Kinetic cross-coupling between non conserved and conserved fields in phase field models

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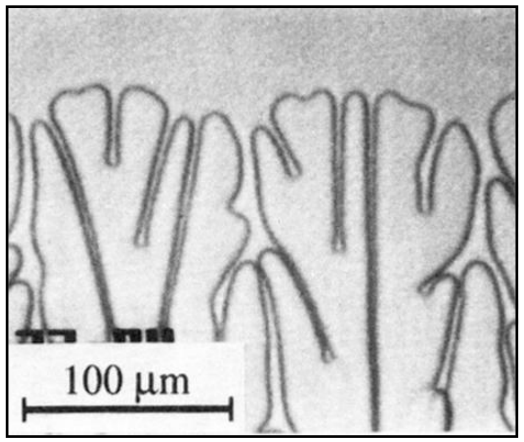
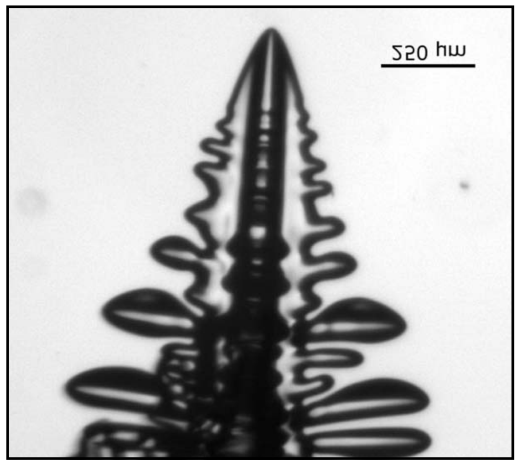
Diffusional growth and kinetic effects

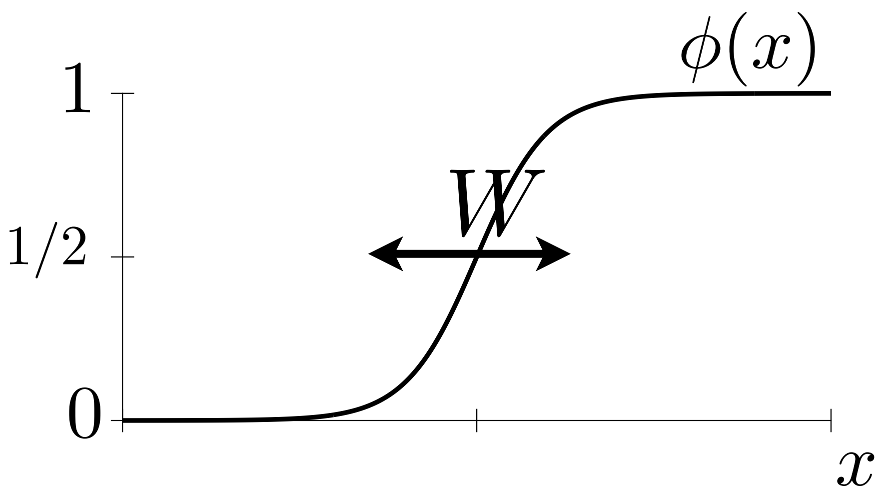




Transport equation in the bulk (diffusion equation)

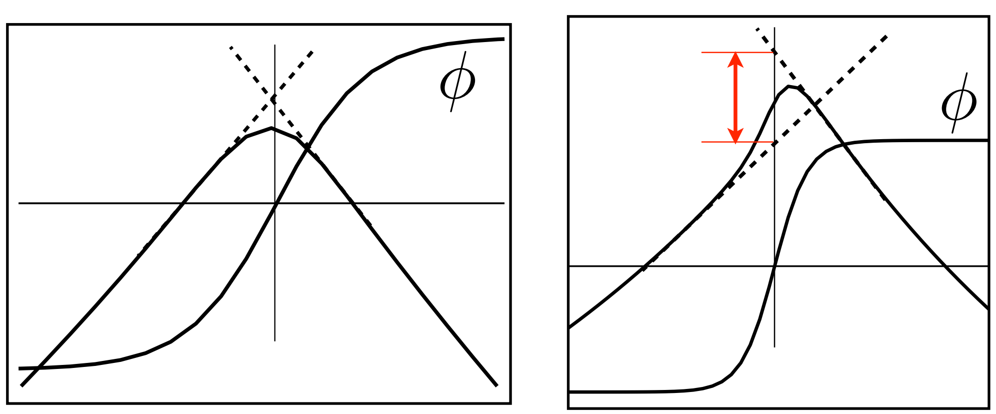
+ boundary conditions at the interfaces :

- energy/mass conservation
- local equilibrium + kinetic effects



<u>thin interface analysis</u> : kinetic effects depend strongly on W

➔ which boundary conditions the phase field model corresponds to ?



