



## Phase-field modelling

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## Drivers for modelling

- Understanding
  - o If you know the basic "rules" underlying some phenomenon you may feel you understand.
  - o To train your intuition by simulations rather than experiments may be a more rapid way to achieve understanding.
- Prediction
  - o Less expensive than experiments
  - o Process control
  - o Compute things that are difficult to measure
- Efficiency
  - o To make measured data useful
  - o To reduce redundancy

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## Historical review of phase-field modelling

- 1990's: Kobayashi's video of dendritic solidification.
- 1893: Van der Waals, capillarity effect of critical systems. Continuum model and the energy of a diffuse interface with an extra term  $\nabla^2 c$ .
- 1956-58: Cahn and Hilliard and Hillert
  - Extra term  $(\nabla c)^2$ , "gradient energy"
  - Equilibrium from variational analysis.
  - Dynamics from a diffusion equation derived from the total free energy. => **Cahn-Hilliard equation**

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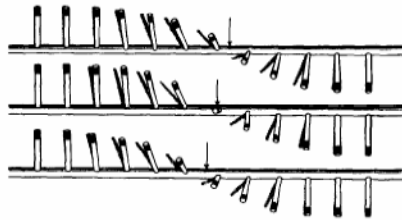


FIG. 1. Schematic drawing of a domain wall advancing. Each rod represents the direction of magnetization of a plane of atoms; each row of rods represents the domain wall at an instant of time. The arrow points to the center of the domain wall.

From Cahn 1960



- 1979: Allen and Cahn, migration of APB, change in order parameter  $\eta$  (non conserved).
    - Dynamics from a postulated equation derived from total free energy.
    - Similar equation postulated by Ginzburg-Landau in the 1950's to represent superconductivity transformation.
- => **AC/GL-equation (Allen-Cahn/Ginzburg-Landau)**



## Phase-field simulations

- In 1980's the AC/GL-equation combined with a modified heat-flow equation to simulate solidification (Stefan problem).  $\eta=1$  for liquid and  $\eta=-1$  for solid:
  - 1985: Collins and Levine,
  - 1986: Caginalp and Fife
  - 1993: Kobayashi

**Elegant formulation of the Stefan problem. A set of partial differential equations solved over the whole domain, no special conditions at the migrating phase interface.**

- 1992: Wheeler et al.:  
Thermodynamic consistency by replacing the heat-flow equation with a Cahn-Hilliard equation derived from the total free energy.



## Now applied to a variety of problems, e.g:

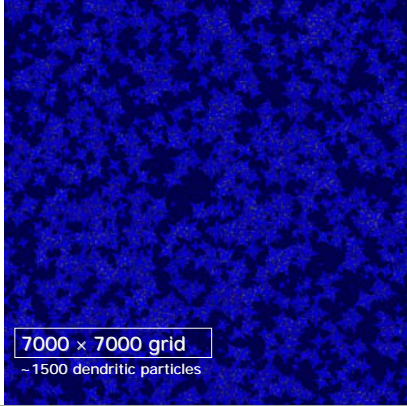


- Effect of elastic strain: Y. Wang, L.-Q. Chen and A. G. Khachaturyan (1993)
- DIGM: J. W. Cahn, P. Fife and O. Penrose (1997)
- Convection during solidification: R. Törnhardt and G. Amberg (1998)
- Solidification of multicomponent super alloys: U. Grafe, B. Böttger, J. Tiaden and S. G. Fries (2000)
- Phase decomposition with ordering: T. Miyazaki (2001)
- Simultaneous heat flow and diffusion: I. Logina, G. Amberg and J. Ågren (2001)
- Large-scale (1500 crystals) solidification: Gránásy, Borzsonyi, Pusztai (2002)
- Grain growth: J. A. Warren, R. Kobayashi, A. E. Lobkovsky and W. C. Carter (2003)
- Solute drag and massive transformation: I. Logina, J. Odqvist, G. Amberg and J. Ågren (2003)
- Sintering: Asp and Ågren (2005)



