Phase Field Method

From fundamental theories to a phenomenological simulation method

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24 June 2003

Outline

- Introduction
- Important concepts:
  - Diffuse interphase-phase field variables
- Thermodynamics of heterogeneous systems
  - Free energy formulation (C-H) -theoretical derivation-interpretation
- Kinetics of heterogeneous systems
  - Linear kinetic theory-conserved versus non-conserved variables

Outline

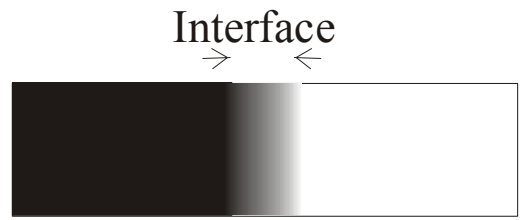
- Phase field microelasticity
  - Stress-free strain-Khachaturyan's approach-generalisation
- Calphad and phase field modeling
- Determination of the other parameters
  - Gradient energy coefficient-kinetic parameters -mechanical parameters
- Conclusions

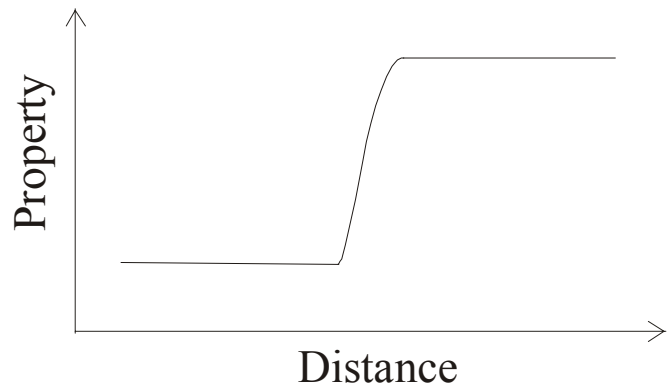
Introduction

- Simulation of phase transformations and other microstructural evolutions:
  - Dendritic solidification, martensitic transformations, recrystallisation, graingrowth, precipitation, …
- Possible to simulate and to predict arbitrary microstructures
- Straight forward to account for various driving forces:
  - Chemical free energy, interfacial energy, elastic strain energy, external fields

Important concepts

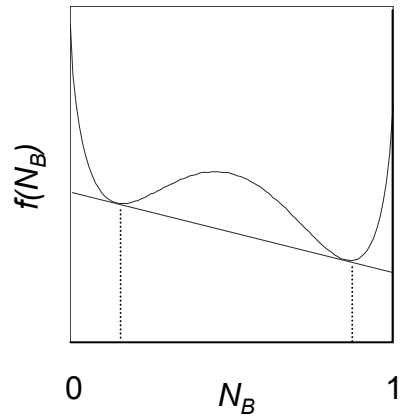
- Diffuse interfaces
  - Introduced by Cahn and Hilliard (1958)
  - Continous variation in properties accross interfaces of finite thickness
  - Free energy for a heterogeneous system:

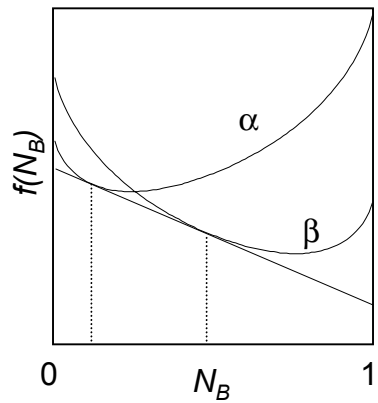




$$F(c,\phi,\eta) \rightarrow F\left(c,\phi,\eta,(\partial c/\partial x_i),(\partial \phi/\partial x_i),(\partial \eta/\partial x_i)\right)$$

