Series lectures of phase-field model

08. Multi-phase model: WBM model

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Free energy of binary two-phase system

- Assume the binary two-phase system, introduce the parameters, concentration $c(\mathbf{r}, t)$ and the non-conserved order parameter $\phi(\mathbf{r}, t)$ and the free energy is

$$f = \int_{\Omega} \left[f(c, \phi) + wg(\phi) + \frac{\varepsilon^2}{2} \left| \nabla \phi \right|^2 \right] d\Omega \tag{1}$$

Governing equations

- Two governing equations are needed. The Ginzburg-Landau equation is

$$\frac{\partial \phi(\mathbf{r},t)}{\partial t} = -M_\phi \frac{\delta f(c,\phi)}{\delta \phi} \tag{2}$$

- The flux of the solute is

$$\mathbf{J} = -M_{\mathsf{d}} \nabla \frac{\delta f(c,\phi)}{\delta c}$$

- Applying the mass conservation,

$$\frac{\partial c(\mathbf{r},t)}{\partial t} = \nabla \cdot M_{\mathsf{d}} \nabla \frac{\delta f(c,\phi)}{\delta c} \tag{3}$$

Wheeler-Boettinger-McFadden model

- Proposed by Wheeler, Boettinger and McFadden.
- Eqs. 2 and 3 are simplified by

$$\frac{1}{M_\phi}\frac{\partial\phi(\mathbf{r},t)}{\partial t} = \varepsilon^2\nabla^2\phi - wg'(\phi) - \frac{\partial f(c,\phi)}{\partial\phi} \tag{4}$$

$$\frac{\partial c(\mathbf{r},t)}{\partial t} = \nabla\cdot\left[M_{\mathsf{d}}\nabla\frac{\partial f(c,\phi)}{\partial c}\right] \tag{5}$$

- The concentration have to be given by mixing rule, excluding dependence of time,

$$c(\mathbf{r}) = c_\alpha(\mathbf{r})h\big(\phi(\mathbf{r})\big) + c_\beta(\mathbf{r})\Big[1 - h\big(\phi(\mathbf{r})\big)\Big]$$

- In WBM model, we assume that

$$c_\alpha(\mathbf{r}) = c_\beta(\mathbf{r}) = c(\mathbf{r})$$

namely, equal concentration condition.

Wheeler-Boettinger-McFadden model

- The driving force for WBM model is gradient (temporal gradient) of diffusion potential where the diffusion potential($\tilde{\mu}$) is

$$\tilde{\mu}(\mathbf{r}, t) = \frac{\partial f(c, \phi)}{\partial c}$$

- Since the concentrations of different phases have to be equal at the interface, and free energy of each phase is not generally equal, therefore, the gradient of diffusion potential have to be abruptly changed in the interface regime.
- Since only one concentration needs to be known per location, required computational resources are low. However, there is a weak point in terms of numerical stability in the interface.

Wheeler-Boettinger-McFadden model

- The free energy is

$$f(c,\phi) = h(\phi) f^{\alpha}(c) + \big(1 - h(\phi)\big) f^{\beta}(c) \tag{6}$$

- The phase field equation is

$$\begin{aligned}\frac{1}{M_\phi}\frac{\partial \phi(\mathbf{r},t)}{\partial t} &= \varepsilon^2 \nabla^2 \phi - w g'(\phi) - \frac{\partial f(c,\phi)}{\partial \phi} \\ &= \varepsilon^2 \nabla^2 \phi - w g'(\phi) - \big(f^{\alpha}(c) - f^{\beta}(c)\big) h'(\phi)\end{aligned}$$

- The diffusion equation is

$$\begin{aligned}\frac{\partial c(\mathbf{r},t)}{\partial t} &= \nabla \cdot M_{\mathsf{d}} \nabla \frac{\partial f(c,\phi)}{\partial c} \\ &= \nabla \cdot M_{\mathsf{d}} \nabla \left[h(\phi) \frac{\partial f^{\alpha}(c)}{\partial c} + \big(1 - h(\phi)\big) \frac{\partial f^{\beta}(c)}{\partial c} \right]\end{aligned}$$