## Large-scale simulation

Gránásy, Börzsönyi, Pusztai, 2002



7000 × 7000 grid  
~1500 dendritic particles

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## Basic formulation

The total Gibbs energy:

$$G = \int_{\Omega} \left( g(\eta, x_k) + \frac{\varepsilon^2}{2} |\nabla \eta|^2 + \frac{\kappa^2}{2} |\nabla x_k|^2 \right) d\Omega$$

At equilibrium  $G$  is minimal, for fixed over - all composition. From variational calculus:

$$\frac{\delta G}{\delta \eta} = \left( \frac{\partial g}{\partial \eta} - \varepsilon^2 \nabla^2 \eta \right) = 0$$

$$\frac{\delta G}{\delta x_k} = \frac{\partial g}{\partial x_k} - \kappa^2 \nabla^2 x_k = 0$$

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## Rate equations

$$J_k = -\sum L_{kj} \nabla \left( \frac{\delta G}{\delta x_j} \right)$$

Cahn-Hilliard equation

$$\dot{c}_k = \nabla \cdot \left[ \sum L_{kj} \nabla \left( \frac{\partial g}{\partial x_j} - \kappa_j^2 \nabla^2 x_j \right) \right]$$

AC/GL-equation:

$$\dot{\eta} = -M_{\eta} \frac{\delta G}{\delta \eta} = -M_{\eta} \left( \frac{\partial g}{\partial \eta} - \varepsilon^2 \nabla^2 \eta \right)$$

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## Materials Data

- Thermodynamics  $G(\eta, x_j, P, T)$
- Diffusivities  $L_{kj}(\eta, x_j, P, T)$
- Phase field mobilities  $M_{\eta}(\eta, x_j, P, T)$
- Gradient-energy parameters:  $\varepsilon, \kappa$

$$D_{kj} = L_{ki} \Psi_{ij}$$

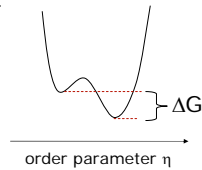
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## Thermodynamics

Early works:  $G(\eta, x_j, P, T) = f(\eta) + h(\eta) \Delta G(T)$   
 $\Delta G$  is the driving force, a function of temperature,  $f(\eta)$  and  $h(\eta)$  rather arbitrarily chosen to give a double well:



## Recent progress in Calphad

- $G(x_j, P, T)$  given for each individual phase of a system based on physical models and large body of experimental data.
- Allows calculation of multicomponent phase diagrams
- Driving force can be calculated for a multicomponent alloy, e.g. a Ni-base super alloy, Grafe et al. (2000)

$$\Delta G = \sum_j x_j^\beta (\mu_j^\alpha - \mu_j^\beta)$$



## More direct approach:

Evaluate  $\delta G / \delta \eta$  and  $\delta G / \delta x_j$  from the expressions for Gibbs energy given by Calphad, see e.g.

- Miyazaki et al. (2001)
- Zhu et al. (2002)
- Loginova et al. (2003)

Allows (in principle) a rather direct treatment of complex "real" alloys.



## One problem with the direct approach:

The Calphad expressions for  $G$  complex. How to speed up the computations of thermodynamic quantities?

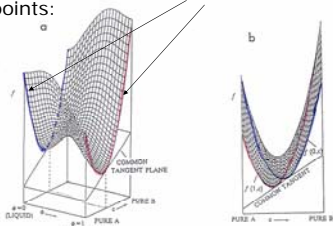
Strandlund (2004) a factor 10-100 times faster calculations by representing  $G$  with artificial neural networks.



## Another problem:

Calphad does not usually give the dependence of  $\eta$  but only the functions at the endpoints:

How to obtain the full Gibbs energy "landscape"?



## Two methods:

- Wheeler et al. (1992):

$$G_m(\eta, x_1, x_2, \dots) = (1 - p(\eta))G_m^\alpha(x_1, x_2, \dots) + p(\eta)G_m^\beta(x_1, x_2, \dots) + h(\eta)W$$

- Steinbach et al. (1998), Kim et al (1999)

$$G_m(\eta, x_1, x_2, \dots) = (1 - p(\eta))G_m^\alpha(x_1^\alpha, x_2^\alpha, \dots) + p(\eta)G_m^\beta(x_1^\beta, x_2^\beta, \dots) + h(\eta)W$$

2(n-1) extra conditions needed

$p(\eta)$  and  $h(\eta)$  polynomials.



