Series lectures of phase-field model

09. Multi-phase model: KKS model

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Kim-Kim-Suzuki model

- In Kim-Kim-Suzuki(KKS) model, the free energy density $f(c, \phi)$, where ϕ is phase-field to distinguish α and β phase.
- c is the composition of the system which is mixture of α and β phases.
- c_α and c_β are compositions of α and β phase, respectively.
- Concentrations and order parameter depend on position **r** and time t. We implicitly represent it.
- The free energy functional is

$$f(c, \phi) = h(\phi) f^\alpha(c_\alpha) + \left[1 - h(\phi)\right] f^\beta(c_\beta) + wg(\phi) \tag{1}$$

- The composition of the system is

$$c(\mathbf{r}, t) = h(\phi) c_\alpha(\mathbf{r}, t) + \left[1 - h(\phi)\right] c_\beta(\mathbf{r}, t) \tag{2}$$

- Under the thermodynamic equilibrium is assumed by

$$\frac{df^\alpha(c_\alpha)}{dc_\alpha} = \frac{df^\beta(c_\beta)}{dc_\beta} \tag{3}$$

Kim-Kim-Suzuki model

- The interpolation function $h(\phi)$ have to be satisfied

$$h(\phi = 0) = 0 \qquad h(\phi = 1) = 1$$

and

$$h'(\phi = 0) = 0 \qquad h'(\phi = 1) = 0$$

we can choose

$$h(\phi) = \phi^3(10 - 15\phi + 6\phi^2) \quad \text{or} \quad h(\phi) = \phi^2(3 - 2\phi)$$

- The double-well potential is

$$g(\phi) = \phi^2(1 - \phi)^2$$

Governing equation using dilute solution approximation

- Introduce the notation for convenience.

$$f_c(c,\phi) = \frac{\partial f(c,\phi)}{\partial c} \qquad f_\phi = \frac{\partial f(c,\phi)}{\partial \phi} \quad f_c^\alpha(c_\alpha) = \frac{df^\alpha}{dc_\alpha}$$

$$f_{cc}^\alpha = \frac{d^2 f^\alpha(c_\alpha)}{dc_\alpha^2} \quad f_{cc}^\beta = \frac{d^2 f^\beta(c_\beta)}{dc_\beta^2} \quad f_{cc} = \frac{\partial^2 f(c,\phi)}{\partial c^2}$$

- Two equations are given by

$$\frac{\partial \phi(\mathbf{r},t)}{\partial t} = M_\phi\left(\epsilon^2\nabla^2\phi - f_\phi\right) \tag{4}$$

$$\frac{\partial c(\mathbf{r},t)}{\partial t} = \nabla\left(M_{\mathrm{d}}\nabla f_c\right) = \nabla\left(\frac{D(\phi)}{f_{cc}}\nabla f_c\right) \tag{5}$$

Governing equation using dilute solution approximation

- Take partial derivative with respect to c of Eq. 2,

$$1 = h(\phi)\frac{\partial c_\alpha}{\partial c} + [1 - h(\phi)]\frac{\partial c_\beta}{\partial c}, \tag{6}$$

- Take partial derivative with respect to c of Eq. 3, we have

$$f_{cc}^{\alpha}\left(\frac{\partial c_\alpha}{\partial c}\right) = f_{cc}^{\beta}\left(\frac{\partial c_\beta}{\partial c}\right)$$

proceed to

$$\frac{\partial c_\beta}{\partial c} = \frac{f_{cc}^{\alpha}}{f_{cc}^{\beta}}\left(\frac{\partial c_\alpha}{\partial c}\right)$$

- Plug it into Eq. 6,

$$\frac{\partial c_\alpha}{\partial c} = \frac{f_{cc}^{\beta}}{[1 - h(\phi)]f_{cc}^{\alpha} + h(\phi)f_{cc}^{\beta}} \tag{7}$$

- Consistently,

$$\frac{\partial c_\beta}{\partial c} = \frac{f_{cc}^{\alpha}}{[1 - h(\phi)]\, f_{cc}^{\alpha} + h(\phi) f_{cc}^{\beta}} \tag{8}$$

- By similar ways,

$$\frac{\partial c_\alpha}{\partial \phi} = \frac{h'(\phi)(c_\alpha - c_\beta) f_{cc}^{\beta}}{[1 - h(\phi)]\, f_{cc}^{\alpha} + h(\phi) f_{cc}^{\beta}} \tag{9}$$

$$\frac{\partial c_\beta}{\partial \phi} = \frac{h'(\phi)(c_\alpha - c_\beta) f_{cc}^{\alpha}}{[1 - h(\phi)]\, f_{cc}^{\alpha} + h(\phi) f_{cc}^{\beta}} \tag{10}$$