Important concepts





- Phase field variables
  - Composition: c_i, N_i
    - Both phases same structure
      - spinodal decomposition
  - Phase field parameter: ϕ
    - Distinction between phases with different structures:
      - phase α: ϕ=0, phase β: ϕ=1
      - solidification
  - Long range order parameter: η
    - Ordering:
      - disordered phase: η=0, ordered phase: $\eta=\eta_0(c)$
      - Ni-superalloys : γ(disorderd fcc) $\rightarrow$ γ'(ordered fcc)
    - Reduction in crystal symmetry
      - high symmetry phase: η=0, low symmetry phase: $\eta=\eta_0(c)$
      - martensitic transformation: cubic$\rightarrow$tetragonal

Thermodynamics of heterogeneous systems

- Free energy formulation (in *J*):

$$F = \frac{1}{\Omega}\int_V \left[f_0(c,\eta) + \kappa(\nabla c)^2 + \alpha(\nabla \eta)^2 \right] dV$$

- Theoretical derivation (Cahn-Hilliard)
  - *f* (*J/mol*) depends on local composition and on composition of immediate environment
  - Taylor expansion around f(c,0,0,…) :

$$f(c,(\partial c/\partial x_i),(\partial^2 c/\partial x_i \partial x_j),\ldots) = f_0(c) + \sum_i L_i(\partial c/\partial x_i) + \sum_{ij} \kappa_{ij}^{(1)}(\partial^2 c/\partial x_i \partial x_j)$$
$$+(1/2)\sum_{ij} \kappa_{ij}^{(2)} \left[(\partial c/\partial x_i)(\partial c/\partial x_j) \right] \ldots$$

with
$$L_i = [\partial f/\partial(\partial c/\partial x_i)]_0,$$
$$\kappa_{ij}^{(1)} = [\partial f/\partial(\partial^2 c/\partial x_i \partial x_j)]_0,$$
$$\kappa_{ij}^{(2)} = [\partial^2 f/\partial(\partial c/\partial x_i)\partial(\partial c/\partial x_j)]_0$$

Thermodynamics of heterogeneous systems

- Most general mathematical expression

$$f(c,(\partial c/\partial x_i),(\partial^2 c/\partial x_i \partial x_j),\ldots) = f_0(c) + \sum_i L_i(\partial c/\partial x_i) + \sum_{ij} \kappa_{ij}^{(1)}(\partial^2 c/\partial x_i \partial x_j) + (1/2)\sum_{ij} \kappa_{ij}^{(2)}\left[(\partial c/\partial x_i)(\partial c/\partial x_j)\right]\ldots$$

- Cubic or isotropic symmetry

$$L_i = 0, \quad \kappa_{ij}^{(1)} = \begin{matrix}\kappa_1 (i=j) \\ 0 (i \neq j)\end{matrix}, \quad \kappa_{ij}^{(2)} = \begin{matrix}\kappa_2 (i=j) \\ 0 (i \neq j)\end{matrix}$$

- Hence for a cubic lattice (*J/mol*):

$$f(c,\nabla c,\nabla^2 c,\ldots) = f_0(c) + \kappa_1 \nabla^2 c + \kappa_2 \left(\nabla c\right)^2 + \ldots$$

Thermodynamics of heterogeneous systems

- Total free energy (*J*):

$$F = \frac{1}{\Omega}\int_V \left[f_0(c) + \kappa_1 \nabla^2 c + \kappa_2 \left(\nabla c\right)^2 + \ldots \right] dV$$

- Divergence theorem: $\int_S \left(\kappa_1 \nabla c \bullet n\right) dS = \int_V \nabla\left(\kappa_1 \nabla c\right) dV$

$$\Rightarrow \int_V \left(\kappa_1 \nabla^2 c\right) dV = -\int_V \left(d\kappa_1 / dc\right)\left(\nabla c\right)^2 dV + \int_S \left(\kappa_1 \nabla c \bullet n\right) dS$$