## Comparison between the two Approaches

Wheeler et al.:

- + Derived from variational principles with few extra assumptions
- + No extra equations need to be solved in interface
- Difficult to treat transformations involving stoichiometric phases
- The alloying contribution to surface energy scales with interface thickness

Steinbach, Kim et al.:

- + No problems with stoichiometric phases
- Extra assumptions must be introduced
- Extra equations need to be solved in interfacial region (more computations needed)
- + Surface energy does not scale with interface thickness



## Diffusion

- Analyze diffusion data in terms of mobilities and thermodynamic factors.
  - Andersson and Ågren (1992)
  - Campbell et al. (2002)

Mobilities represented as functions of  $\eta$ !

$$D_{kj} = L_{ki} \Psi_{ij}$$



## The properties of the phase interface - The interfacial energy

$$\sigma = 2 \int_{-\infty}^{+\infty} (g(\eta, x_1, x_2, \dots) - \sum_j x_j \mu_j) dz$$

$$= \int_{-\infty}^{+\infty} \left[ \varepsilon^2 \left| \frac{\partial \eta}{\partial z} \right|^2 + \sum_j \kappa_j^2 \left| \frac{\partial x_j}{\partial z} \right|^2 \right] dz$$

$$\sigma \cong \varepsilon^2 / \ell$$



## Effect of Curved Interfaces

- Sharp interface: Contribute to the driving force by

$$\sigma V_m (1/\rho_1 + 1/\rho_2)$$

- Allen and Cahn

$$\nabla^2 \eta = (1/\rho_1 + 1/\rho_2)$$



## The gradient term when several (independent) variables

$n$  variables  $\varphi_j$  and  $\sum_j \varphi_j = 1$ .

Several possibilities (all equivalent when only 1 independent variable  $\varphi_i$ ). E.g.:

$$\sum_j^{\infty-1} \kappa_j (\nabla \varphi_j)^2$$

or

$$\sum_i \sum_j \kappa_{ij} |\nabla \varphi_i| |\nabla \varphi_j|$$



## Finite diffusion inside interface

- If properties are realistically chosen there will be a solute drag effect and eventually a transition to partitionless transformation.

- Loginova et al. (2003)

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High T

Intermediate T

Low T

Loginova et al. 2003  
 $\gamma \rightarrow \alpha$  in Fe-C

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### Surface-energy driven processes

Two grains:  
dihedral angle

dihedral angle

Grain1 Grain2

$$2\sigma_{sg} \cos(\theta/2) = \sigma_{ss}$$

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a  $\sigma_{sg} = \sigma_{ss} : \theta = 120^\circ$

b

c  $\sigma_{sg} = \sigma_{ss} / 2 : \theta = 0^\circ$

d  $\sigma_{sg} = 2\sigma_{ss} : \theta = 151^\circ$

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### Surface-energy driven processes

Interfaces shown

Density shown

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## Anisotropy

The total Gibbs energy:

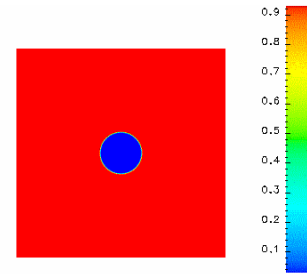
$$G = \int_{\Omega} \left( g(\eta, x_k) + \frac{\varepsilon^2}{2} |\nabla \eta|^2 + \frac{\kappa^2}{2} |\nabla x|^2 \right) d\Omega$$

$$\varepsilon = \bar{\varepsilon} (1 + \gamma \cos(k\beta))$$

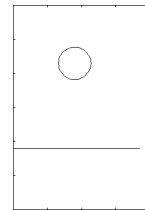
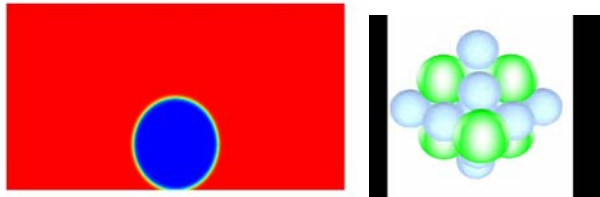
$\beta$  = angle between interface normal and crystal lattice.