Governing equation using dilute solution approximation

- Take partial derivative with respect to ϕ of Eq. 1, under equilibrium

$$\frac{df^\alpha(c_\alpha)}{dc_\alpha} = \frac{df^\beta(c_\beta)}{dc_\beta} = \tilde{\mu}$$

it have to be diffusion potential $\tilde{\mu}$. We have

$$\begin{aligned} f_\phi(c,\phi) &= \frac{\partial f(c,\phi)}{\partial \phi} + h(\phi)\tilde{\mu}\frac{\partial c_\alpha}{\partial \phi} + \left[1 - h(\phi)\right]\tilde{\mu}\frac{\partial c_\beta}{\partial \phi} \\ &= -h'(\phi)\left[f^\alpha(c_\alpha) - f^\beta(c_\beta)\right] + wg'(\phi) \\ &+ \tilde{\mu}\underbrace{\left[h(\phi)\frac{\partial c_\alpha}{\partial \phi} + \left[1 - h(\phi)\right]\frac{\partial c_\beta}{\partial \phi}\right]}_{h'(\phi)\left(c_\alpha - c_\beta\right)} \\ &= -h'(\phi)\left[f^\alpha(c_\alpha) - f^\beta(c_\beta) - \tilde{\mu}\left(c_\alpha - c_\beta\right)\right] + wg'(\phi) \end{aligned} \tag{11}$$

- Take the derivative with respect to c of Eq. 3,

$$f_{cc}(c,\phi) = f_{cc}^{\alpha}\left(\frac{\partial c_\alpha}{\partial c}\right) = \frac{f_{cc}^{\alpha} f_{cc}^{\beta}}{\left[1-h(\phi)\right] f_{cc}^{\alpha} + h(\phi) f_{cc}^{\beta}}$$

- Take the derivative with respect to ϕ of Eq. 3,

$$f_{c\phi}(c,\phi) = f_{cc}^{\alpha}\left(\frac{\partial c_\alpha}{\partial \phi}\right) = \frac{f_{cc}^{\alpha} f_{cc}^{\beta} h'(\phi)(c_\alpha - c_\beta)}{\left[1-h(\phi)\right] f_{cc}^{\alpha} + h(\phi) f_{cc}^{\beta}}$$

- Therefore, we have

$$\frac{f_{c\phi}(c,\phi)}{f_{cc}(c,\phi)} = h'(\phi)(c_\alpha - c_\beta) \tag{12}$$

Governing equation using dilute solution approximation

- Take partial derivative with respect to c of Eq. 1 with $f_c^\alpha = f_c^\beta = \tilde{\mu}$, we have the diffusion potential $\tilde{\mu}$.

$$
\begin{aligned}
f_c(c,\phi) &= h(\phi)\tilde{\mu}\frac{\partial c_\alpha}{\partial c} + \left[1 - h(\phi)\right]\tilde{\mu}\frac{\partial c_\beta}{\partial c} \\
&= \frac{h(\phi)\tilde{\mu}f_{cc}^\beta + \left[1 - h(\phi)\right]\tilde{\mu}f_{cc}^\alpha}{\left[1 - h(\phi)\right]f_{cc}^\alpha + h(\phi)f_{cc}^\beta} = \tilde{\mu} = f_c^\beta = f_c^\alpha
\end{aligned}
$$

Governing equations for KKS equation

- With Eqs. 5 and 12,

$$\begin{aligned}\frac{\partial c(\mathbf{r},t)}{\partial t} &= \nabla \cdot \frac{D(\phi)}{f_{cc}} \nabla f_c \\ &= \nabla \cdot \frac{D(\phi)}{f_{cc}} \left(f_{cc} \nabla c + f_{c\phi} \nabla \phi \right) \\ &= \nabla \cdot D(\phi) \nabla c + \nabla \cdot \frac{D(\phi) f_{c\phi}}{f_{cc}} \nabla \phi \\ &= \nabla \cdot D(\phi) \nabla c + \nabla \cdot D(\phi) h'(\phi) \left(c_\alpha - c_\beta \right) \nabla \phi\end{aligned}$$

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

Governing equations for KKS equation

- With Eq. 2.

$$\frac{\partial c(\mathbf{r},t)}{\partial t} = \nabla \cdot D(\phi)\nabla\Big[h(\phi)c_\alpha + \big(1-h(\phi)\big)c_\beta\Big] + \nabla \cdot D(\phi)h'(\phi)\big(c_\alpha - c_\beta\big)\nabla\phi = \nabla \cdot D(\phi)\Big[h(\phi)\nabla c_\alpha + \big(1-h(\phi)\big)\nabla c_\beta\Big]$$