- $\nabla c \bullet n = 0$ at the boundary $\Rightarrow$

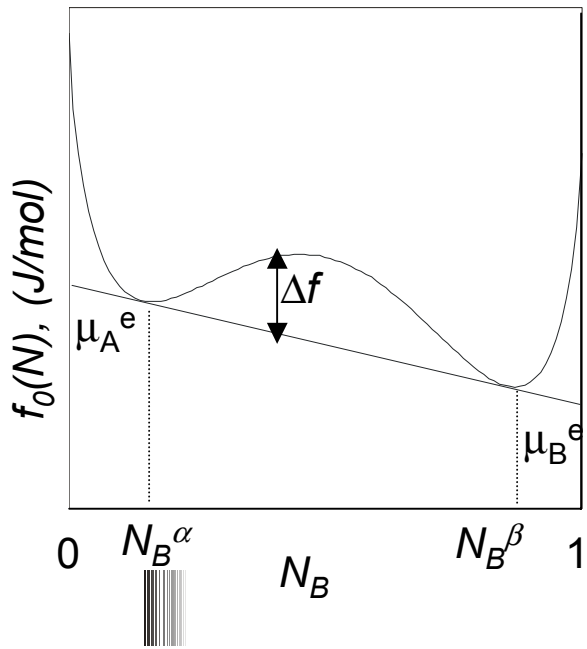
$$F = \frac{1}{\Omega}\int_V \left[f_0 + \kappa\left(\nabla c\right)^2 \right] dV$$

Thermodynamics of heterogeneous systems

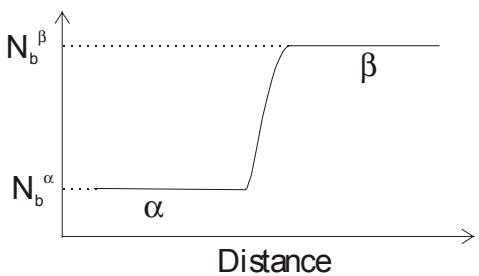
- Flat interfase (C-H):
  - 1D: $F = A\frac{1}{\Omega}\int_{-\infty}^{+\infty}\left[f_0(N_B) + \kappa\left(dN_B/dx\right)^2 \right]dx$
  - Free energy of a flat interfase:

$$\sigma = \frac{1}{\Omega}\int_{-\infty}^{+\infty}\left[f_0(N_B) + \kappa\left(dN_B/dx\right)^2 - \left(N_B\mu_B^e + (1-N_B)\mu_A^e\right)\right]dx$$

$$\sigma = \frac{1}{\Omega}\int_{-\infty}^{+\infty}\left[\Delta f(N_B) + \kappa\left(dN_B/dx\right)^2 \right]dx$$



  - Equilibrium:σ minimal



$$\Delta f(N_B) = \kappa\left(dN_B/dx\right)^2$$

$$\sigma = \frac{2}{\Omega}\int_{N_B^\alpha}^{N_B^\beta}\left[\kappa\Delta f(N_B)\right]^{1/2} dx \Rightarrow \delta \propto \kappa^{1/2}$$

Thermodynamic equilibrium in heterogeneous systems

$$F = \frac{1}{\Omega}\int_V \left[f_0(c,\eta) + \kappa(\nabla c)^2 + \alpha(\nabla \eta)^2 \right] dV$$

- η, ϕ not conserved $\Rightarrow \quad \dfrac{\partial F}{\partial \phi} = 0$
- c conserved $\Rightarrow \quad \dfrac{\partial F}{\partial c} = cte$
- Euler's equation

$$F(y(x)) = \int L(x, y(x), y'(x))dx \Rightarrow \frac{\partial F}{\partial y(x)} = \frac{\partial L}{\partial y} - \frac{d}{dx}\frac{\partial L}{\partial y'(x)} = 0$$

- $\Rightarrow \quad \dfrac{\partial F}{\partial \phi} = \dfrac{\partial f_0}{\partial \phi} - 2\alpha\nabla^2\phi = 0$ and $\dfrac{\partial F}{\partial c} = \dfrac{\partial f_0}{\partial c} - 2\kappa\nabla^2 c = cte$