## Anisotropy



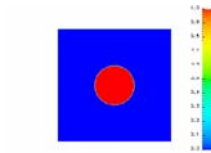
## Wetting and spreading





## Dynamic solute drag

- Initial state: A circular grain with  $\phi=1$  surrounded by another grain where  $\phi=0$ . Homogenous concentration of  $x_B=0.01$ .



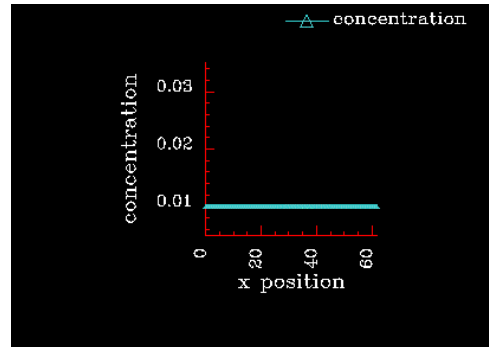
Phase-field at  $t=0$

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Large grain

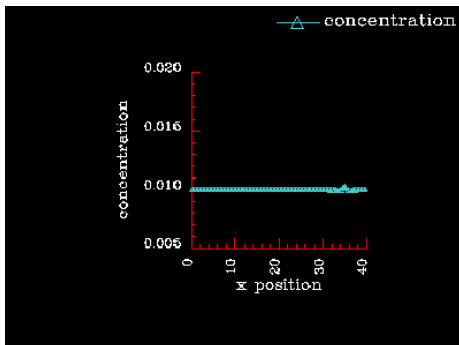


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Small grain



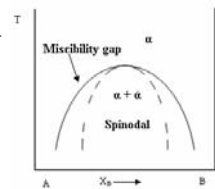
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## Theory spinodal decomposition

- The spinodal is the limit of stability.
- Inside the miscibility gap a two-phase mixture forms by phase separation:
  - separation by nucleation and growth mechanisms
  - separation by simple diffusional clustering mechanisms



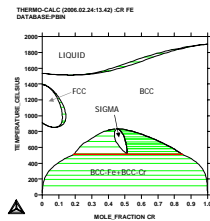
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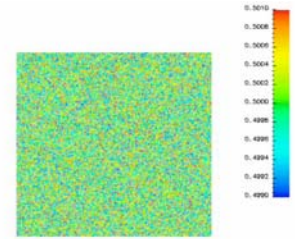


## Theory spinodal decomposition

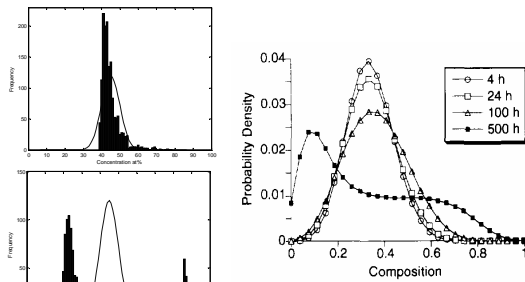
- In what kind of system do we expect to find a spinodal?
- BCC-Fe and BCC-Cr do not mix
- Miscibility gap and spinodal in Fe-Cr system
- Spinodal up to  $\sim 560^\circ\text{C}$



## Spinodal decomposition I Fe-Cr



## Result - comparison



Ref: Hyde et al, Acta metall. mater, vol.43, no 9, pp 3403-3413, 1995.



## Summary – Key Issues

In order to become a general engineering simulation tool:

- The thermodynamic and kinetic properties of interfaces must be expressed with realistic models.
- Numerical approaches capable of resolving the fine details of the interface and the large-scale behaviour of bulk phases simultaneously must be developed.
- Computationally efficient evaluation of thermodynamic functions.
- Include rigid body motion and fluid flow.