- The change in solute concentration at a point, for example in a binary system, is determined by the sum of the solute changes in the two phases.
- With Eqs. 4 and 11,

$$\frac{1}{M_\phi}\frac{\partial\phi}{\partial t} = \varepsilon^2\nabla^2\phi - wg'(\phi) + \underbrace{\Big[f^\alpha(c_\alpha) - f^\beta(c_\beta) - \big(c_\alpha - c_\beta\big)\tilde{\mu}\Big]h'(\phi)}_{\text{thermodynamic driving force}}$$

Equilibrium concentration of KKS model

- In binary system, in one-dimensional system three conditions have to be satisfied under the equilibrium.

$$\frac{d}{dx}\left(M_{\mathsf{d}}\frac{d\tilde{\mu}}{dx}\right) = 0$$

$$\varepsilon^2\frac{d^2\phi}{dx^2} - wg'(\phi) + h'(\phi)\left[f^\alpha(c_\alpha^{\mathsf{e}}) - f^\beta(c_\beta^{\mathsf{e}}) - (c_\alpha^{\mathsf{e}} - c_\beta^{\mathsf{e}})\tilde{\mu}^{\mathsf{e}}\right] = 0 \quad (13)$$

$$\tilde{\mu} = \frac{df^\beta(c_\beta)}{dc_\beta} = \frac{df^\alpha(c_\alpha)}{dc_\alpha}$$

- Integrate the second equation with respect to x,

$$\frac{\varepsilon^2}{2}\left(\frac{d\phi}{dx}\right)^2\Bigg|_{-\infty}^{+\infty} - wg(\phi)\Bigg|_1^0 + h(\phi)\Bigg|_1^0\left[f^\alpha(c_\alpha^{\mathsf{e}}) - f^\beta(c_\beta^{\mathsf{e}}) - (c_\alpha^{\mathsf{e}} - c_\beta^{\mathsf{e}})\tilde{\mu}^{\mathsf{e}}\right] = 0$$

Equilibrium concentration of KKS model

- First and second terms are gone, we have

$$f^\alpha(c^{\mathrm{e}}_\alpha) - f^\beta(c^{\mathrm{e}}_\beta) - (c^{\mathrm{e}}_\alpha - c^{\mathrm{e}}_\beta)\tilde{\mu}^{\mathrm{e}} = 0 \tag{14}$$

it is

$$\tilde{\mu}^{\mathrm{e}} = f^\alpha_c = f^\beta_c = \frac{f^\alpha(c^{\mathrm{e}}_\alpha) - f^\beta(c^{\mathrm{e}}_\beta)}{c^{\mathrm{e}}_\alpha - c^{\mathrm{e}}_\beta}$$

which converges to the common tangent condition, which is given by thermodynamic equilibrium condition.

- The concentration within the interface is given by

$$\tilde{c}^{\mathrm{e}} = h(\phi)c^{\mathrm{e}}_\beta + \big(1 - h(\phi)\big)c^{\mathrm{e}}_\alpha$$

Interface width of KKS model

- When Eq. 14 is satisfied, Eq. 13 becomes under the equilibrium

$$\varepsilon^2 \frac{d^2\phi}{dx^2} - wg'(\phi) = 0 \tag{15}$$

which differs from WBM model. In KKS model, $f_\phi(c, \phi)$ term disappears. The solution of Eq. 15 is

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

- When the order parameter varies from ϕ_a to ϕ_b at interface, the interface width 2ξ is

$$2\xi = \frac{\varepsilon}{\sqrt{2w}} \int_{\phi_a}^{\phi_b} \frac{d\phi}{\sqrt{g(\phi)}}$$

Interface width of KKS model

- Let

$$g(\phi) = \phi^2(1-\phi)^2$$

then we have the solution

$$\phi(x) = \frac{1}{2}\left[1 - \tanh\left(\frac{\sqrt{w}}{\sqrt{2}\varepsilon}x\right)\right]$$

