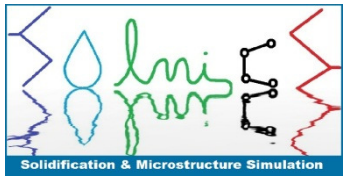
KATHOLIEKE UNIVERSITEIT
LEUVEN



Quantitative phase-field modeling of growth and coarsening in polycrystalline materials

N. Moelans

Department of Metallurgy and Materials Engineering, KU Leuven, Belgium

KATHOLIEKE UNIVERSITEIT LEUVEN

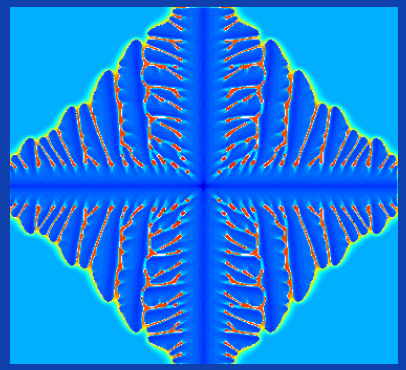
Outline

- Some aspects of model formulation
  - 2-phase versus multi-phase and multi-grain
- Application example
  - Slag/oxide crystallization

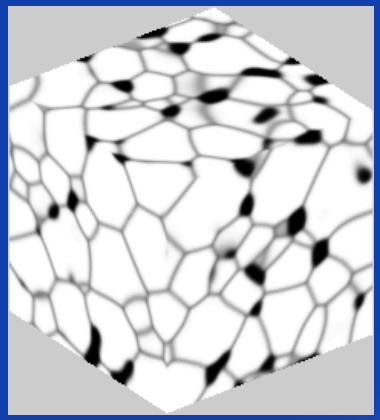
KATHOLIEKE UNIVERSITEIT LEUVEN

'Quantitative' phase-field models

- **Physics bulk and interfaces are reproduced accurately in the simulations**
  - **Effect model description and parameters – Physics**
  - **Numerical issues**



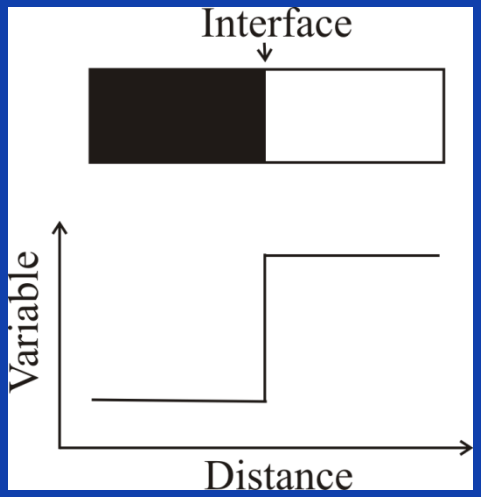
- **Predictive ?**
  - **Depends on availability and accuracy of input data**
    - **Requires composition and orientation dependence**
  - **Features on the mesoscale**



KATHOLIEKE UNIVERSITEIT LEUVEN

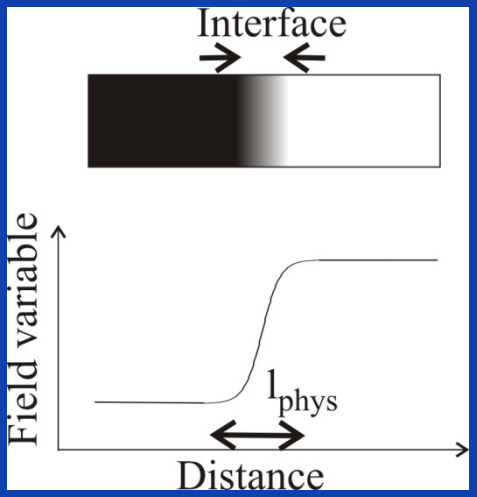
Sharp – Diffuse – Thin interface models

Sharp Interface



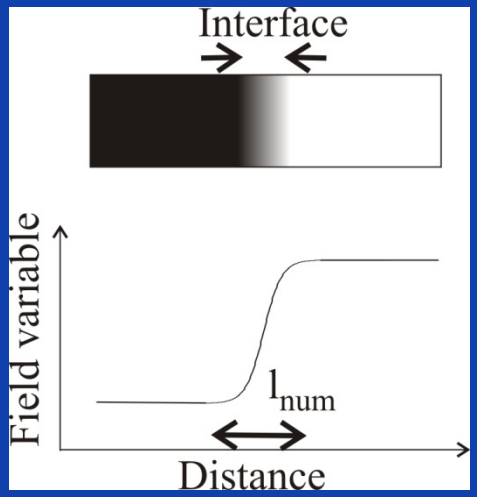
- Discontinuity
- (Semi) 1-D problems
- Problem specific

Diffuse interface



- Complex morphologies
- Segregation, solute drag, trapping, lattice mismatch, …
- However, l_{phys} (<1nm) <<< R_{grain} (μm-mm)
- Mostly qualitative

Thin interface



- l_{num} *independent*
- $l_{phys} << l_{num} << R_{grain}$
- *Karma and Rappel (1996), Tiaden et al. (1996), Kim and Kim (1999), Karma (2001), Kazaryan et al. (2000)*

Solidification & Microstructure Simulation

KATHOLIEKE UNIVERSITEIT
LEUVEN

Solidification & Microstructure Simulation

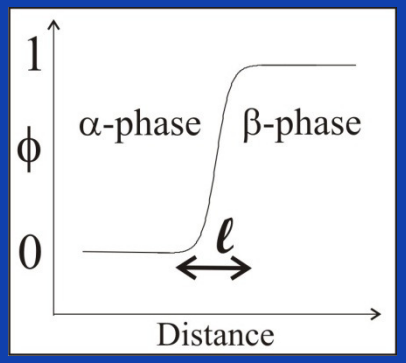
Some aspects of model formulation

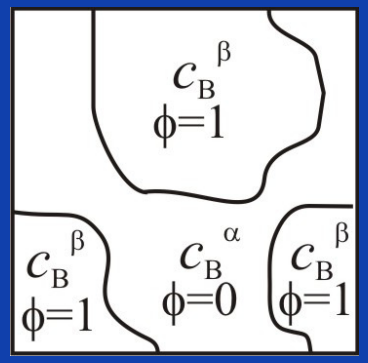
- **Two-phase systems : single phase-field**
- **Multi-grain/phase systems : multiple phase-field**

KATHOLIEKE UNIVERSITEIT LEUVEN

2-phase systems

- **Field variables:** $\phi(\vec{r},t)$ $c_k(\vec{r},t)$



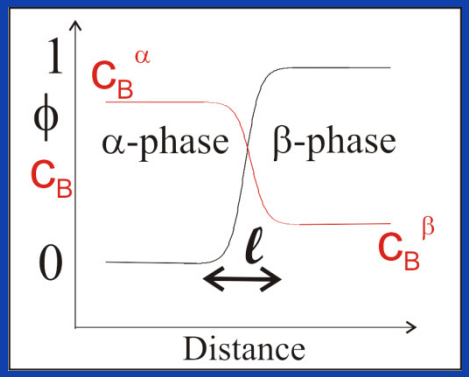


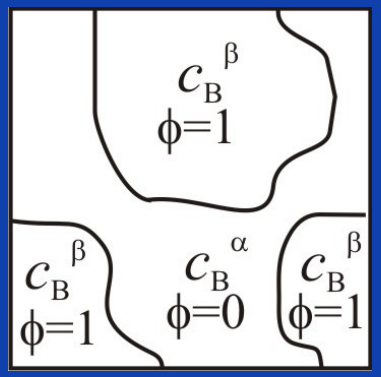
- ***Phase α: $\phi = 0$***
- ***Phase β: $\phi = 1$***
- ***Composition: c_B***

KATHOLIEKE UNIVERSITEIT LEUVEN

2-phase systems

- **Field variables:** $\phi(\vec{r},t)$ $c_k(\vec{r},t)$





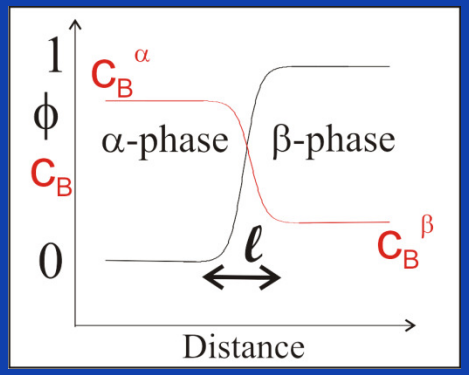
- ***Phase α: ϕ = 0***
- ***Phase β: ϕ = 1***
- ***Composition: c_B***

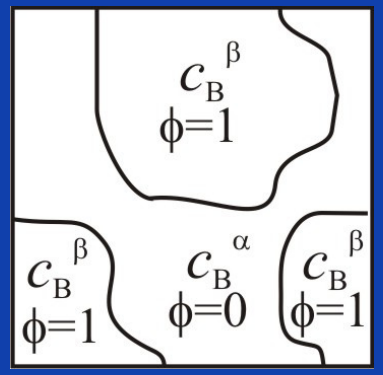
Solidification & Microstructure Simulation

KATHOLIEKE UNIVERSITEIT LEUVEN

2-phase systems

- **Field variables:** $\phi(\vec{r},t)$ $c_k(\vec{r},t)$



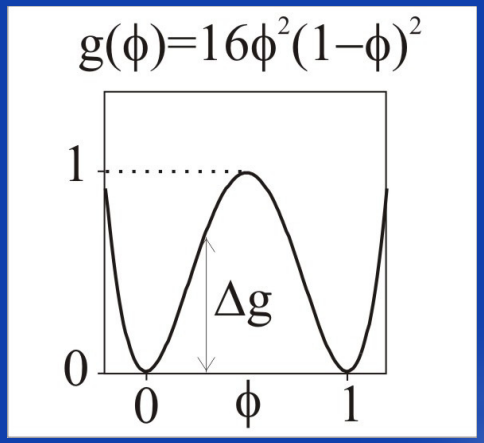


- ***Phase α: ϕ = 0***
- ***Phase β: ϕ = 1***
- ***Composition: c_B***

- **Free energy**

$$F = \int_V \left[f_{chem}(c,\phi) + \underbrace{W g(\phi) + \frac{\varepsilon^2}{2} |\nabla \phi|^2}_{\text{Interfacial energy}} \right] d\vec{r}$$