Wheeler-Boettinger-McFadden model

- The relation between the diffusivity of solute and mobility is

$$M_{\mathsf{d}} = \frac{D(\phi)}{d^2 f/dc^2} = \frac{D(\phi)}{f_{cc}}$$

then the diffusion equation becomes

$$\begin{aligned}\frac{\partial c(\mathbf{r}, t)}{\partial t} &= \nabla \cdot \frac{D(\phi)}{f_{cc}} \nabla \frac{\partial f(c, \phi)}{\partial c} \\ &= \nabla \cdot \frac{D(\phi)}{f_{cc}} \left(f_{cc} \nabla c + f_{c\phi} \nabla \phi \right) \\ &= \nabla \cdot D(\phi) \nabla c + \nabla \cdot \frac{f_{c\phi} D(\phi)}{f_{cc}} \nabla \phi\end{aligned}$$

- The first term in RHS means the diffusion by concentration gradient and second term indicates the solute redistribution at the interface.

- Under the equilibrium, two equations have to be satisfied.

$$\varepsilon^2 \frac{d^2\phi(\mathbf{r},t)}{dx^2} = wg'(\phi) + f_\phi(c,\phi) \tag{7}$$

$$\frac{d}{dx}\left[M_{\mathsf{d}} \frac{d}{dx} f_c(c,\phi) \right] = 0$$

where

$$f_\phi(c,\phi) = \frac{\partial f(c,\phi)}{\partial \phi} \qquad f_c(c,\phi) = \frac{\partial f(c,\phi)}{\partial c}$$

- The diffusion potential at equilibrium is

$$f_c(c,\phi) = \tilde{\mu}^{\mathsf{e}}$$

Equilibrium concentration of WBM model

- Take integration of Eq. 7 with respect to x,

$$\frac{\varepsilon^2}{2}\left(\frac{d\phi}{dx}\right)^2\Bigg|_{x=-\infty}^{x=\infty} = wg(\phi)\Bigg|_{x=-\infty}^{x=\infty} + \int_{-\infty}^{\infty} f_\phi(c,\phi)\frac{d\phi}{dx}dx$$

- At $x \to \pm\infty$, then $\phi = 0$ or 1 and

$$\frac{d\phi}{dx} = 0 \qquad g(1) = g(0) = 0$$

therefore, we have

$$\int_{\beta}^{\alpha} f_\phi(c,\phi)d\phi = 0$$

with α, β means two bulk regions.

- By chain rule,

$$df(\phi, c) = f_\phi d\phi + f_c dc \to f_\phi d\phi = df - \tilde{\mu}^{\mathsf{e}} dc$$

Equilibrium concentration of WBM model

- Therefore,

$$\int_{\beta}^{\alpha} f_{\phi}(c,\phi)d\phi = \int_{\beta}^{\alpha} \left(df - \tilde{\mu}^{\mathsf{e}} dc\right) = \int_{\beta}^{\alpha} df - \tilde{\mu}^{\mathsf{e}} \int_{\beta}^{\alpha} dc = 0$$

Assume that left side is bulk solid and left side is bulk liquid,

$$f\left(c_{\alpha},0\right) - f\left(c_{\beta},1\right) - \left(c_{\alpha} - c_{\beta}\right)\tilde{\mu}^{\mathsf{e}} = 0$$

- From Eq. 6,

$$f\left(c_{\beta},1\right) = f^{\beta}\left(c_{\beta}\right) \qquad f\left(c_{\alpha},0\right) = f^{\alpha}\left(c_{\alpha}\right)$$

the diffusion potential under equilibrium is

$$\tilde{\mu}^{\mathsf{e}} = \frac{f^{\alpha}\left(c_{\alpha}\right) - f^{\beta}\left(c_{\beta}\right)}{c_{\alpha} - c_{\beta}}$$

Equilibrium concentration of WBM model

- Take the derivative with respect to c of Eq. 6,

$$f_c^\alpha(c_\alpha^\mathsf{e}) = f_c^\beta(c_\beta^\mathsf{e}) = \frac{f^\alpha(c_\alpha^\mathsf{e}) - f^\beta(c_\beta^\mathsf{e})}{c_\alpha^\mathsf{e} - c_\beta^\mathsf{e}}$$

- At the interface, the solute concentration vary continuously from c_β^e to c_α^e.

