Series lectures of phase-field model

10. Multi-phase model: Grand Potential Model

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Grand Potential Model

- For KKS model, for liquid-solid two-phase system, the concentration is

$$c = h(\phi)c_s + \left[1 - h(\phi)\right]c_l$$

the local(bulk) free energy is

$$f_{\text{loc}}(\phi, c, T) = h(\phi)f_s(c_s, T) + \left[1 - h(\phi)\right]f_l(c_l, T) + Wg(\phi)$$

where c_s and c_l are concentrations of solid and liquid phases.

- Under the equilibrium,

$$\frac{\partial f_s}{\partial c_s} = \frac{\partial f_l}{\partial c_l}$$

- The gradient energy is given by

$$f_{\text{grad}}(\nabla\phi) = \frac{\kappa}{2}\left|\nabla\phi\right|^2$$

- The free energy density is

$$f(\phi, \nabla\phi, c, T) = f_{\text{loc}}(\phi, c_s, c_l, T) + f_{\text{grad}}(\nabla\phi)$$

Grand Potential Model

- The free energy density is

$$F = \int_V f(\phi, \nabla\phi, c, T) dV$$

- The evolution of the material is modeled in terms of derivatives of the grand potential Ω rather than the Gibbs free energy F,

$$\omega(\mu, \psi, \nabla\psi, T) = \omega_{\text{loc}}(\mu_s, \mu_l, \psi, T) + \omega_{\text{grad}}(\nabla\psi)$$

$$\Omega = \int \omega(\mu_s, \mu_l, \psi, \nabla\psi, T) dV$$

where $\omega_{\text{grad}}(\nabla\psi)$ is identical to $f_{\text{grad}}(\nabla\phi)$ for the KKS model.

Grand Potential Model

- The grand potential density is

$$\omega_{\mathrm{loc}}(\mu_s, \mu_l, \psi, T) = h(\psi)\omega_s(\mu_s, T) + \big[1 - h(\psi)\big]\omega_l(\mu_l, T) + Wg(\psi)$$

with

$$\mu_l = \frac{\delta f_{\mathrm{loc}}}{\delta c_l} \qquad \mu_s = \frac{\delta f_{\mathrm{loc}}}{\delta c_s}$$

$$c_l = -\frac{\delta \omega_{\mathrm{loc}}}{\delta \mu_l} \qquad c_s = -\frac{\delta f_{\mathrm{loc}}}{\delta \mu_s}$$

and for solution, we have

$$\mu = \frac{\delta F}{\delta c} \qquad c = -\frac{\delta \Omega}{\delta \mu}$$

The grand potential densities ω_s and ω_l are obtained from Legendre transforms of the free energy densities f_s and f_l.

Grand Potential Model

- The relation between the two potentials is given by

$$\omega = f - \mu c$$

and

$$\Omega = F - \int \mu c dV$$

or

$$F = \Omega + \int \mu c dV \tag{1}$$

- With assumption $\phi = \psi$,

$$\frac{\partial}{\partial \phi} = \frac{\partial \psi}{\partial \phi}\frac{\partial}{\partial \psi} + \frac{\partial \mu}{\partial \phi}\frac{\partial}{\partial \mu} = \frac{\partial}{\partial \psi} + \frac{\partial \mu}{\partial \phi}\frac{\partial}{\partial \mu}$$

- Consistently,

$$\frac{\partial}{\partial \nabla \phi} = \frac{\partial}{\partial \nabla \psi} + \frac{\partial \mu}{\partial \nabla \phi}\frac{\partial}{\partial \mu}$$

Grand Potential Model

- Proceed to

$$
\begin{aligned}
\frac{\delta\Omega}{\delta\phi} &= \frac{\partial\omega}{\partial\phi} - \nabla\cdot\frac{\partial\omega}{\partial\nabla\phi} \\
&= \left[\frac{\partial\omega}{\partial\psi} + \frac{\partial\mu}{\partial\phi}\frac{\partial\omega}{\partial\mu}\right] - \nabla\cdot\left[\frac{\partial\omega}{\partial\nabla\psi} + \frac{\partial\mu}{\partial\nabla\phi}\frac{\partial\omega}{\partial\mu}\right] \\
&= \frac{\partial\omega}{\partial\psi} - \nabla\cdot\frac{\partial\omega}{\partial\nabla\psi} + \frac{\partial\mu}{\partial\phi}\frac{\partial\omega}{\partial\mu} - \nabla\cdot\left[\frac{\partial\mu}{\partial\nabla\phi}\frac{\partial\omega}{\partial\mu}\right] \\
&= \frac{\delta\Omega}{\delta\psi} + \frac{\partial\mu}{\partial\phi}\frac{\partial\omega}{\partial\mu} - \nabla\cdot\left[\frac{\partial\mu}{\partial\nabla\phi}\frac{\partial\omega}{\partial\mu}\right]
\end{aligned}
$$