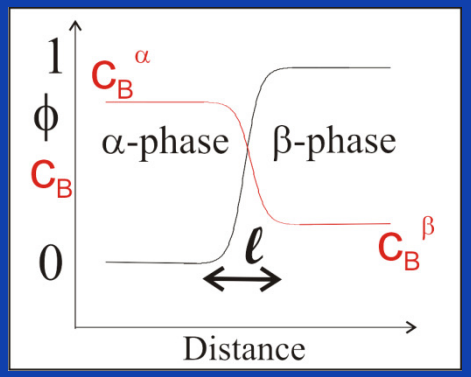
Double well function

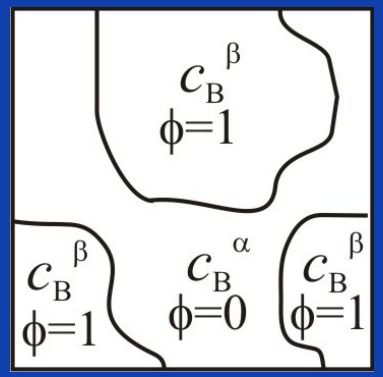


KATHOLIEKE UNIVERSITEIT LEUVEN

2-phase systems

- **Field variables:** $\phi(\vec{r},t)$ $c_k(\vec{r},t)$





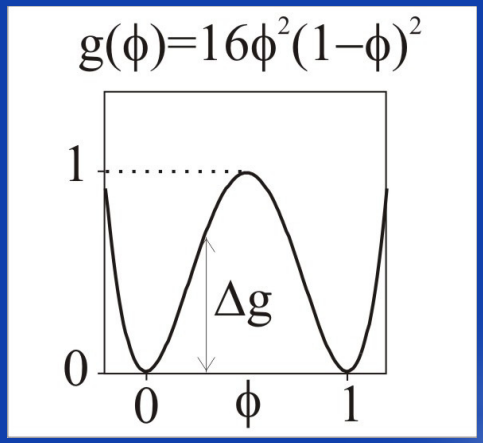
- ***Phase α: ϕ = 0***
- ***Phase β: ϕ = 1***
- ***Composition: c_B***

- **Free energy**

$$F = \int_V \left[f_{chem}(c,\phi) + \underbrace{W g(\phi) + \frac{\varepsilon^2}{2} |\nabla\phi|^2}_{\text{Interfacial energy}} \right] d\vec{r}$$

$$\Rightarrow \gamma = \frac{2\sqrt{2}}{3}\sqrt{W}\varepsilon, \qquad \ell \propto \frac{\varepsilon}{\sqrt{2W}}$$

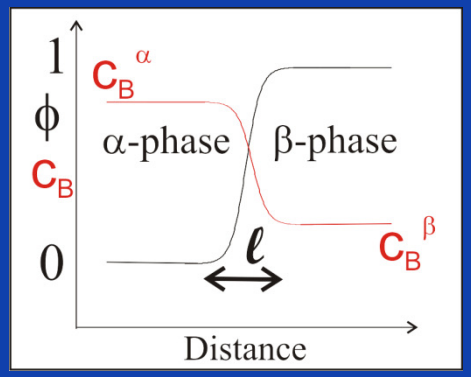
Double well function

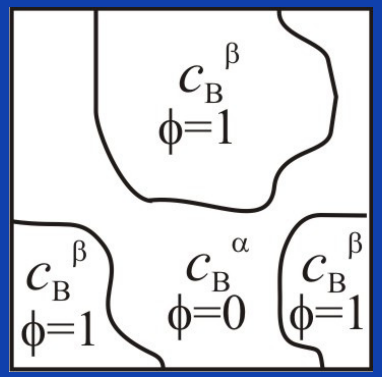


KATHOLIEKE UNIVERSITEIT LEUVEN

2-phase systems

- **Field variables:** $\phi(\vec{r},t) \quad c_k(\vec{r},t)$





- ***Phase α: ϕ = 0***
- ***Phase β: ϕ = 1***
- ***Composition: c_B***

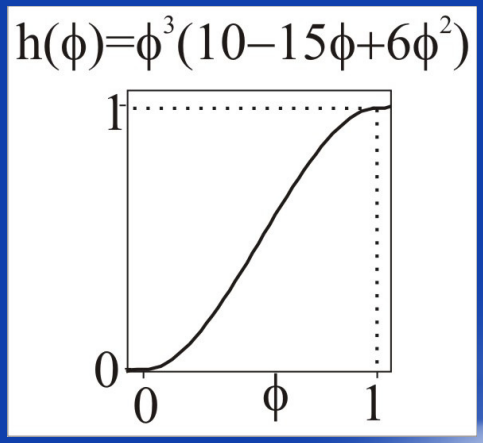
- **Free energy**

$$F = \int_V \left[\underbrace{f_{chem}(c,\phi)} + W g(\phi) + \frac{\varepsilon^2}{2} |\nabla \phi|^2 \right] d\vec{r}$$

Bulk energy

$$f_{chem} = h(\phi)\, f^{\beta}(c,T) + \left[1 - h(\phi)\right] f^{\alpha}(c,T)$$

Interpolation function



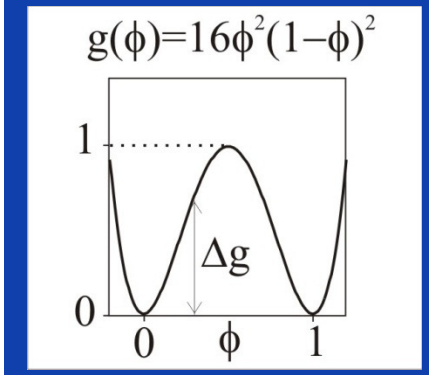
KATHOLIEKE UNIVERSITEIT LEUVEN

Decoupling bulk and interfacial energy

- **Free energy**

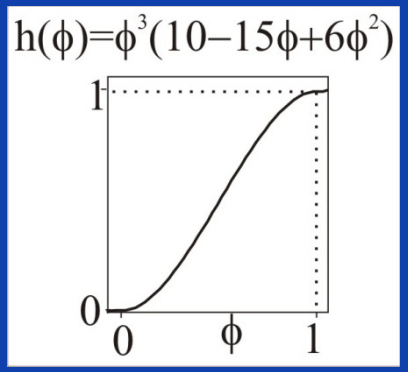
$$F = \int_V \left[\underbrace{f_{chem}(c,\phi)} + Wg(\phi) + \frac{\varepsilon^2}{2} |\nabla\phi|^2 \right] d\vec{r}$$