- When

$$\phi_a = 0.1 \qquad \phi_b = 0.9$$

we have

$$2\xi = \frac{4\varepsilon}{\sqrt{2w}} \ln 3$$

Interface energy of KKS model

- For KKS model,

$$\frac{G^{\mathsf{xs}}}{A} = \int_{-\infty}^{\infty} \Bigg[h(\phi) f^{\beta}(c_{\beta}^{\mathsf{e}}) + (1 - h(\phi)) f^{\alpha}(c_{\alpha}^{\mathsf{e}}) + w g(\phi) + \left(\frac{\varepsilon^2}{2} \frac{d\phi}{dx} \right)^2 \Bigg] dx - \int_{-\infty}^{0} f^{\beta}(c_{\beta}^{\mathsf{e}}) dx - \int_{0}^{\infty} f^{\alpha}(c_{\alpha}^{\mathsf{e}}) dx$$

- The number of excessive solute atoms per area is

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

Interface width of KKS model

- Proceed to

$$
\begin{aligned}
v_m \frac{\Gamma^{\mathsf{xs}}}{A} \tilde{\mu}^{\mathsf{e}} = \Bigg[\int_{-\infty}^{\infty} \Big(h(\phi) c_\beta^{\mathsf{e}} + (1 - h(\phi)) c_\alpha^{\mathsf{e}} \Big) dx \\
- \int_{-\infty}^{0} c_\beta^{\mathsf{e}} dx - \int_{0}^{\infty} c_\alpha^{\mathsf{e}} dx \Bigg] \frac{f^\alpha(c_\alpha^{\mathsf{e}}) - f^\beta(c_\beta^{\mathsf{e}})}{c_\alpha^{\mathsf{e}} - c_\beta^{\mathsf{e}}}
\end{aligned}
$$

- Then the interface energy is

$$
\sigma = \varepsilon^2 \int_{-\infty}^{\infty} \left(\frac{d\phi}{dx} \right)^2 dx = -\varepsilon^2 \int_0^1 \left(\frac{d\phi}{dx} \right) d\phi = \varepsilon \sqrt{2w} \int_0^1 \sqrt{g(\phi)} d\phi \tag{16}
$$

- Compare to WBM model, $W(\phi)$ term disappears!

Gibbs-Thompson effect under the equilibrium

- When spherical R β phase is under the equilibrium on the α phase,

$$\tilde{\mu}^{\mathsf{e},R} = \frac{df^{\alpha}(c_{\alpha}^{\mathsf{e},R})}{dc} = \frac{df^{\beta}(c_{\beta}^{\mathsf{e},R})}{dc}$$

- When we transfer the origin of coordinates from the center of curvature to the center of interface $\phi = 1/2$, we have

$$\frac{\varepsilon^2}{R+r}\frac{d\phi}{dr} + \varepsilon^2\frac{d^2\phi}{dr^2} - wg'(\phi) + h'(\phi)\Big(f^{\alpha}(c_{\alpha}^{\mathsf{e},R}) - f^{\beta}(c_{\beta}^{\mathsf{e},R}) - (c_{\alpha}^{\mathsf{e},R} - c_{\beta}^{\mathsf{e},R})\tilde{\mu}^{\mathsf{e},R}\Big) = 0$$

Gibbs-Thompson effect under the equilibrium

- Integrate over whole space, second and third terms are vanished,

$$
\begin{aligned}
\varepsilon^2 \int_{-\infty}^{\infty} \frac{1}{R+r}\left(\frac{d\phi}{dr}\right)^2 dr &= \frac{\varepsilon^2}{R}\int_{-\infty}^{\infty} \frac{1}{1+r/R}\left(\frac{d\phi}{dr}\right)^2 dr \\
&= \frac{\varepsilon^2}{R}\int_{-\infty}^{\infty}\left(1-\frac{r}{R}\right)\left(\frac{d\phi}{dr}\right)^2 dr + \mathcal{O}(\delta_2^2) \\
&= \frac{\varepsilon^2}{R}\int_{-\infty}^{\infty}\left(\frac{d\phi}{dr}\right)^2 dr - \frac{\varepsilon^2}{R^2}\int_{-\infty}^{\infty} r\left(\frac{d\phi}{dr}\right)^2 dr + \mathcal{O}(\delta_2^2)
\end{aligned}
$$

- If $g(\phi)$ is symmetric with respect to $\phi = 1/2$, $d\phi/dr$ is odd function with respect to r, therefore, $r(d\phi/dr)^2$ is an even function, therefore, the second term is gone.
- The first integration of RHS becomes σ/R.

Gibbs-Thompson effect under the equilibrium

- Neglecting δ_2^2 term and more,

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

  which converges to result of sharp interface analysis.
- KKS model reproduce Gibbs-Thomson effect with conditions
  1. The curvature radius of interface R is the distance from the origin of curvature to $\phi = 1/2$
  2. $g(\phi)$ is symmetric with respect to $\phi = 1/2$.
  3. The interface have to be narrow enough.