Series lectures of phase-field model

03. Cahn-Hilliard Equation I

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Growth of a precipitate

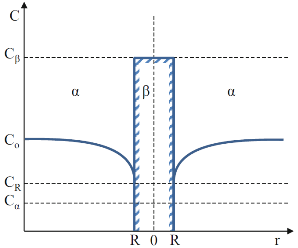
- Diffusion equation (Fick's 2nd law)

$$\frac{\partial c(\mathbf{r},t)}{\partial t} = D\nabla^2 c(\mathbf{r},t)$$

- Mass balance at the interface

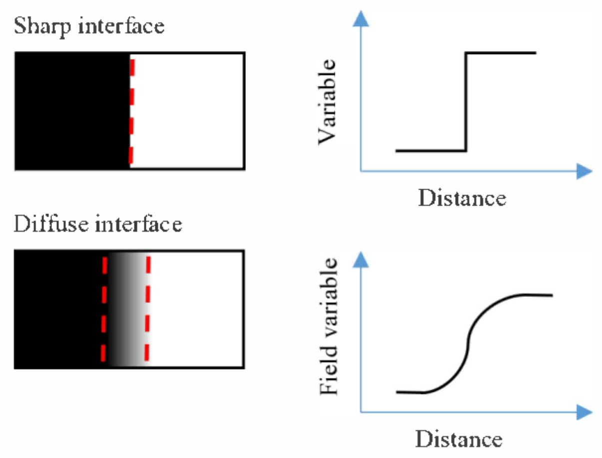
$$\frac{dR}{dt}(c^\beta - c^\alpha) = D\frac{\partial c(\mathbf{r},t)}{\partial r}\bigg|_{r=R(t)}$$

- Free boundary problems



Sharp interface approach

Write one (or many) PDE that holds everywhere, in both phases and at the interface. Do not need to track the location of the boundary.



Phase-field model

- Conserved order parameter: Cahn-Hilliard equation
- Non-conserved order parameter: Allen-Cahn equation

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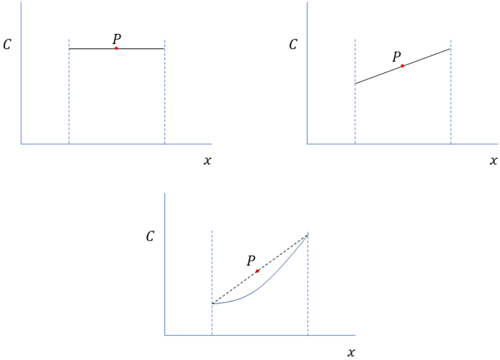
Derivation of Cahn-Hilliard equation

- Cahn-Hilliard (JCP, 1958): Consider the energy associated with gradients in composition.



Derivation of Cahn-Hilliard equation

- The chemical potential is function of $\frac{d^2c}{dx^2}$

$$f = f\left(c, \frac{dc}{dx}, \frac{d^2c}{dx^2}, \cdots\right)$$

- By Taylor's expansion with omitting higher-order terms,

$$f(c, dc/dx) = f(c, 0) + L\frac{dc}{dx} + \kappa\left(\frac{dc}{dx}\right)^2$$

where

$$L = \frac{\partial f}{\partial(dc/dx)} \qquad \kappa = \frac{1}{2}\frac{\partial f}{\partial\big((dc/dx)^2\big)}$$

- $L = 0$ for centrosymmetric crystal, $f(c)$ is free energy per volume.

$$F = A\int_V \left[f(c) + \kappa\left(\frac{dc}{dx}\right)^2\right] dV$$

Derivation of Cahn-Hilliard equation

- For 1-D case

$$F = A\int_{x_1}^{x_2}\left[f(c)+\kappa\left(\frac{dc}{dx}\right)^2\right]dx$$

$$\delta F = A\int_{x_1}^{x_2}\left[\frac{\partial f(c)}{\partial c}\delta c+\kappa\delta\left(\frac{dc}{dx}\right)^2\right]dx$$

$$= A\int_{x_1}^{x_2}\left[\frac{\partial f(c)}{\partial c}\delta c+2\kappa\left(\frac{dc}{dx}\right)\delta\left(\frac{dc}{dx}\right)\right]dx$$