Phase field models for diffusional growth

$\longrightarrow \phi$: non-conserved field

$\longrightarrow C$: conserved field $\qquad \dot{C} + \boldsymbol{\nabla} \cdot \mathbf{J} = 0$

$$F = \int_V dV \, \left\{ f(\phi) + W^2 |\nabla \phi|^2 + g(\phi, C) \right\}$$

thermodynamic coupling between phase field and diffusion field

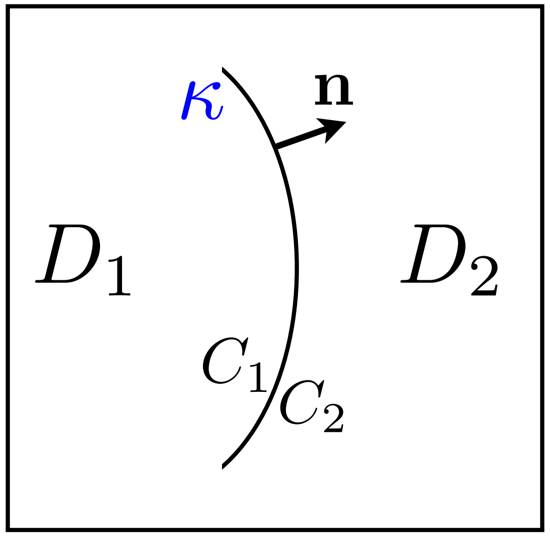
<u>classical phase field model</u> :

$$-\frac{\delta F}{\delta \phi} = \tau \dot{\phi}$$

$$-\boldsymbol{\nabla} \frac{\delta F}{\delta C} = \frac{\mathbf{J}}{D(\phi)}$$

$\longrightarrow$ 2 velocity scales : $W/\tau \; , \; D/W$

Macroscopic approach (sharp-interface description) of diffusional transformations in binary alloys $A_{1-C}B_C$



Diffusion equation in the bulk : $\dot{C} = D_i \boldsymbol{\nabla}^2 C$

Conservation of mass at the interface :

$$D_1(\boldsymbol{\nabla} C_1 \cdot \mathbf{n}) + V C_1 = D_2(\boldsymbol{\nabla} C_2 \cdot \mathbf{n}) + V C_2 = J_B$$

total number of atoms

number of solute atoms

Interface kinetics :

$$\Phi_2 - \Phi_1 = \mathcal{A} V + \mathcal{B} J_B + d_0 \kappa$$

$$\mu_2 - \mu_1 = \mathcal{B} V + \mathcal{C} J_B$$

grand potential:

$$\Phi_i = f_i(C_i) - C_i \mu_i$$

chemical potential:

$$\mu_i = f_i'(C_i)$$

$\longrightarrow$ 3 velocity scales describing interface kinetics

Non diagonal model (1)

classical diagonal model :

$$-\frac{\delta \mathcal{F}}{\delta \phi} = \tau \dot{\phi} + 0$$

$$-\boldsymbol{\nabla} \frac{\delta \mathcal{F}}{\delta C} = 0 + \frac{\mathbf{J}}{D(\phi)}$$

non diagonal model : $-\frac{\delta \mathcal{F}}{\delta \phi} = \tau \dot{\phi} + (MW \boldsymbol{\nabla} \phi) \cdot \mathbf{J}$

$$-\boldsymbol{\nabla} \frac{\delta \mathcal{F}}{\delta C} = (MW \boldsymbol{\nabla} \phi) \dot{\phi} + \frac{\mathbf{J}}{D(\phi)}$$

$\longrightarrow$ 3 velocity scales :

$W/\tau \ , \ D/W \ , \ 1/M$

positiveness of the Onsager matrix: $M^2 < \frac{\tau}{\max[D(\phi) W^2 (\nabla \phi)^2]}$

