\alpha/12\langle 112\rangle$ partial dislocation. Reprinted with permission from [153] by Elsevier Science Ltd., Oxford, England.

High Index Interfaces

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

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

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Coherent Interfaces: The Cahn Hillard Model

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

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

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

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

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Coherent Interfaces: The Cahn Hillard Model

$$\boldsymbol{f}(\boldsymbol{c}, \nabla \boldsymbol{c}, \nabla^2 \boldsymbol{c}, \ldots) = \boldsymbol{f}_0 + \sum_i \boldsymbol{L}_i \nabla_i \boldsymbol{c} + \sum_{i,j} \boldsymbol{k}_{ij}^{(1)} \frac{\partial^2 \boldsymbol{c}}{\partial x_i \partial x_j} + \frac{1}{2} \sum_{i,j} \boldsymbol{k}_{ij}^{(2)} \frac{\partial \boldsymbol{c}}{\partial x_i} \frac{\partial \boldsymbol{c}}{\partial x_j} + \cdots$$

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

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

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

$$L_i = 0$$

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

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

$$\boldsymbol{f}(\boldsymbol{c}, \nabla \boldsymbol{c}, \nabla^2 \boldsymbol{c}, \ldots) = \boldsymbol{f}_0 + \sum_i \boldsymbol{k}^1 \frac{\partial^2 \boldsymbol{c}}{\partial^2 x_i} + \sum_i \boldsymbol{k}^2 \left(\frac{\partial \boldsymbol{c}}{\partial x_i} \right)^2 + \cdots = \boldsymbol{f}_0 + \boldsymbol{k}^1 \nabla^2 \boldsymbol{c} + \boldsymbol{k}^2 (\nabla \boldsymbol{c})^2 + \cdots$$

Coherent Interfaces: The Cahn Hillard Model

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

Divergence Theorem:

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

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

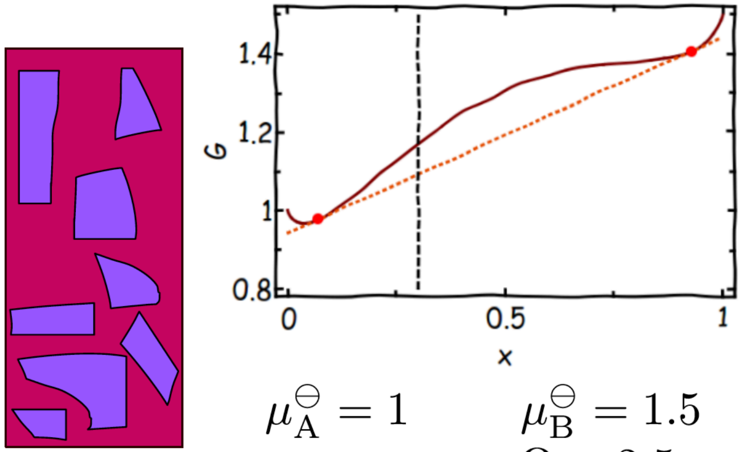
$$k = k^2 - \frac{dk^1}{dc} = \frac{\partial^2 f}{\partial \left(|\nabla c|^2\right)^{1/2}} - \frac{d}{dc} \left(\frac{\partial f}{\partial (\nabla^2 c)}\right)$$

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**)



$$\mu^{\ominus}_{A} = 1 \qquad \mu^{\ominus}_{B} = 1.5$$
$$RT = 1 \qquad \Omega = 2.5$$

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

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Coherent Interfaces: The Cahn Hillard Model

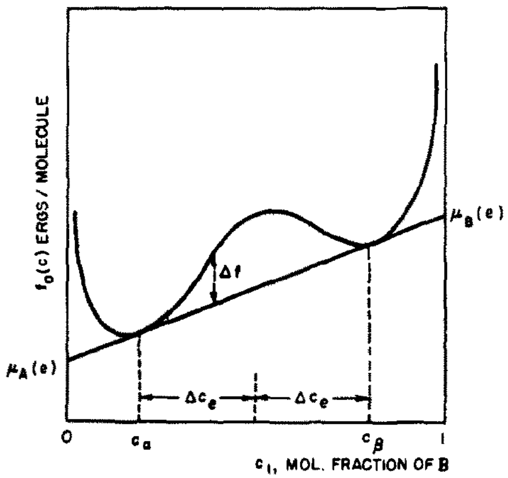

FIG. 1. $f_0(c)$ for $T < T_c$.