Kinetics of heterogeneous systems

- c_i, N_i conserved
  - Mass balance $\frac{\partial c_k}{\partial t} = -\nabla \vec{J}_k$
  - Linear kinetic theory (Onsager) $\vec{J_k} = -\sum_j M_{jk} \nabla \frac{\partial F}{\partial c_j}$
  - Cahn-Hilliard equation $\frac{\partial c}{\partial t} = \nabla \bullet M \nabla \left[\frac{\partial f_0}{\partial c} - 2\kappa \nabla^2 c \right]$

Kinetics of heterogeneous systems

- η, ϕ not conserved
  - Linear Kinetic theory: $\frac{d\eta}{dt} = -L\frac{\partial F}{\partial \eta}$
    - Cahn-Allen equation: $\frac{d\phi}{dt} = -L\left(\frac{\partial f_0}{\partial \phi} - 2\alpha\nabla^2\phi\right)$
    - Time dependant Ginzburg-Landau equation:

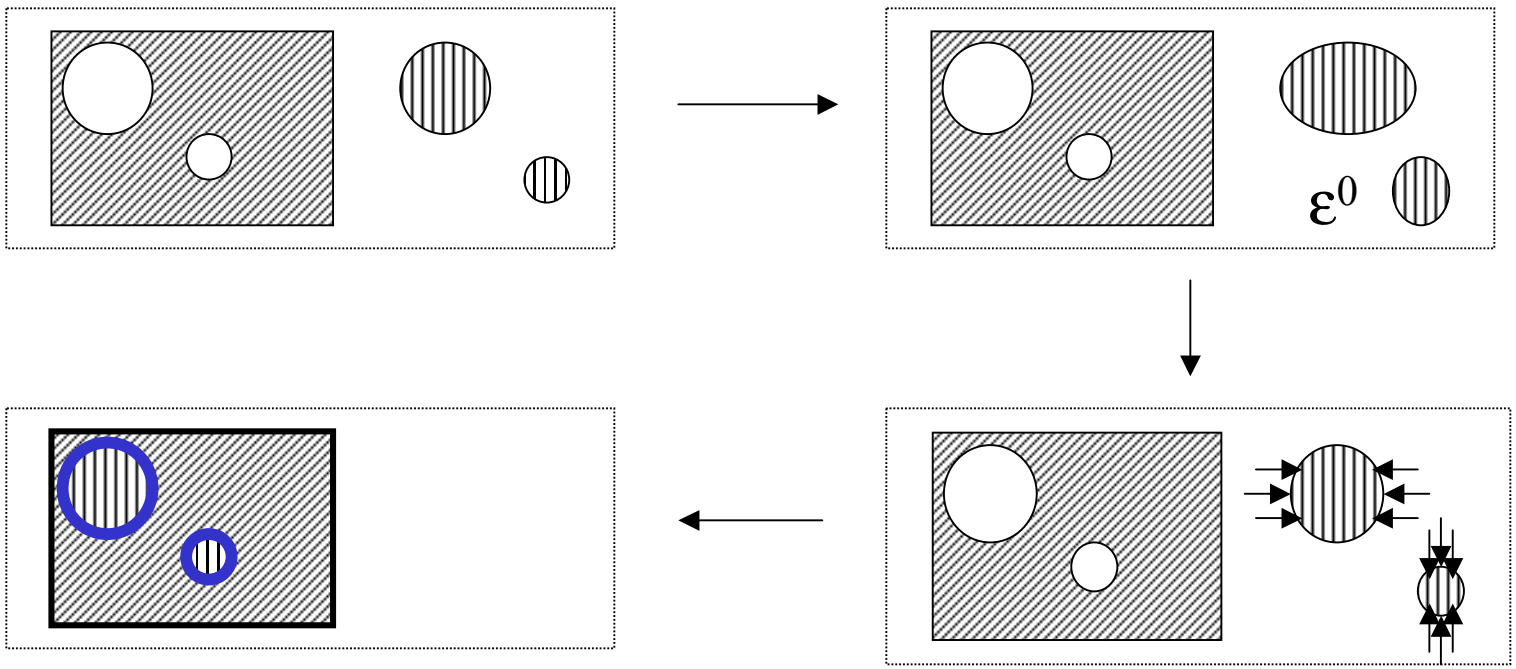
$$\frac{d\eta}{dt} = -L\left(\frac{\partial f_0}{\partial \eta} - 2\alpha\nabla^2\eta\right)$$