- By integrating by parts

$$\int_{x_1}^{x_2}\left[\left(\frac{dc}{dx}\right)\delta\left(\frac{dc}{dx}\right)\right]dx = \frac{dc}{dx}\delta c\Big|_{x_1}^{x_2} - \int_{x_1}^{x_2}\frac{d^2c}{dx^2}\delta c dx$$

when $\frac{dc}{dx}$ is 0 when $x = x_1, x_2$ then

$$\int_{x_1}^{x_2} 2\kappa\left(\frac{dc}{dx}\right)\delta\left(\frac{dc}{dx}\right)dx = -2\kappa\int_{x_1}^{x_2}\frac{d^2c}{dx^2}\delta c dx$$

- At equilibrium,

$$\frac{\delta F}{\delta c} = A \int_{x_1}^{x_2} \left[\frac{\partial f(c)}{\partial c} - 2\kappa \frac{d^2 c}{dx^2} \right] dx = 0$$

therefore,

$$\frac{\partial f(c)}{\partial c} - 2\kappa \frac{d^2 c}{dx^2} = 0$$

- For the case of non-conserved order parameter(η), means no constrain on the average value of η, we can state

$$\frac{\partial f(\eta)}{\partial \eta} - 2\kappa \frac{d^2 \eta}{dx^2} = 0$$

- For conserved order parameter, such as composition(c), it have to be conserved

$$\int_{x_1}^{x_2} \left[c(x) - c_0 \right] dx = 0$$

where c_0 is the nominal alloy composition.

Derivation of Cahn-Hilliard equation

- Then we have

$$F = A \int_{x_1}^{x_2} \left[f(c) + \kappa \left(\frac{dc}{dx} \right)^2 - \lambda \big(c(x) - c_0 \big) \right] dx$$

- Take variation

$$\delta F = A \int_{x_1}^{x_2} \left[\delta \left[f(c) + \kappa \left(\frac{dc}{dx} \right)^2 \right] - \lambda \delta \big(c(x) - c_0 \big) \right] dx$$

$$= A \int_{x_1}^{x_2} \left[\frac{\partial f}{\partial c} - 2\kappa \frac{d^2 c}{dx^2} - \lambda \right] \delta c dx$$

therefore, we reach the Euler-Lagrange equation

$$\lambda = \frac{\partial f}{\partial c} - 2\kappa \frac{d^2 c}{dx^2}$$

- λ have to be uniform at equilibrium.

Derivation of Cahn-Hilliard equation

- If λ is not uniform, flux have to be present. Therefore, we can write

$$J_{\mathsf{A}} = -M\nabla\lambda = -M\nabla\left(\frac{\partial f}{\partial c_{\mathsf{A}}} - 2\kappa\frac{\partial^2 c_{\mathsf{A}}}{\partial x^2}\right)$$

where

$$f = c_0[\mu_{\mathsf{A}} c_{\mathsf{A}} + \mu_{\mathsf{B}} c_{\mathsf{B}}]$$

Derivation of Cahn-Hilliard equation

- Applying mass conservation equation

$$\begin{aligned}\frac{\partial c}{\partial t} &= -\frac{\partial J}{\partial x} \\ &= \frac{d}{dx} \cdot \left[M \frac{\partial}{\partial x} \left(\frac{\partial f}{\partial c} - 2\kappa \frac{\partial^2 c}{\partial x^2} \right) \right]\end{aligned}$$

we reach the Cahn-Hilliard equation in one-dimensional system.

Derivation of Cahn-Hilliard equation

- Assume constant mobility,

$$\begin{aligned}
\frac{\partial c}{\partial t} &= M\frac{\partial}{\partial x}\left[\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial c} - 2\kappa\frac{\partial^2 c}{\partial x^2}\right)\right] \\
&= M\frac{\partial}{\partial x}\left[\frac{\partial^2 f}{\partial c^2}\frac{\partial c}{\partial x} - 2\kappa\frac{\partial^3 c}{\partial x^3}\right] \\
&= M\left[\frac{\partial}{\partial x}\left(\frac{\partial^2 f}{\partial c^2}\frac{\partial c}{\partial x}\right) - 2\kappa\frac{\partial^4 c}{\partial x^4}\right]
\end{aligned}$$

- Unfortunately, closed form of the solution does not exist generally.