$$f_{chem} = h(\phi) f^{\beta}(c,T) + \left[1 - h(\phi)\right] f^{\alpha}(c,T)$$



Double well

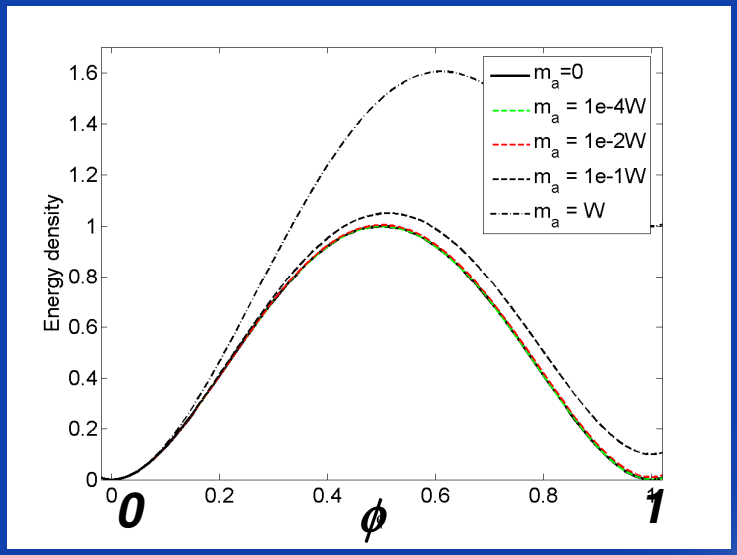
+



Bulk energy with

- *h(ϕ) with zero slope at 0 and 1*

=

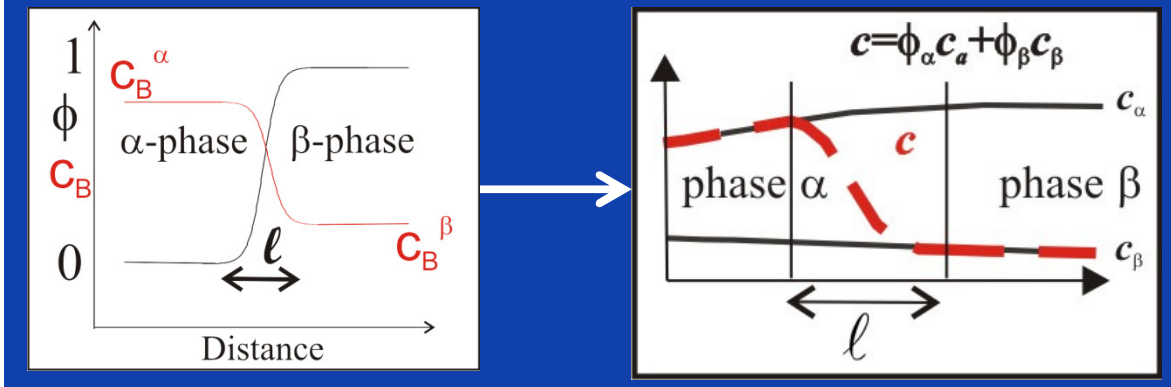


Homogeneous energy denstiy : minima remain at 0 and 1

KATHOLIEKE UNIVERSITEIT LEUVEN

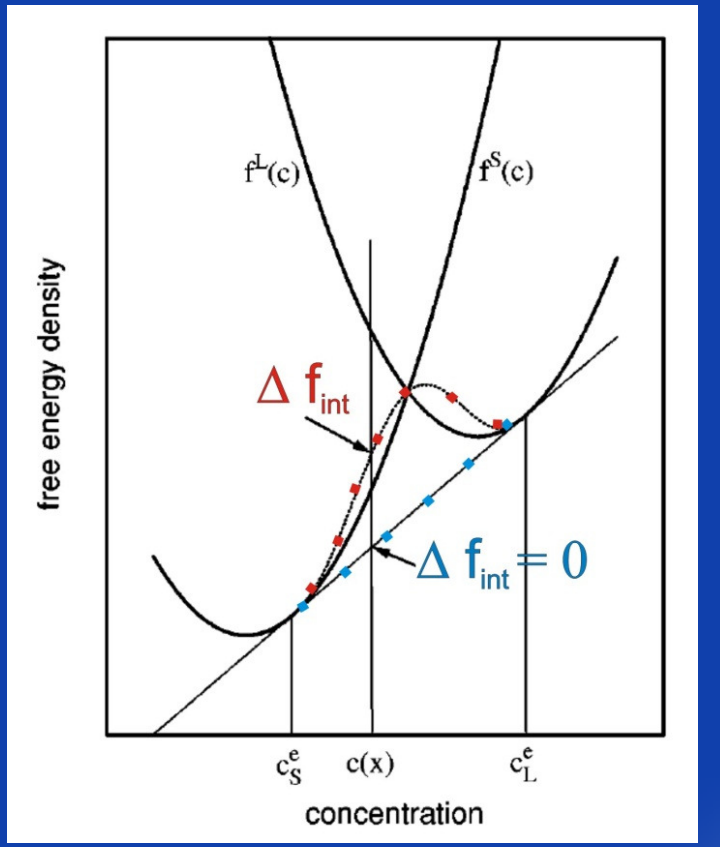
Decoupling bulk and interfacial energy

- **Interface treated as mixture of 2 phases – KKS approach**
  - **c-field for each phase** $c \rightarrow c^{\alpha}, c^{\beta}$



  - **Equal diffusion or chemical potential**
  - **Bulk energy**

$$\Rightarrow f_{chem} = h(\phi) f^{\beta}(c^{\beta}) + \left[1 - h(\phi)\right] f^{\alpha}(c^{\alpha})$$



Kim et al., PRE, 6 (1999) p 7186; Tiaden et al., Physica D, 115 (1998) p73

KATHOLIEKE UNIVERSITEIT LEUVEN

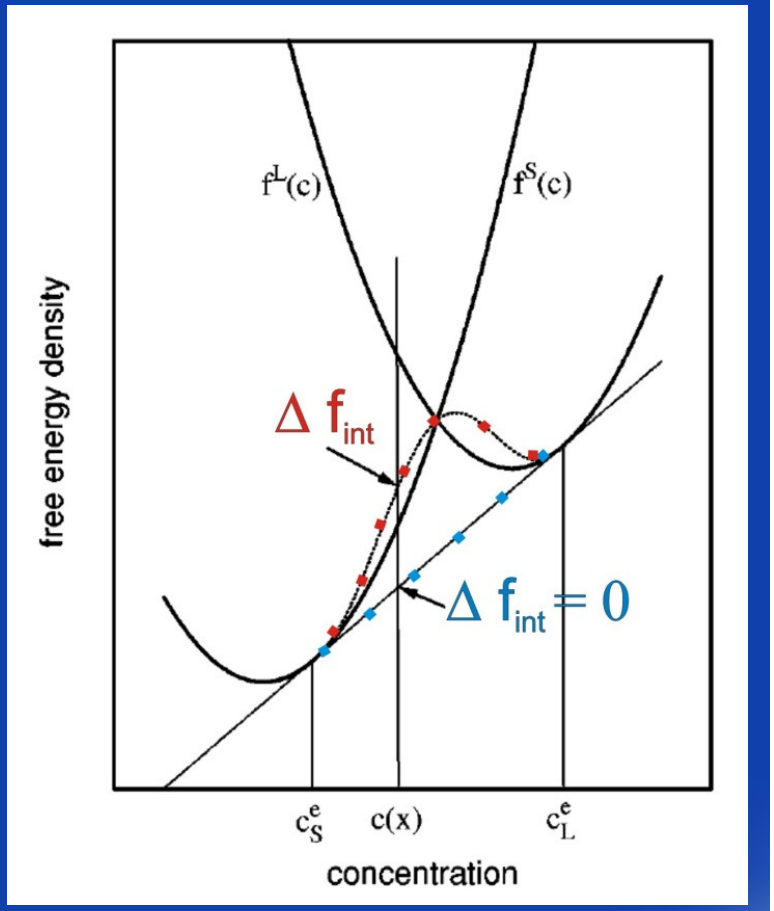
Decoupling bulk and interfacial energy

- **Alternative formulation for dilute alloys**

Karma 2001A. Karma, PRL, 87 (2001) n° 115701; Echebarria et al., PRE, 70 (2004) n°061604

- **Unified approach using a grand-canonical functional**

M. Plapp, PRE, 84 (2011) n°031601



KATHOLIEKE UNIVERSITEIT LEUVEN

Kinetics -- general

- **Interface movement (Allen - Cahn)** $$\frac{\partial \varphi}{\partial t} = -L\frac{\partial F}{\partial \varphi}$$

$$\frac{\partial \phi}{\partial t} = -L\left[W\frac{\partial g}{\partial \phi} - \varepsilon\nabla\phi + \frac{\partial h}{\partial \phi}\left(f^{\beta} - f^{\alpha}\right)\right]$$

Curvature driven *Bulk energy driven*

- **Diffusion** $$\frac{\partial c_k}{\partial t} = \nabla\cdot\sum_{l}^{C-1}\left[h(\phi)M_{kl}^{\beta} + [1-h(\phi)]M_{kl}^{\alpha}\right]\nabla\tilde{\mu}_l$$

  - **Diffusion potentials :** $\tilde{\mu}_l = \mu_l - \mu_C$
  - **Diffusion mobilities/coefficients :** $D^{\rho} = M^{\rho}G^{\rho}$, $G_{kl}^{\rho} = \frac{\partial^2 f^{\rho}}{\partial c_k \partial c_l}$

Multicomponent diffusion formalism of J.-O. Andersson, J. Ågren, J. Appl. Phys., J. Appl. Phys, 72 (1992) p1350

KATHOLIEKE UNIVERSITEIT LEUVEN

Decoupling bulk and interfacial kinetics

- **Anomalous nonequilibrium effects, such as discontinuity in μ_i for $D_l$neq D_S**

$$\propto \ell, v_n, \vec{j}_n$$

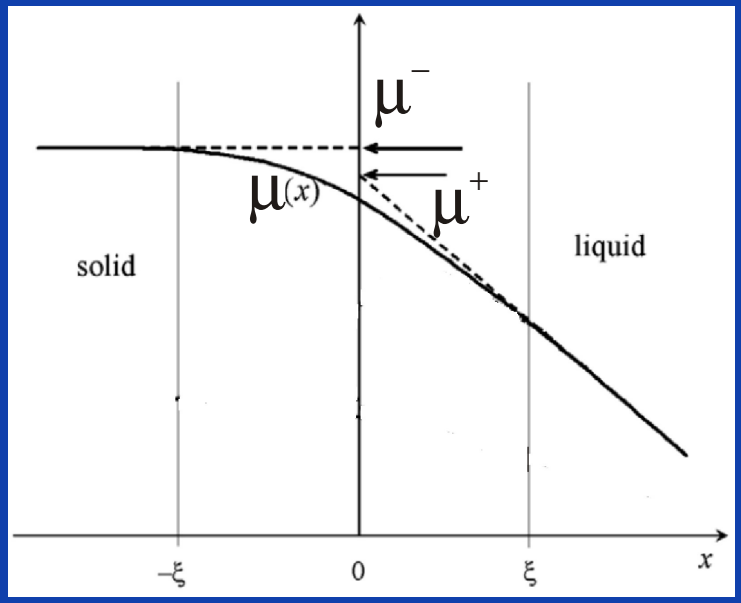
  - **Non-variational anti-trapping current**

$$\vec{j}_a = \alpha\sqrt{\frac{\kappa}{W}}\left(1-\frac{D_S}{D_L}\right)\frac{\partial\phi}{\partial t}\frac{\nabla\phi}{|\nabla\phi|}$$

  - **But still 'Kapitza' effect for**

$$\vec{j}_n \gg v_n$$

M. Plapp, Phil. Mat. 91 (2011) p25



- *Anomalous effects: R.F. Almgren, SIAM J. Appl. Math., 59 (1999) p2086.*
- *Anti-trapping, dilute, D_S=0: A.Karma, PRL, 87, 115701 (2001); B. Echebarria et al., PRE, 70, 061604 (2004)*
- *Anti-trapping, dilute, D≠ 0: M. Ohno and K. Matsuura, Phys. Rev. E 79 (2009) No 031603*
- *Anti-trapping multi-comp, D_S=0: S.G. Kim, Acta Mater. 55, p4391 (2007)*

KATHOLIEKE UNIVERSITEIT
LEUVEN

Solidification & Microstructure Simulation

Some aspects of model formulation

- **Two-phase systems : single phase-field**
- **Multi-grain/phase systems : multiple phase-field**

KATHOLIEKE UNIVERSITEIT LEUVEN

Multi-grain and multi-phase structures

- **Single phase-field models -> Multiple phase-field models**

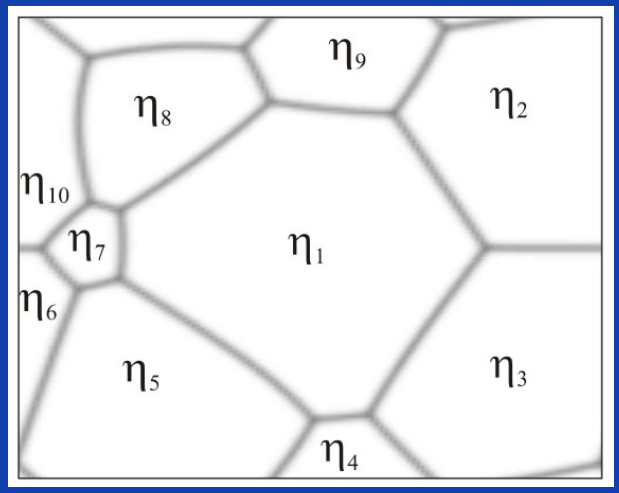
$$\varphi \rightarrow \{\varphi_1, \varphi_2, \varphi_3, \ldots \varphi_p\}$$