- Equivalent formulation: Langevin equations

$$\frac{\partial c}{\partial t} = \nabla \bullet M\nabla\left[\frac{\partial f_0}{\partial c} - 2\kappa\nabla^2 c\right] + \zeta(\vec{r},t)$$

Phase field microelasticity theory

- Important for phase transformations in solids



- Elastic contribution to free energy

$$F^{tot} = F^{chem} + F^{el} \qquad F^{el} = \frac{1}{2}\int_V C_{ijkl}\varepsilon_{ij}^{el}\varepsilon_{kl}^{el}dV$$

Phase field microelasticity theory

- Khachaturyan's approach $\rightarrow F^{el}(c,\eta)$
  - Stress-free strain: $\varepsilon_{ij}^{0}(c_k,\eta_l)$

$$\varepsilon_{ij}^{0}(\vec{r}) = \varepsilon^{0c}\partial c(\vec{r})\delta_{ij} + \varepsilon^{0\eta}\eta^2$$

  - Elastic strain/total strain: $\varepsilon_{ij}^{el}(\vec{r}) = \varepsilon_{ij}^{tot}(\vec{r}) - \varepsilon_{ij}^{0}(\vec{r})$
  - Total strain is sum of homogeneous and heterogeneous strains

$$\varepsilon_{ij}^{tot}(\vec{r}) = \overline{\varepsilon_{ij}} + \partial\varepsilon_{ij}(\vec{r})$$

$$\int_V \partial\varepsilon_{ij}(\vec{r})dV \rightarrow \overline{\varepsilon_{ij}}$$

$$\partial\varepsilon_{ij}(\vec{r}) = \frac{1}{2}\left[\frac{\partial u_i(\vec{r})}{\partial r_l} + \frac{\partial u_j(\vec{r})}{\partial r_i}\right]$$

Homogeneous strain=macroscopic strain

Phase field microelasticity theory

- Mechanical equilibrium is established much faster than chemical equilibrium
  - Elasticity theory:

$$\frac{\partial \sigma_{ij}^{el}(\vec{r})}{\partial r_j} = 0 \quad \sigma_{ij}^{el}(\vec{r}) = C_{ijkl}\left[\varepsilon_{ij}^{el}(\vec{r})\right] = C_{ijkl}\left[\varepsilon_{ij}^{tot}(\vec{r}) - \varepsilon_{ij}^{0}(\vec{r})\right]$$

$$\rightarrow \quad u_i(\vec{r})$$

$$\rightarrow F^{el} = \frac{1}{2}\int_V C_{ijkl}\varepsilon_{ij}^{el}(c(\vec{r}),\eta(\vec{r}))\varepsilon_{kl}^{el}(c(\vec{r}),\eta(\vec{r}))dV$$

- Extension to elastically inhomogeneous systems:

$$C_{ijkl}(\vec{r}) = C_{ijkl}^{\alpha}\frac{c_{eq}^{\beta} - c(\vec{r})}{c_{eq}^{\beta} - c_{eq}^{\alpha}} + C_{ijkl}^{\beta}\frac{c(\vec{r}) - c_{eq}^{\alpha}}{c_{eq}^{\beta} - c_{eq}^{\alpha}}$$

Generalisation to a phenomenological theory

- Multiple components and multiple phases: c_k, ϕ_l or η_l
- For condensed matter f(J/mol)$\approx$$G_m$(J/mol)

  $\Rightarrow$CALPHAD approach to obtain free energy expressions

$$G = \int_V \left[\frac{G_m(c_k, \phi_l)}{V_m} + \sum_k \frac{\kappa_k^2}{2} (\nabla c_k)^2 + \sum_l \frac{\alpha_l^2}{2} (\nabla \phi_l)^2 \right] dV$$