Grand Potential Model

- With Eq.1,

$$\begin{aligned}
\frac{\delta F}{\delta \phi} &= \frac{\delta \Omega}{\delta \phi} + \frac{\delta \int \mu c}{\delta \phi} \\
&= \left(\frac{\delta \Omega}{\delta \psi} + \frac{\partial \mu}{\partial \phi}\frac{\partial \omega}{\partial \mu} - \nabla \cdot \left[\frac{\partial \mu}{\partial \nabla \phi}\frac{\partial \omega}{\partial \mu} \right] \right) + \frac{\delta \mu c}{\delta \phi} \\
&= \frac{\delta \Omega}{\delta \psi} + \frac{\partial \mu}{\partial \phi}\frac{\delta \Omega}{\delta \mu} - \nabla \cdot \left[\frac{\partial \mu}{\partial \nabla \phi}\frac{\delta \Omega}{\delta \mu} \right] + c\frac{\partial \mu}{\partial \phi} - \nabla \cdot c\frac{\partial \mu}{\partial \nabla \phi} \\
&= \frac{\delta \Omega}{\delta \psi} - \frac{\partial \mu}{\partial \phi}c + \nabla \cdot \left[\frac{\partial \mu}{\partial \nabla \phi}c \right] + c\frac{\partial \mu}{\partial \phi} - \nabla \cdot c\frac{\partial \mu}{\partial \nabla \phi} \\
&= \frac{\delta \Omega}{\delta \psi}
\end{aligned}$$

Grand Potential Model

- We have assumed no gradient of μ in ω, so that

$$\frac{\delta\Omega}{\delta\mu} = \frac{\partial\omega}{\partial\mu}$$

- The Ginzburg-Landau Equation is

$$\frac{\partial\phi}{\partial t} = -M\frac{\delta F}{\delta\phi}$$

is identical to

$$\frac{\partial\psi}{\partial t} = -M\frac{\delta\Omega}{\delta\psi}$$

- The solute can be obtained by

$$\frac{\partial c}{\partial t} = \frac{\partial c}{\partial \psi}\frac{\partial \psi}{\partial t} + \frac{\partial c}{\partial \mu}\frac{\partial \mu}{\partial t}$$

Grand Potential Model

- The free energy is

$$f_s = (c_s - 0.25)^2 \qquad f_l = (c_l - 0.75)^2 + 0.1c_l$$

then

$$\mu_s = \frac{\partial f_s}{\partial c_s} = 2c_s - 0.5 \qquad \mu_l = \frac{\partial f_l}{\partial c_l} = 2c_l - 1.4$$

so

$$\omega_s(c_s) = f_s - \mu_s c_s = 0.625 - c_s^2 \qquad \omega_l(c_l) = f_l - \mu_l c_l = 0.5625 - c_l^2$$

and

$$c_s = 0.5\mu_s + 0.25 \qquad c_l = 0.5\mu_l + 0.7$$

- Under the equilibrium, $\mu = \mu_s = \mu_l$, we have

$$c_s = 0.5\mu + 0.25 \qquad c_l = 0.5\mu + 0.7 \tag{2}$$

- Therefore, the grand potentials are given by

$$\omega_s(c_s) = 0.625 - c_s^2 = -0.25\mu - 0.25\mu^2$$

$$\omega_l(c_l) = 0.5625 - c_l^2 = 0.0725 - 0.7\mu - 0.25\mu^2$$

- Under the equilibrium,

$$\omega_s(c_s) = \omega_l(c_l)$$

then

$$-0.25\mu - 0.25\mu^2 = 0.0725 - 0.7\mu - 0.25\mu^2$$

then we have

$$\mu_e = 0.16111$$

Grand Potential Model

- Introduce

$$h(\phi) = 3\phi^2 - 2\phi^3$$

and with Eq. 2

$$\begin{aligned} c &= c_s h(\phi) + c_l \left[1 - h(\phi)\right] \\ &= 0.5\mu + 0.7 - 0.45 \times \left(3\phi^2 - 2\phi^3\right) \\ &= 0.7 + 0.9\phi^3 - 1.35\phi^2 + 0.5\mu \end{aligned}$$

and the chemical potential

$$\mu = -1.8\phi^3 + 2.7\phi^2 - 1.4 + 2c$$