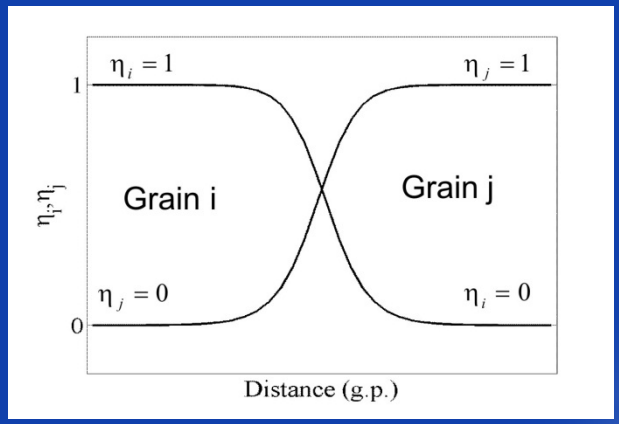
  - **Model extension**

$$F(\phi_1, \phi_2, \phi_3, \ldots, |\nabla \phi_1|^2, |\nabla \phi_2|^2, \ldots)$$

    - **Different types of interfaces**
    - **Triple and higher order junctions**

  - **Numerically**
    - **Homogeneous accuracy**
    - **Thin interface asymptotics for all interfaces** $\rightarrow \ell_{num} = cte$

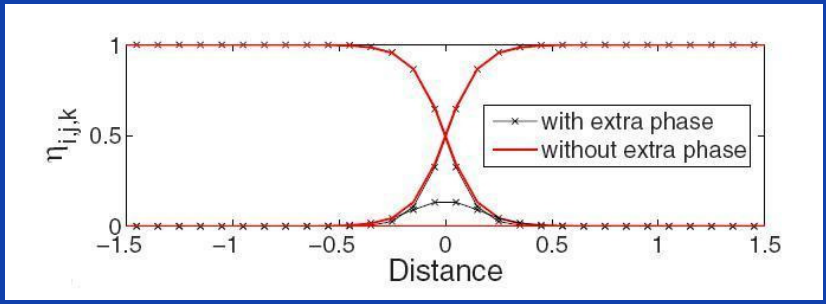




KATHOLIEKE UNIVERSITEIT LEUVEN

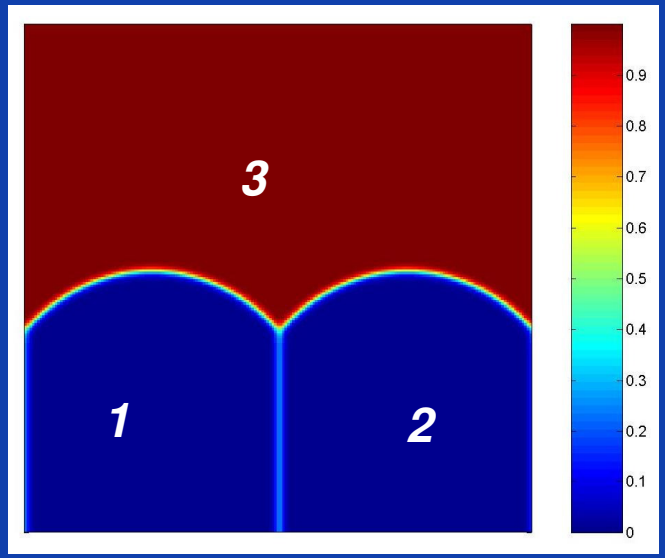
Multi-grain and multi-phase models: major difficulties

- **Third-phase contributions**
  - $\sigma_{12} = \sigma_{13} = 7/10\ \sigma_{12}$



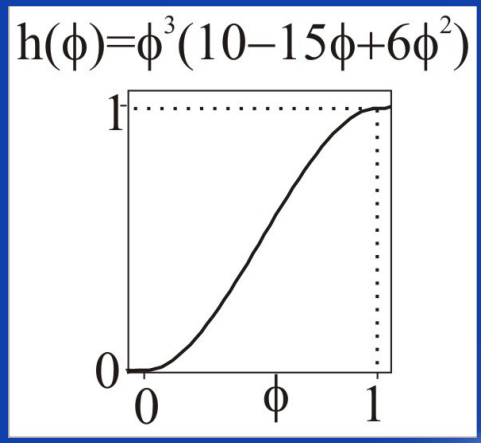
  - → **Careful choice of multi-well function and gradient contribution**

η_3



- **Interpolation function**
  - **Zero-slope at equilibrium values of the phase fields**
  - **Thermodynamic consistency**

$$f_{chem} = \sum_{i=1}^{p} h_i(\eta_1, \eta_2, \ldots) f^i(c,T) \quad \Rightarrow \sum_{i=1}^{p} h_i(\eta_1, \eta_2, \ldots) = 1$$



KATHOLIEKE UNIVERSITEIT
LEUVEN

Solidification & Microstructure Simulation

Some aspects of model formulation

- Two-phase/grain model
- **Multi-grain model**
- Multi-phase multi-grain model

KATHOLIEKE UNIVERSITEIT LEUVEN

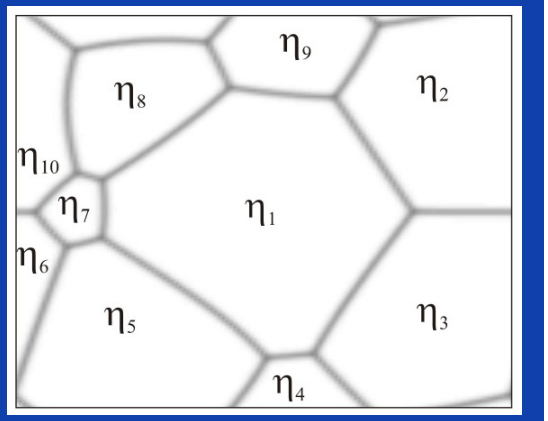
Anisotropic grain growth model

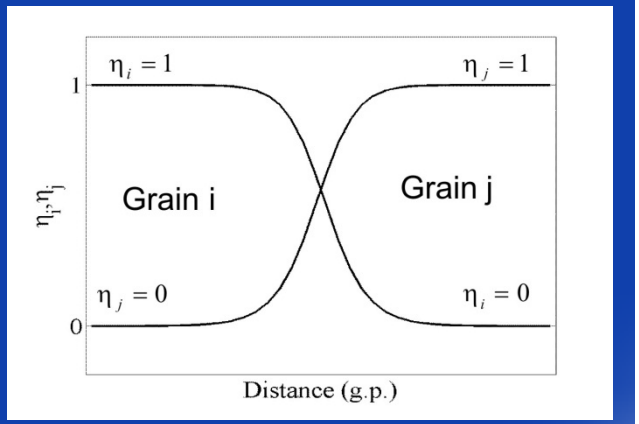
- **Phase fields** $\eta_1, \eta_2, \ldots, \eta_i(\vec{r}, t), \ldots, \eta_p$
  - **With grain i**
    $$(\eta_1, \eta_2, \ldots, \eta_i, \ldots, \eta_p) = (0, 0, \ldots, 1, \ldots, 0)$$
- **Free energy**

$$F_{interf} = \int_V m\left(\sum_{i=1}^{p}\left(\frac{\eta_i^4}{4} - \frac{\eta_i^2}{2}\right) + \sum_{i=1}^{p}\sum_{j<i}^{p}\gamma_{i,j}\eta_i^2\eta_j^2 + \frac{1}{4}\right) + \frac{\kappa(\eta)}{2}\sum_{i=1}^{p}(\nabla\eta_i)^2 dV$$

$$\kappa(\eta) = \sum_{i=1}^{p}\sum_{j<i}^{p}\kappa_{i,j}\eta_i^2\eta_j^2 \Big/ \sum_{i=1}^{p}\sum_{j<i}^{p}\eta_i^2\eta_j^2$$

  - **For each grain boundary** $\eta_i^2\eta_j^2 \neq 0 \Rightarrow \kappa(\eta) = \kappa_{i,j}$





- **Inclination dependence**

$$\gamma_{i,j}(\psi_{i,j}), \kappa_{i,j}(\psi_{i,j}), L_{i,j}(\psi_{i,j}), \qquad \psi_{i,j} = \frac{\nabla\eta_i - \nabla\eta_j}{|\nabla\eta_i - \nabla\eta_j|}$$

A. Kazaryan et al., PRB, 61 (2000) p14275

Solidification & Microstructure Simulation

KATHOLIEKE UNIVERSITEIT LEUVEN

Non-variational approach – equal interface width

- **Ginzburg-Landau type equations**

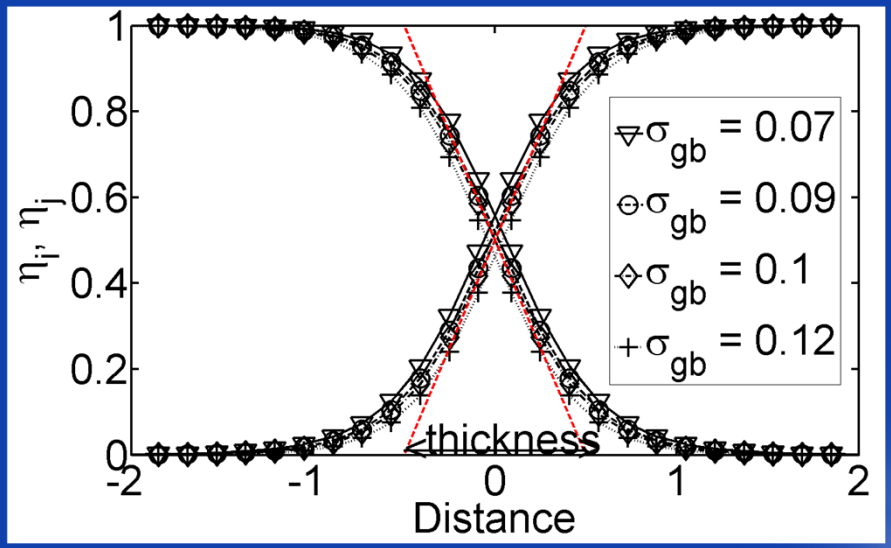
$$\frac{\partial \eta_i(\vec{r},t)}{\partial t} = -L(\eta)\left[m\left(\eta_i^3 - \eta_i + 2\eta_i \sum_{j\neq i} \gamma_{i,j}\eta_j^2 \right) - \kappa(\eta)\nabla^2\eta_i \right]$$