- Interfacial energy

$$G = \int_V \left[\frac{G_m(c_k, \phi_l)}{V_m} + \sum_p \sum_{ij} \frac{\kappa_{pij}^2(c_k, \phi_l)}{2} (\partial^2 c_p / \partial x_i \partial x_j)^2 + \sum_r \sum_{ij} \frac{\alpha_{rij}^2(c_k, \phi_l)}{2} (\partial^2 \phi_r / \partial x_i \partial x_j)^2 \right] dV$$

CALPHAD and the phase field method

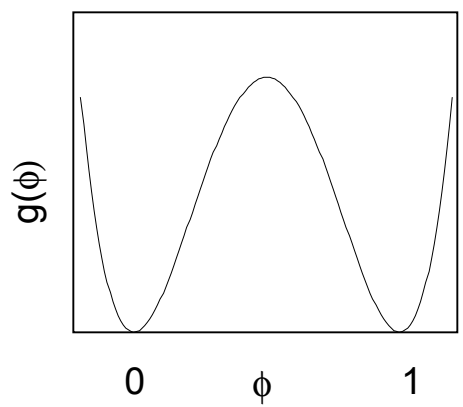
- Transformation $\alpha(\phi=0) \rightarrow \beta(\phi=1)$
  - Calphad:

$$G_m(c_k,0,T) = G_m^{\alpha}(c_k,T)$$
$$G_m(c_k,1,T) = G_m^{\beta}(c_k,T)$$
$$0 < \phi < 1 \rightarrow G_m(c_k,\phi,T)?$$

  - Wheeler-Boettinger

$$G_m(c_k,\phi) = \big(1-p(\phi)\big)G_m^{\alpha}(c_k) + p(\phi)G_m^{\beta}(c_k) + g(\phi)W(c_k)$$

    - $p(\phi)$ smooth function with $p(0)=0, p(1)=1$, for example $p(\phi) = \phi^2(3-2\phi)$
    - double well $g(\phi) = \phi^2(1-\phi)^2$



CALPHAD and the phase field method

- Landau expansion polynomial

$$f(c,\eta_k) = f(c,0) + \sum_i B_i(c)\eta_i + \sum_{ij} C_{ij}(c)\eta_i\eta_j + \sum_{ijk} D_{ijk}(c)\eta_i\eta_j\eta_k + \sum_{ijkl} E_{ijkl}(c)\eta_i\eta_j\eta_k\eta_l + \ldots$$

  - Symmetry (for example cubic→tetragonal phase transformation)

$$f(c,\eta_k) = f(c,0) + C(c)\sum_k \eta_k^2 + E(c)\sum_k \eta_k^4 + G(c)\left(\sum_k \eta_k^2\right)^3$$

  - Calphad: $f(c,0) \approx G_m^{cubic}(c)$

  - Other parameters must be determined by fitting

Determination of the other parameters

- The gradient energy coefficient $F = \frac{1}{\Omega}\int_V \left[f_0(c,\eta) + \kappa(\nabla c)^2 + \alpha(\nabla \eta)^2 \right] dV$
  - Experimental measurement of interfacial energy and thickness
  - From theoretical calculation (starting from regular solution model, first principles)
- Kinetic parameters
  - Mobilities in the Cahn-Hilliard equation $\vec{J} = -M\nabla\frac{\partial F}{\partial c}$
    - Relation between mobilities and diffusivities: $D_B = RTM_B$
    - DICTRA-software
  - Relaxation parameter in TDGL equation $\frac{d\eta}{dt} = -L\frac{\partial F}{\partial \eta}$
    - Very hard to determine
- Elastic parameters
  - Elastic moduli C_{ijkl}
    - From mechanical experiments
  - Stress-free strains
    - Related to the difference in lattice parameters between different phases

Conclusions

- The Phase field method for modeling microstructural evolutions has become very popular
- Achievements
  - A consistent and general theory (thermodynamics, kinetics) has been worked out
  - Simulations for simple cases give promising results
  - Link with CALPHAD and DICTRA
- Remaining problems:
  - Systems with multiple components and phases with different orienations
  - Determination of the parameters
  - Computational intensive method