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Non diagonal model (2)

$$\underbrace{\left[1 - \frac{D(\phi)(MW\boldsymbol{\nabla}\phi)^2}{\tau}\right]}_{\text{determinant} > 0} \dot{\phi} = -\frac{1}{\tau}\frac{\delta\mathcal{F}}{\delta\phi} + \frac{MWD(\phi)}{\tau}\boldsymbol{\nabla}\phi \cdot \boldsymbol{\nabla}\frac{\delta\mathcal{F}}{\delta C}$$

$$\dot{C} = \boldsymbol{\nabla} \cdot \left[D(\phi)\boldsymbol{\nabla}\frac{\delta\mathcal{F}}{\delta C} + MWD(\phi)\dot{\phi}\boldsymbol{\nabla}\phi\right]$$

Non diagonal model (2)

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$$\dot{C} = \boldsymbol{\nabla}\cdot\left[D(\phi)\boldsymbol{\nabla}\frac{\delta\mathcal{F}}{\delta C} + \underbrace{MW\,D(\phi)\dot{\phi}\boldsymbol{\nabla}\phi}_{\text{same structure as anti-trapping current}}\right]$$

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one-sided model: $D_1 \ll D_2$

$$\cancel{D_1(\boldsymbol{\nabla}C_1\cdot\mathbf{n})}+VC_1=J_B=D_2(\boldsymbol{\nabla}C_2\cdot\mathbf{n})+VC_2$$

$\longrightarrow$ $J_B = VC_1^{eq}$ $\longrightarrow$ no requirement concerning Onsager symmetry

Thin interface limit

$$\mathcal{A} = \int_{-\infty}^{\infty} dx\ [\tau - 2MWC_{eq}(x)][\phi'_{eq}(x)]^2 + \int_{-\infty}^{\infty} dx\ \left[\frac{C_{eq}^2(x)}{D(\phi_{eq})} - \frac{(C_1^{eq})^2}{2D_1} - \frac{(C_2^{eq})^2}{2D_2}\right]$$

$$\mathcal{B} = \int_{-\infty}^{\infty} dx\ MW[\phi'_{eq}(x)]^2 - \int_{-\infty}^{\infty} dx\ \left[\frac{C_{eq}(x)}{D(\phi_{eq})} - \frac{C_1^{eq}}{2D_1} - \frac{C_2^{eq}}{2D_2}\right]$$

$$\mathcal{C} = \int_{-\infty}^{\infty} dx\ \left[\frac{1}{D(\phi_{eq})} - \frac{1}{2D_1} - \frac{1}{2D_2}\right]$$

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Equilibrium profiles : $\begin{cases} \phi_{eq}(x) = \tanh\left(\dfrac{x}{\sqrt{2}W}\right) \\ C_{eq}(x) = \bar{C} + \Delta C\ \dfrac{p[\phi_{eq}(x)]}{2} \end{cases}$

$$\bar{C} = \frac{C_1^{eq} + C_2^{eq}}{2}$$

$$\Delta C = C_1^{eq} - C_2^{eq}$$

Switching function : $p(\phi) = \dfrac{15}{8}\left(\phi - 2\phi^3/3 + \phi^5/5\right)$

Contrast of diffusivity

$$\frac{1}{D(\phi)} = \frac{1}{\bar{D}} + \frac{1}{\Delta D} q(\phi) \qquad \text{with} \begin{cases} \frac{1}{\bar{D}} = \frac{1}{2D_1} + \frac{1}{2D_2} \; ; \; \frac{1}{\Delta D} = \frac{1}{2D_1} - \frac{1}{2D_2} \\ q(\phi) = -q(-\phi) \; ; \; q(\pm 1) = \pm 1 \end{cases}$$

$$\mathcal{A} = \frac{\alpha\tau}{W}\left(1 - \beta \Delta C^2 \frac{W^2}{\bar{D}\tau}\right) - 2\bar{C}\mathcal{B}$$

$$\mathcal{B} = \alpha M - \gamma \Delta C \frac{W}{\Delta D}$$

$$\mathcal{C} = 0$$

$$\alpha = W \int_{-\infty}^{\infty} dx \left[\phi'_{eq}(x)\right]^2$$

$$\beta = \frac{1}{\alpha} \int_{-\infty}^{\infty} \frac{dx}{4W} \left[1 - p^2(\phi_{eq})\right]$$

$$\gamma = \int_{-\infty}^{\infty} \frac{dx}{2W} \left[p(\phi_{eq}) q(\phi_{eq}) - 1\right]$$