  - **Non-variational with respect to η-dependence of κ**
  - **Similar to Monte Carlo Potts approach**

- **Definition 'grain boundary width'**

$$l_{num} = \frac{1}{|\frac{d\eta_i}{dx}|_{max}} = \frac{1}{|\frac{d\eta_j}{dx}|_{max}}$$

→High controllability of numerical accuracy ($l_{num}/R < 5$)



KATHOLIEKE UNIVERSITEIT LEUVEN

Grain boundary properties

- **Grain boundary energy**

$$\gamma_{gb,\theta_{i,j}} = g(\gamma_{i,j})\sqrt{m\kappa_{i,j}}$$

- **Grain boundary mobility**

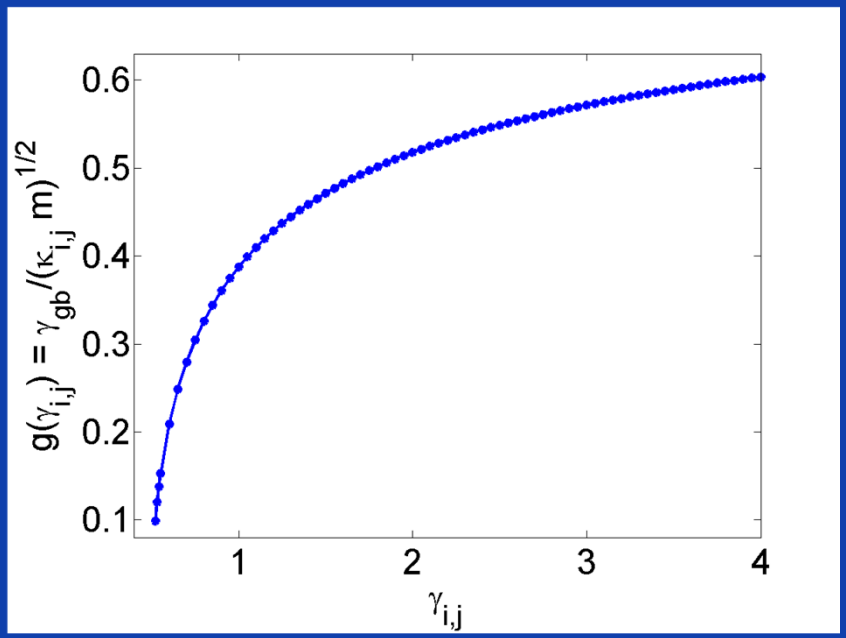
$$\mu_{gb,\theta_{i,j}} = L_{i,j}\sqrt{\frac{\kappa_{i,j}}{m(g(\gamma_{i,j}))^2}}$$

- **Grain boundary width**

$$l = \frac{4}{3}\sqrt{\frac{\kappa_{i,j}}{m(g(\gamma_{i,j}))^2}}$$

- **Iterative algorithm**

$$\ell_{gb}, [\gamma_{gb,\theta}], [\mu_{gb,\theta}] \rightarrow m, [\kappa_{i,j}], [\gamma_{i,j}], [L_{i,j}]$$



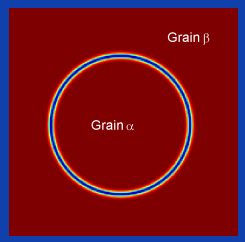
$g(\gamma_{i,j})$ calculated numerically

N. Moelans, B. Blanpain, P. Wollants, PRL, 101, 0025502 (2008); PRB, 78, 024113 (2008)

KATHOLIEKE UNIVERSITEIT LEUVEN

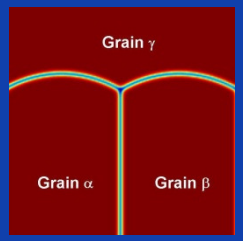
Numerical validation

- **Shrinking grain:**



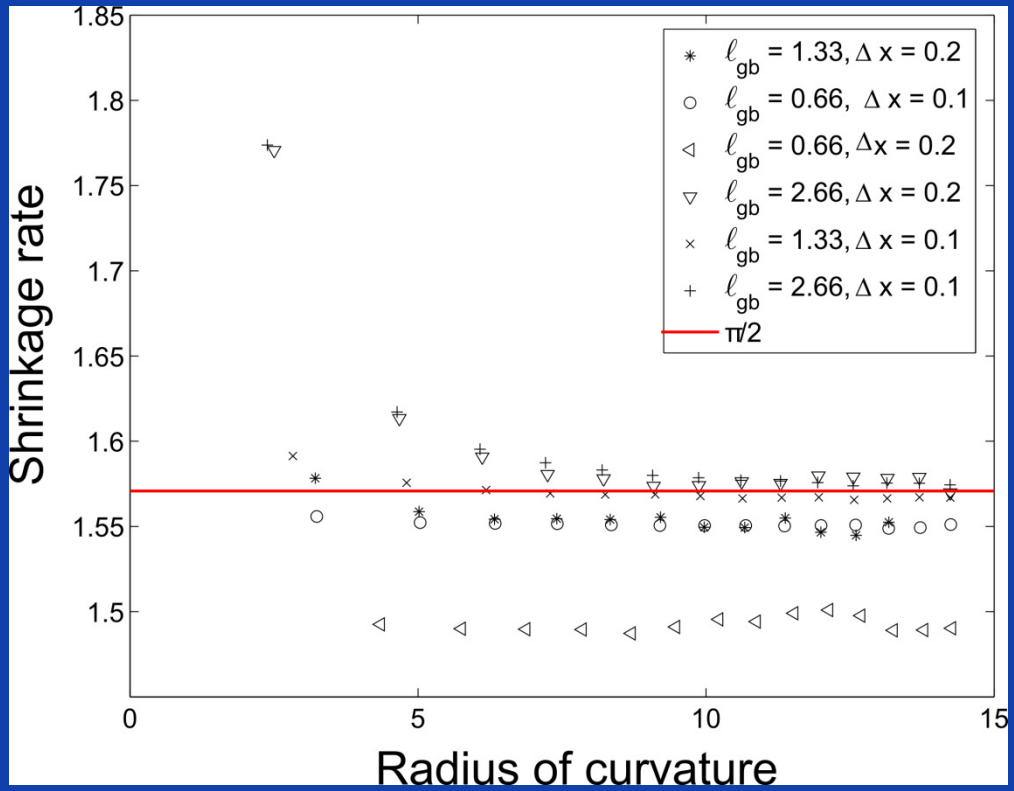
$$\frac{dA_\alpha}{dt} = -2\pi\mu_{\alpha\beta}\sigma_{\alpha\beta}$$

- **Triple junction angles:**



$$\frac{dA_\alpha}{dt} = -\mu_{\alpha\gamma}\sigma_{\alpha\beta}$$

$$\sigma_{\alpha\gamma} = \sigma_{\beta\gamma}, \mu_{\alpha\gamma} = \mu_{\beta\gamma}$$



- **Observations**
  - **Accuracy controlled by** $\ell_{num} / \Delta x$ **for** $\ell_{num} / R \leq 5$
  - **Diffuse interface effects for** $\ell_{num} / R \geq 5$
  - **Angles outside [100°-140°] require larger** $\ell_{num} / \Delta x$ **for same accuracy**

Solidification & Microstructure Simulation

KATHOLIEKE UNIVERSITEIT LEUVEN

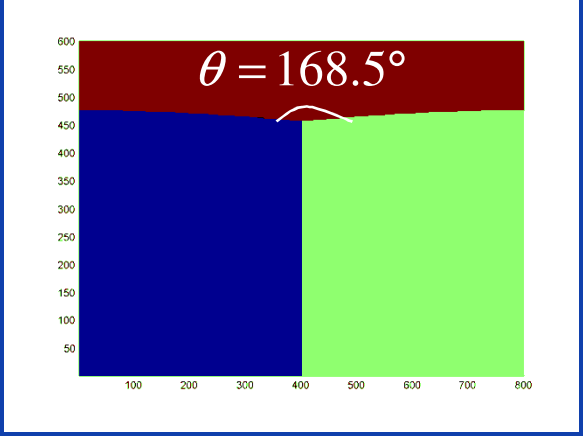
Variational approach – interface width varies with interface energy

- **Anisotropy only through** $\gamma_{i,j}$, κ=*cte*
  - **Energy**

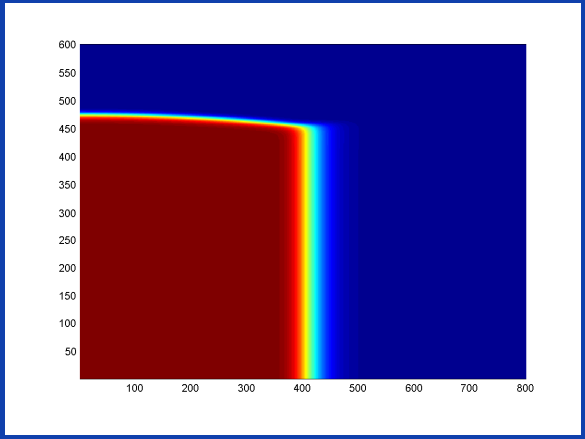
$$F = \int_V \left[m\left(\sum_{i=1}^{p}\left(\frac{\eta_i^4}{4} - \frac{\eta_i^2}{2} \right) + \sum_{i=1}^{p}\sum_{j<i}^{p} \gamma_{i,j}\eta_i^2\eta_j^2 + \frac{1}{4} \right) + \frac{\kappa}{2}\sum_{i=1}^{p}(\vec{\nabla}\eta_i)^2 \right] dV$$