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

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

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

Coherent Interfaces: The Cahn Hillard Model

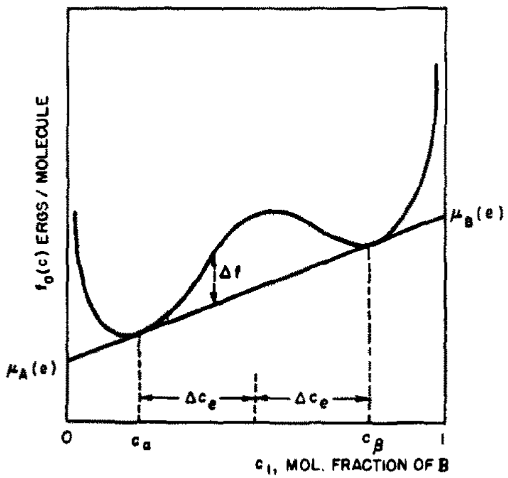

FIG. 1. $f_0(c)$ for $T < T_c$.

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

Euler equation:

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

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

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

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

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

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

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Coherent Interfaces: The Cahn Hillard Model

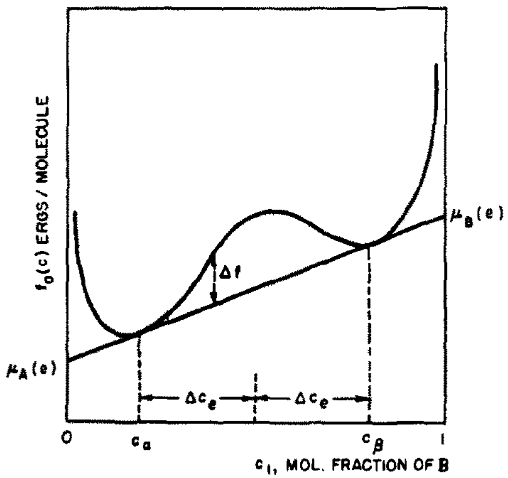


FIG. 1. $f_0(c)$ for $T < T_c$.

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

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

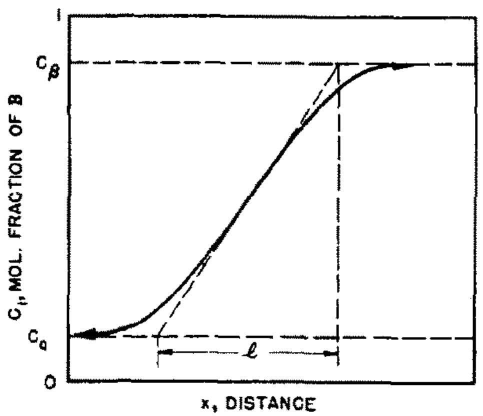
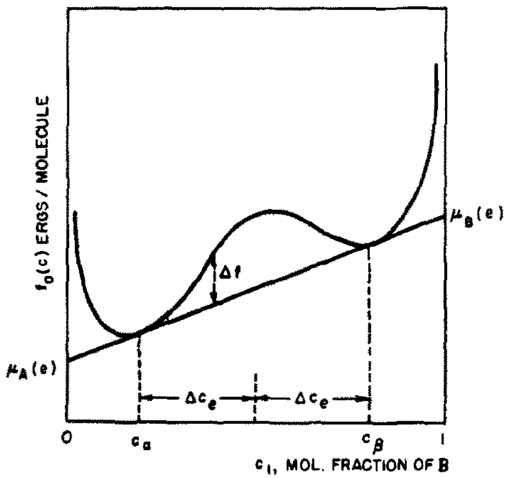


FIG. 2. Interface profile.