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$$\mathcal{B} = \alpha M - \gamma \Delta C \frac{W}{\Delta D}$$

$$\mathcal{C} = 0$$

Almgren: $\mu_2 - \mu_1 = \mathcal{B}V + \mathcal{C}J_B = 0$

if $\mathcal{B} = 0$ i.e. $M = \dfrac{\gamma \Delta C}{\alpha} \dfrac{W}{\Delta D}$

then $\Phi_2 - \Phi_1 = \mathcal{A}V + d_0\kappa$

with $\mathcal{A} = \dfrac{\alpha\tau}{W}\left(1 - \beta \Delta C^2 \dfrac{W^2}{\bar{D}\tau}\right)$

$$\alpha = W \int_{-\infty}^{\infty} dx \left[\phi'_{eq}(x)\right]^2$$

$$\beta = \frac{1}{\alpha}\int_{-\infty}^{\infty} \frac{dx}{4W}\left[1 - p^2(\phi_{eq})\right]$$

$$\gamma = \int_{-\infty}^{\infty} \frac{dx}{2W}\left[p(\phi_{eq})q(\phi_{eq}) - 1\right]$$

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Karma-Rappel: $1/\Delta D = 0$

➔ $\mathcal{B} = \mathcal{C} = 0$ if $M = 0$

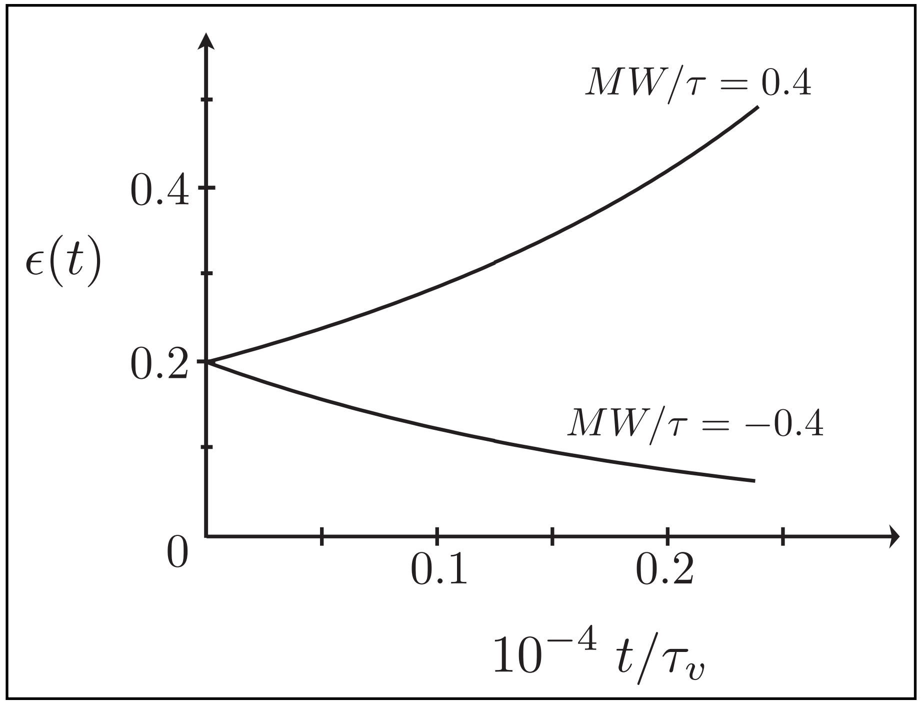
Conclusion

- The kinetic cross coupling is necessary to fully describe interface kinetics.

➔ allows to have the same number of degrees of freedom in phase field model and sharp-interface description

➔ solves problems:

- elimination of temperature jump when finite contrast of diffusivity
- introduce the Ehrlich-Schwoebel effect in MBE
- tuning the solute trapping effect in alloys



➔ open question:

introduction of kinetic cross coupling for multi-phase systems (treatment of the triple junction ?)