  - **Kinetic equations**

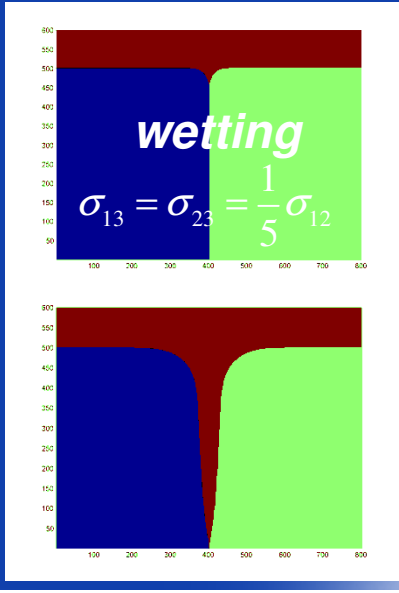
$$\frac{\partial \eta_i(\vec{r},t)}{\partial t} = -L(\eta)\left[m\left(\eta_i^3 - \eta_i + 2\eta_i \sum_{j\neq i} \gamma_{i,j}\eta_j^2 \right) - \kappa\nabla^2\eta_i \right]$$



$\sigma_{13} = \sigma_{23} = 5\sigma_{12}$



η_1



KATHOLIEKE UNIVERSITEIT
LEUVEN

Solidification & Microstructure Simulation

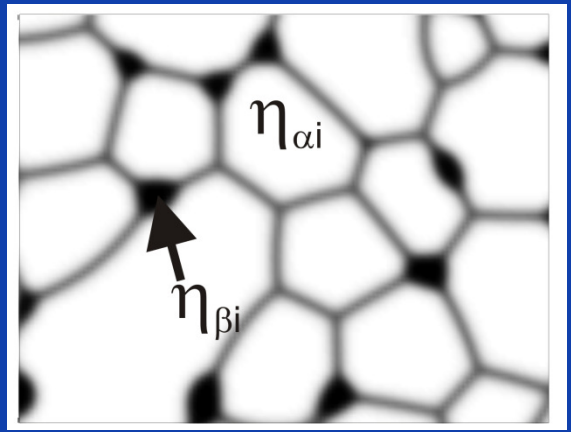
Some aspects of model formulation

- **Two-phase/grain model**
- **Multi-grain model**
- **Multi-phase multi-grain model**

KATHOLIEKE UNIVERSITEIT LEUVEN

Extension to multi-component multi-phase alloys

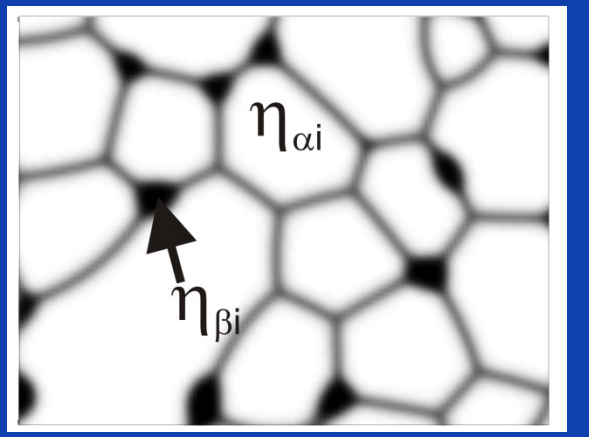
- **Phase field variables:**
  - **Grains** $\eta_{\alpha 1}, \eta_{\alpha 2}, \ldots, \eta_{\alpha i}(\vec{r}, t), \ldots,$ $\eta_{\beta 1}, \eta_{\beta 2}, \ldots \eta_p$
  - **Composition** $x_A, x_B(\vec{r}, t), \ldots, x_{C-1}$



KATHOLIEKE UNIVERSITEIT LEUVEN

Extension to multi-component multi-phase alloys

- **Phase field variables:**
  - **Grains** $\eta_{\alpha 1}, \eta_{\alpha 2}, \ldots, \eta_{\alpha i}(\vec{r}, t), \ldots,$ $\eta_{\beta 1}, \eta_{\beta 2}, \ldots \eta_p$
  - **Composition** $x_A, x_B(\vec{r}, t), \ldots, x_{C-1}$



- **Bulk energy:** $f_{bulk}(x_k, \eta_{\rho i}) = \sum_{\rho} \phi_\rho f^\rho(x_k^\rho)$
  - **with**

$$\begin{cases} \dfrac{\partial f^\beta(x_k^\beta)}{\partial x_k^\beta} = \dfrac{\partial f^\alpha(x_k^\alpha)}{\partial x_k^\alpha} = \ldots = \tilde{\mu}_k \\ x_k = \sum_\rho \phi_\rho x_k^\rho \end{cases}$$

KKS approach

and $\phi_\rho = \dfrac{\sum_i \eta_{\rho i}^2}{\sum_{\pi=\alpha,\beta,\ldots} \sum_i \eta_{\pi i}^2}$

Interpolation function

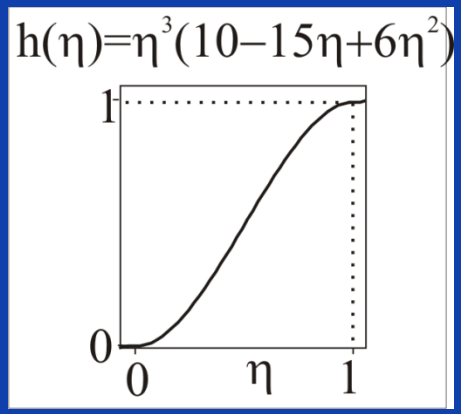
KATHOLIEKE UNIVERSITEIT LEUVEN

Free energy for multi-phase systems

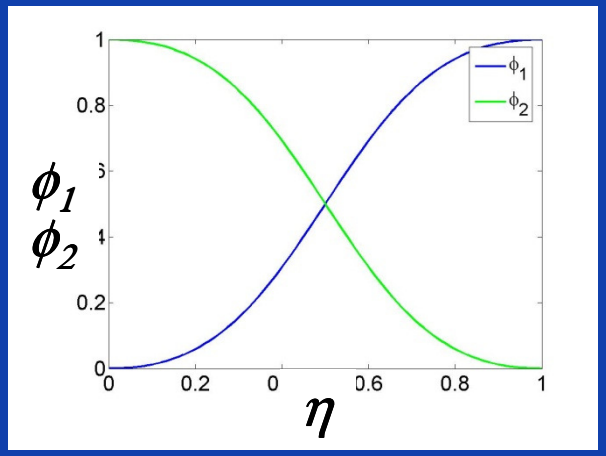
- **Bulk energy:** $f_{bulk}(x_k, \eta_{\rho i}) = \sum_{\rho} h_\rho(\eta_{\rho i}) f^\rho(x_k^\rho)$

  - **With** $h_\rho(\eta_{\rho i}) = \phi_\rho = \dfrac{\sum_i \eta_{\rho i}^2}{\sum_{\pi=\alpha,\beta,\ldots} \sum_i \eta_{\pi i}^2}$ **and** $f^\rho(x_k^\rho) = \dfrac{G_m^\rho(x_k^\rho)}{V_m}$

Replaces the standard function for 2-phase systems



Interpolation function for 2-phase system



Interpolation functions for multi-phase system

N. Moelans, Acta Mater, 59, 1077-1086, 2011

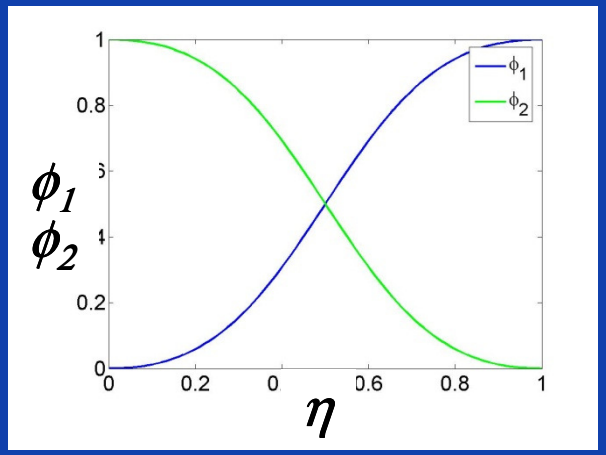
KATHOLIEKE UNIVERSITEIT LEUVEN

Free energy for multi-phase systems

- **Interpolation function**

$$h_\rho(\eta_{\rho i}) = \phi_\rho = \frac{\sum_i \eta_{\rho i}^2}{\sum_{\pi=\alpha,\beta,\ldots} \sum_i \eta_{\pi i}^2}$$

$$\begin{cases} \sum_\rho \phi_\rho = 1 \Rightarrow & \text{'phase fractions'} \\ \dfrac{\partial \phi_\rho}{\partial \eta}\Big|_{\eta=0,\eta=1} = 0 \Rightarrow & \text{Minima remain at } (0,0,\ldots,1,\ldots,0) \end{cases}$$