$$h(\phi)\frac{df^\beta(c)}{dc} + \left(1 - h(\phi)\right)\frac{df^\alpha(c)}{dc} = \frac{f^\alpha(c_\alpha^\mathsf{e}) - f^\beta(c_\beta^\mathsf{e})}{c_\alpha^\mathsf{e} - c_\beta^\mathsf{e}}$$

Interface width of WBM model

- Multiply $d\phi/dx$ to Eq. 7 and integrate with respect to x at interval $[-\infty, x]$.

$$\frac{\varepsilon^2}{2}\left(\frac{d\phi}{dx}\right)^2\Bigg|_{x=-\infty}^{x=x} = wg(\phi)\Bigg|_{x=-\infty}^{x=x} + \int_{-\infty}^{x} f_\phi \frac{d\phi}{dx}dx$$

- In the limit $x \to -\infty$

$$\phi = 1 \qquad \frac{d\phi}{dx} = 0 \qquad g(\phi = 1) = 0$$

therefore,

$$\begin{aligned}\frac{\varepsilon^2}{2}\left(\frac{d\phi}{dx}\right)^2 &= wg(\phi) + \int_1^{\phi} f_\phi d\phi = wg(\phi) + \int_{\beta}^{x=x} \left(df - \tilde{\mu}^{\mathsf{e}}\right)dc \\ &= wg(\phi) + \Big(f\left(c, \phi\right) - f\left(c_\beta^{\mathsf{e}}, 1\right)\Big) - \left(c - c_\beta^{\mathsf{e}}\right)\tilde{\mu}^{\mathsf{e}}\end{aligned}$$

Interface width of WBM model

- When concentration is represented by order parameter ϕ is $\tilde{c}(\phi)$ then

$$\begin{aligned}\frac{\varepsilon^2}{2}\left(\frac{d\phi}{dx}\right)^2 &= wg(\phi) + f\left(\tilde{c}(\phi),\phi\right) - f\left(c_\beta^{\mathrm{e}},1\right) - \left(\tilde{c}(\phi) - c_\beta^{\mathrm{e}}\right)\tilde{\mu}^{\mathrm{e}} \\ &\equiv wg(\phi) + W(\phi)\end{aligned} \tag{8}$$

  where

$$W(\phi) = f\left(\tilde{c}(\phi),\phi\right) - f\left(c_\beta^{\mathrm{e}},1\right) - \left(\tilde{c}(\phi) - c_\beta^{\mathrm{e}}\right)\tilde{\mu}^{\mathrm{e}}$$

  and $wg(\phi)$ is double-well potential.

- When $\phi = 1$, we have

$$\tilde{c}(\phi) = c_\beta^{\mathrm{e}} \qquad W(\phi = 1) = 0$$

- When $\phi = 0$, we have

$$\tilde{c}(\phi) = c_\alpha^{\mathrm{e}} \qquad W(\phi = 0) = 0$$

Interface width of WBM model

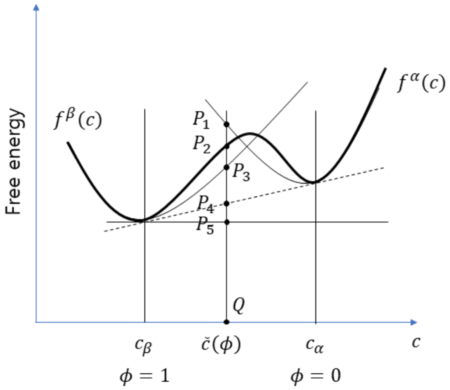

Figure: Free energy of two phase system

Interface width of WBM model

- In Figure in previous slide,

$$\overline{P_1Q} = f^{\alpha}\big(\tilde{c}(\phi)\big) \qquad \overline{P_3Q} = f^{\beta}\big(\tilde{c}(\phi)\big)$$

- From Eq. 6,

$$f\big(\tilde{c}(\phi), \phi\big) = h(\phi) f^{\beta}\big(\tilde{c}(\phi)\big) + \big(1 - h(\phi)\big) f^{\alpha}\big(\tilde{c}(\phi)\big) = \overline{P_2Q}$$

which $f\big(\tilde{c}(\phi), \phi\big)$ depends on $h(\phi)$ which is volume fraction of β phase.