Coherent Interfaces: The Cahn Hillard Model



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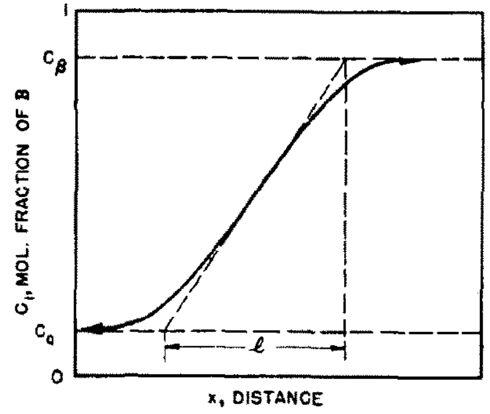

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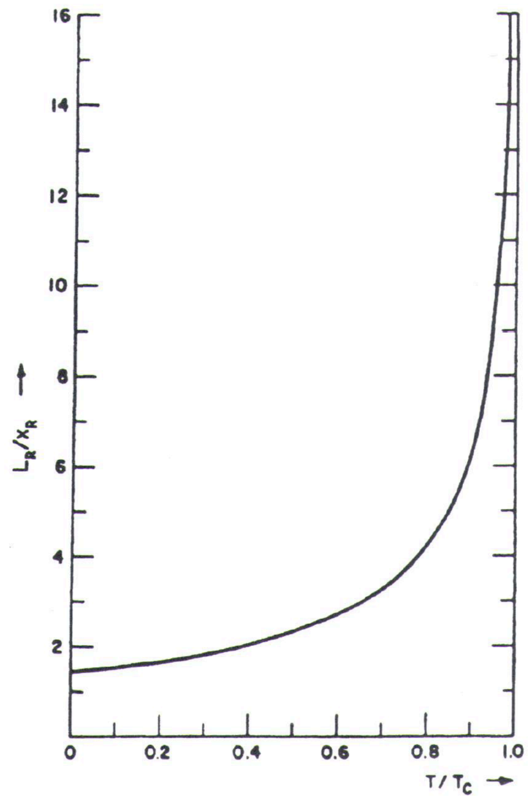

$$\gamma = 2N_V \int_{c_\alpha}^{c_\beta} \left(k\Delta f(c)\right)^{1/2} dc$$

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

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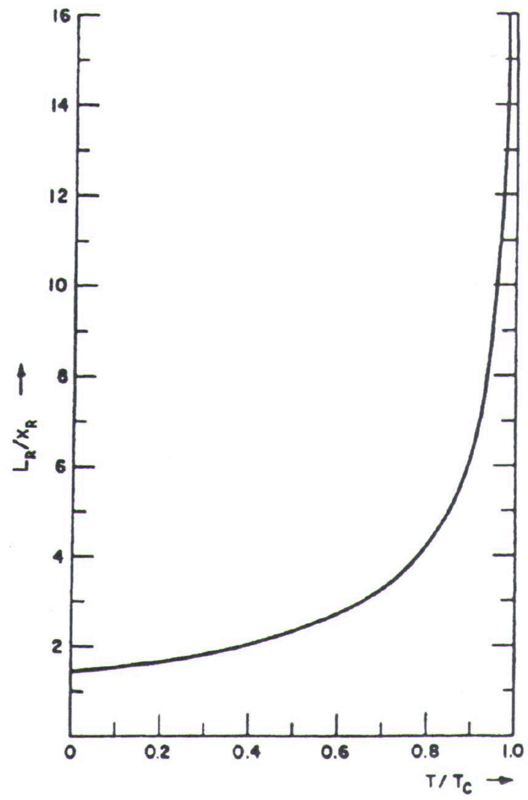
Coherent Interfaces: The Cahn Hillard Model



Coherent Interfaces: The Cahn Hillard Model

Conclusions