Interpolation functions for multi-phase system

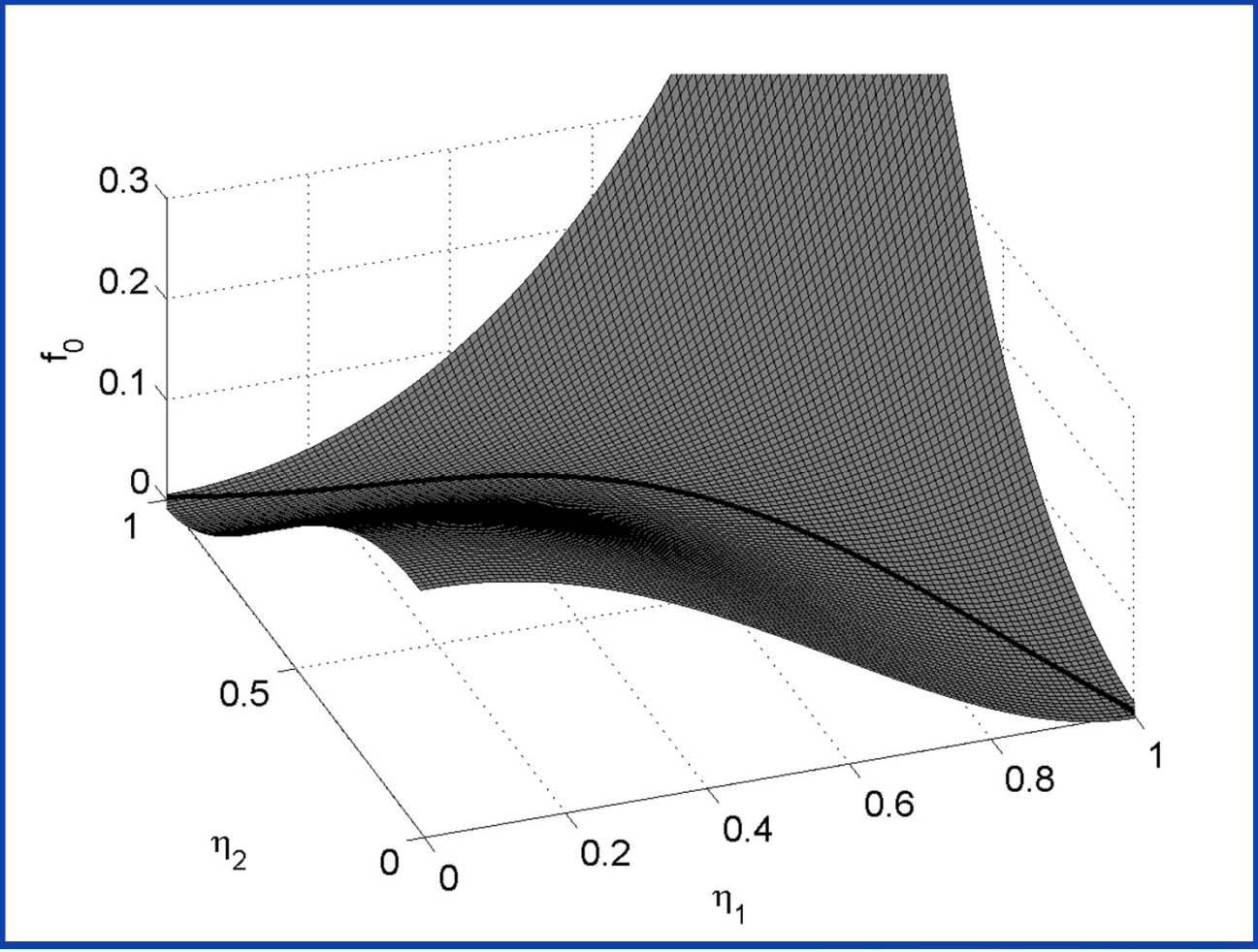
N. Moelans, Acta Mater, 59, 1077-1086, 2011

Solidification & Microstructure Simulation

KATHOLIEKE UNIVERSITEIT LEUVEN

Free energy for multi-phase systems

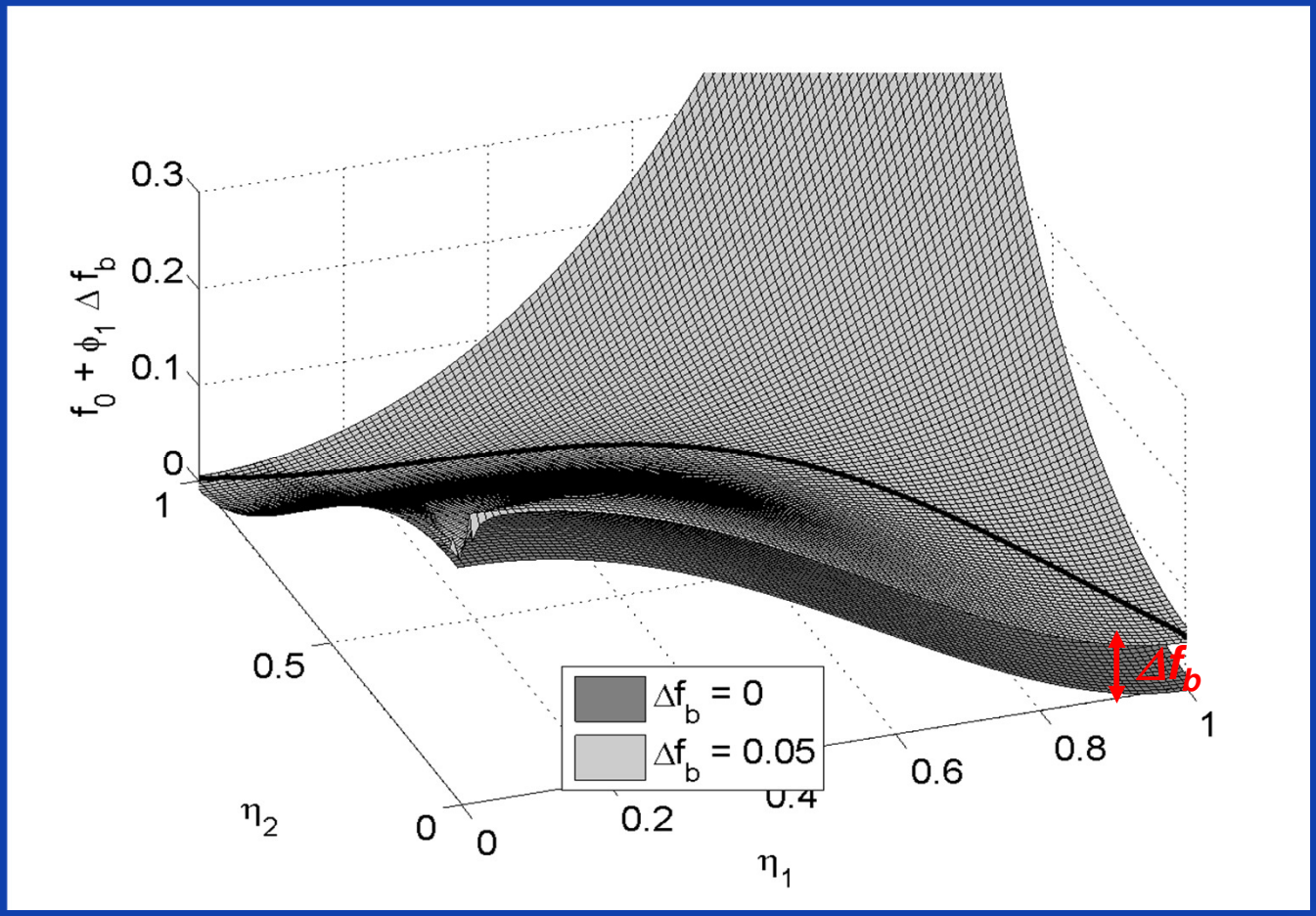
- **Only Interfacial energy :** $f = f_0(\eta_\alpha, \eta_\beta)$



KATHOLIEKE UNIVERSITEIT LEUVEN

Free energy for multi-phase systems

- **Interfacial + bulk energy :** $f = f_0(\eta_\alpha, \eta_\beta) + \phi_\alpha f^\alpha + \phi_\beta f^\beta$



KATHOLIEKE UNIVERSITEIT LEUVEN

Equations for interface movement

- **Interface movement:**

$$\frac{\partial \eta_{i\rho}}{\partial t} = -L \frac{\delta F(\eta_{i\rho}, x_k)}{\delta \eta_{i\rho}}$$

  - **Grain boundary between grain ρ,i and ρ,j**

$$\frac{\partial \eta_{\rho i}}{\partial t} = -L\left(\frac{\partial f_{interf}}{\partial \eta_{\rho i}} - \kappa_{i,j}\nabla^2 \eta_{\rho i}\right) = -L g_{\text{int}}(\eta, \nabla\eta)$$

  - **Between phase α and β**

$$\frac{\partial \eta_{\alpha i}}{\partial t} = -L\left(g_{\text{int}}(\eta, \nabla\eta) + \frac{\nu \eta_{\alpha i}^{\nu-1}\eta_{\beta j}^{\nu}}{\left(\eta_{\alpha}^{\nu} + \eta_{\beta}^{\nu}\right)^2}\left(f^{\alpha}(x^{\alpha}) - f^{\beta}(x^{\beta}) - (x^{\alpha} - x^{\beta})\tilde{\mu}\right)\right)$$

Curvature driven *Bulk energy driven*

Solidification & Microstructure Simulation

KATHOLIEKE UNIVERSITEIT LEUVEN

Diffusion equations

- **Diffusion flux (of the form** $\vec{J}_k = -\sum_{l=1}^{C-1} M_{kl} \nabla(\mu_l - \mu_C) = -\sum_{l=1}^{C-1} M_{kl} \nabla \tilde{\mu}_l$ **)**

  J.-O. Andersson, J. Ågren, J. Appl. Phys., J. Appl. Phys, 72 (1992) p1350

  - **E.g. for binary A-B**

$$\vec{J}_B = \frac{-1}{V_m}\left(\sum_{\rho} \phi_\rho M^\rho + \sum_{\rho,i \neq \sigma,j} M_{interf} \eta_{\rho,i}^2 \eta_{\sigma,j}^2 \right) \nabla \tilde{\mu}_B$$

Bulk diffusion *Interface diffusion*

  - **Relation with interdiffusivities** $M^\rho = D^\rho \Big/ \frac{\partial^2 f^\rho}{\partial x_B^2}$
  - **Relation with atomic mobilities** $M^\rho = x_B(1-x_B)(x_B \beta_A^\rho + (1-x_A)\beta_B^\rho)$
  - **Relation with pipe interdiffusivities** $M_{interf} = 3\left(\frac{D_{interf}}{\partial^2 f^m / \partial x_B^2}\right)\left(\frac{\delta_{gb}}{\delta_{num}}\right)$

- **Mass conservation**

$$\frac{\partial x_B}{\partial t} = \nabla \cdot \left[\left(\sum_{\rho} \phi_\rho M^\rho + \sum_{\rho,i \neq \sigma,j} M_s \eta_{\rho,i}^2 \eta_{\sigma,j}^2 \right) \nabla \tilde{\mu}_B \right]$$

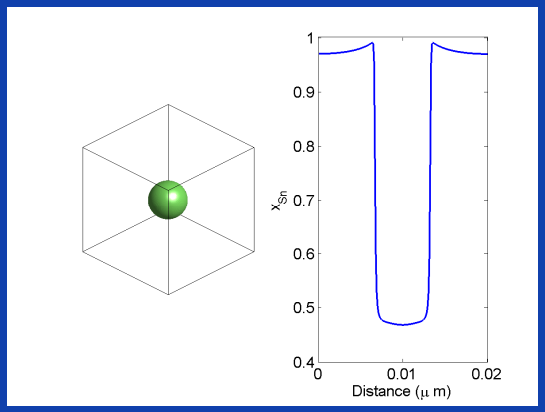
Solidification & Microstructure Simulation