- We have

$$\overline{P_5Q} = f(c_{\beta}, 1)$$

- Since $\tilde{\mu}^{\mathsf{e}}$ is slope of common tangent line,

$$\overline{P_4P_5} = \big(\tilde{c}(\phi) - c_{\beta}^{\mathsf{e}}\big)\tilde{\mu}^{\mathsf{e}}$$

therefore,

$$W(\phi) = \overline{P_2Q} - \overline{P_5Q} - \overline{P_4P_5} = \overline{P_2P_4}$$

Interface width of WBM model

- From Eq. 8,

$$\frac{d\phi}{dx} = -\frac{\sqrt{2}}{\varepsilon}\sqrt{wg(\phi) + W(\phi)} \tag{9}$$

- When the width of interface is 2ξ in other words, $\phi_a < \phi < \phi_b$,

$$\begin{aligned} 2\xi &= \int_{-\xi}^{\xi} dx \\ &= -\frac{\varepsilon}{\sqrt{2}}\int_{\phi_b}^{\phi_a} \frac{d\phi}{\sqrt{wg(\phi) + W(\phi)}} \\ &= \frac{\varepsilon}{\sqrt{2}}\int_{\phi_a}^{\phi_b} \frac{d\phi}{\sqrt{wg(\phi) + W(\phi)}} \end{aligned} \tag{10}$$

- From Eq. 8, we have

$$wg(\phi) + f\left(\tilde{c}(\phi), \phi\right) = \frac{\varepsilon^2}{2}\left(\frac{d\phi}{dx}\right)^2 + f\left(c_\beta^{\mathsf{e}}, 1\right) + \left(\tilde{c}(\phi) - c_\beta^{\mathsf{e}}\right)\tilde{\mu}^{\mathsf{e}}$$

- Plug it into 1,

$$F = \int_\Omega \left[\varepsilon^2\left(\frac{d\phi}{dx}\right)^2 + f\left(c_\beta^{\mathsf{e}}, 1\right) + \left(\tilde{c}(\phi) - c_\beta^{\mathsf{e}}\right)\tilde{\mu}^{\mathsf{e}}\right] d\Omega$$

- The excess energy per area is

$$\frac{G^{\mathsf{xs}}}{A} = \int_{-\infty}^{\infty} \left[\varepsilon^2\left(\frac{d\phi}{dx}\right)^2 + f\left(c_\beta^{\mathsf{e}}, 1\right) + \left(\tilde{c}(\phi) - c_\beta^{\mathsf{e}}\right)\tilde{\mu}^{\mathsf{e}}\right] dx - \int_{-\infty}^{0} f^\beta\left(c_\beta^{\mathsf{e}}\right) dx - \int_0^\infty f^\alpha\left(c_\alpha^{\mathsf{e}}\right) dx$$

Interface width of WBM model

- The number of excess solute atoms at interface is

$$\frac{\Gamma^{\mathsf{xs}}}{A} = \frac{1}{v_m}\left[\int_{-\infty}^{\infty} \tilde{c}(\phi)dx - \int_{-\infty}^{0} c_\beta^{\mathsf{e}} dx - \int_{0}^{\infty} c_\alpha^{\mathsf{e}} dx\right]$$

- The interface energy is

$$\sigma = \varepsilon^2 \int_{-\infty}^{\infty} \left(\frac{d\phi}{dx}\right)^2 dx$$

proceed to

$$\sigma = \varepsilon^2 \int_{1}^{0} \left(\frac{d\phi}{dx}\right)^2 \frac{dx}{d\phi} d\phi = \varepsilon^2 \int_{1}^{0} \left(\frac{d\phi}{dx}\right) d\phi$$

- With Eq. 9,

$$\sigma = \varepsilon\sqrt{2} \int_{0}^{1} \sqrt{wg(\phi) + W(\phi)} d\phi \qquad (11)$$

Interface width of WBM model

- From Eqs. 10 and 11,

$$2\xi = \frac{\sigma}{2} \frac{\int_{\phi_a}^{\phi_b} \frac{d\phi}{\sqrt{wg(\phi)+W(\phi)}}}{\int_0^1 \sqrt{wg(\phi)+W(\phi)}d\phi}$$

- $wg(\phi)$ is manageable, however, $W(\phi)$ is not. It is determined by the formulation of free energy of each phase.
- Interface energy depends on bulk energy in WBM, which is quite challenging.