KATHOLIEKE UNIVERSITEIT LEUVEN

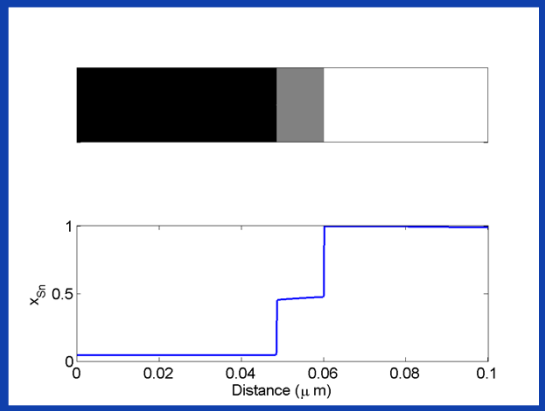
Effect of diffuse interface width: Numerical validation

- **Triple junction**

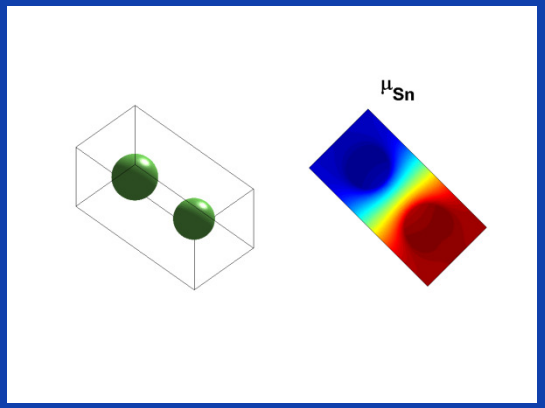
- **Growing sphere**



- **Intermediate phase**



- **Coarsening**



- **Processes for which v(t) ↘**
  - **Accuracy controlled by** $\ell_{num} / \Delta x$

    (≈1.3% for 6 g.p., <1% for 10 g.p.)
  - **Diffuse interface effects for** $\ell_{num} / R > 5$
  - **Angles outside [100°-140°] require larger resolution for same accuracy**

N. Moelans, Acta Mater, 59, 1077-1086, 2011

Solidification & Microstructure Simulation

KATHOLIEKE UNIVERSITEIT LEUVEN

Model comparison

- **Multi-phase-field model**
  - **Phase fields** $\varphi_1, \varphi_2, \varphi_3, \ldots \varphi_p, \quad \sum_{i=1}^{p} \varphi_i = 1$
  - **Interfacial energy**

$$f_{\text{int}} = \sum_{i \neq j} \frac{4\sigma_{i,j}}{\eta_{i,j}} \left\{ \frac{\eta_{i,j}^2}{\pi^2} \left| \nabla \phi_i \cdot \nabla \phi_j \right| + \phi_i \phi_j \right\} + \sum_{i \neq j} \sum_{k \neq i,j} W_{ijk} \phi_i \phi_j \phi_k$$

$$0 < \phi_{i,j} < 1$$

- **Multi-order parameter models**
  - **Order parameters** $\eta_1, \eta_2, \ldots, \eta_i(\vec{r}, t), \ldots, \eta_p, \quad \left(\sum_{i=1}^{p} \eta_i \neq 1 \right)$
  - **Interfacial energy**

$$f_{\text{int}} = m \left(\sum_{i=1}^{p} \left(\frac{\eta_i^4}{4} - \frac{\eta_i^2}{2} \right) + \sum_{i=1}^{p} \sum_{j<i}^{p} \gamma_{i,j} \eta_i^2 \eta_j^2 + \frac{1}{4} \right) + \frac{\kappa(\eta)}{2} \sum_{i=1}^{p} (\vec{\nabla} \eta_i)^2$$

$$\kappa(\eta) = \sum_{i=1}^{p} \sum_{j<i}^{p} \kappa_{i,j} \eta_i^2 \eta_j^2 \Big/ \sum_{i=1}^{p} \sum_{j<i}^{p} \eta_i^2 \eta_j^2$$

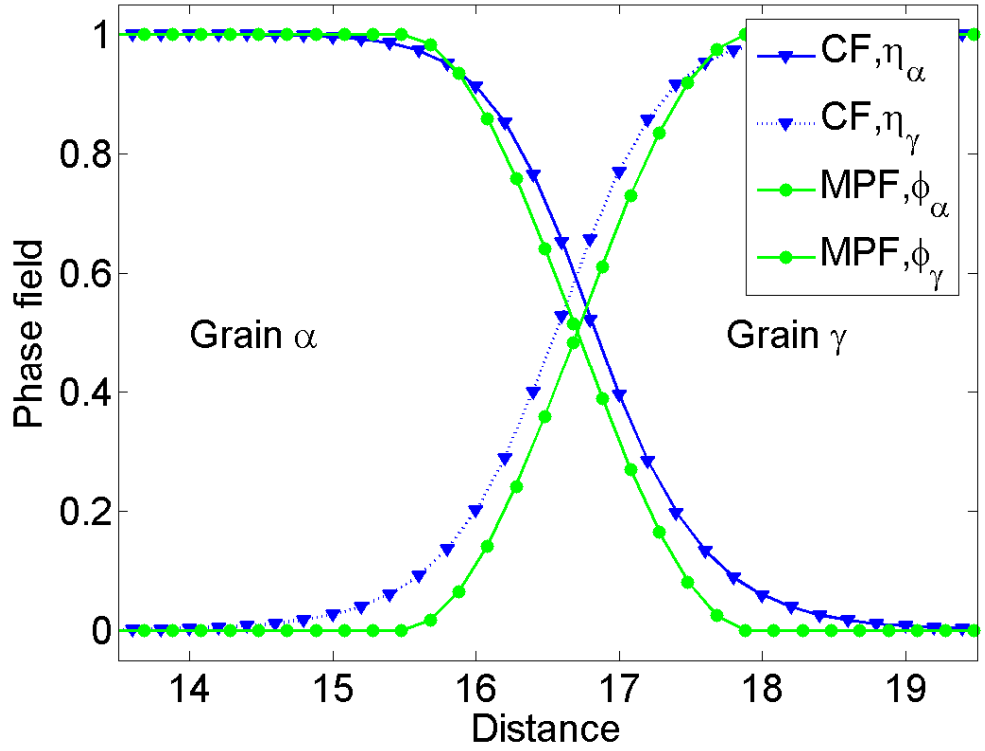
N. Moelans, F. Wendler, B. Nestler, Comp. Mater. Sci. 46 (2009) p479

Solidification & Microstructure Simulation

KATHOLIEKE UNIVERSITEIT LEUVEN

Model comparison : individual interface

- For 'equivalent' model parameters



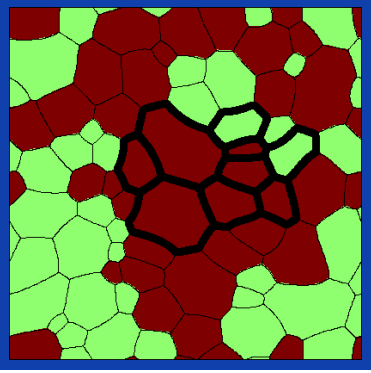
- Similar accuracy for 2- and 3-grain structures for grain boundary movement
- Choice W_{ijk} in MPF affects triple-junction angles
- MPF can reproduce very low and high angles more accurate than the non-variational CF

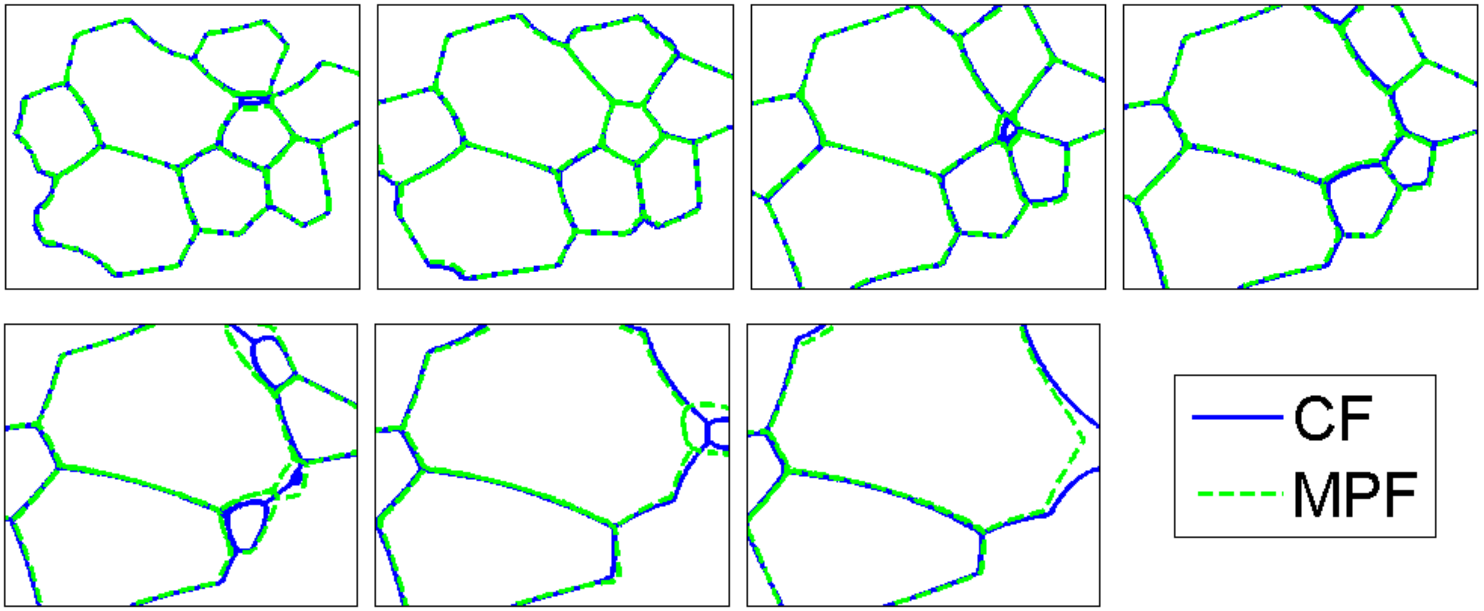
N. Moelans, F. Wendler, B. Nestler, Comp. Mater. Sci. 46 (2009) p479

KATHOLIEKE UNIVERSITEIT LEUVEN

Model comparison : grain assemblies

- 2 orientation variants



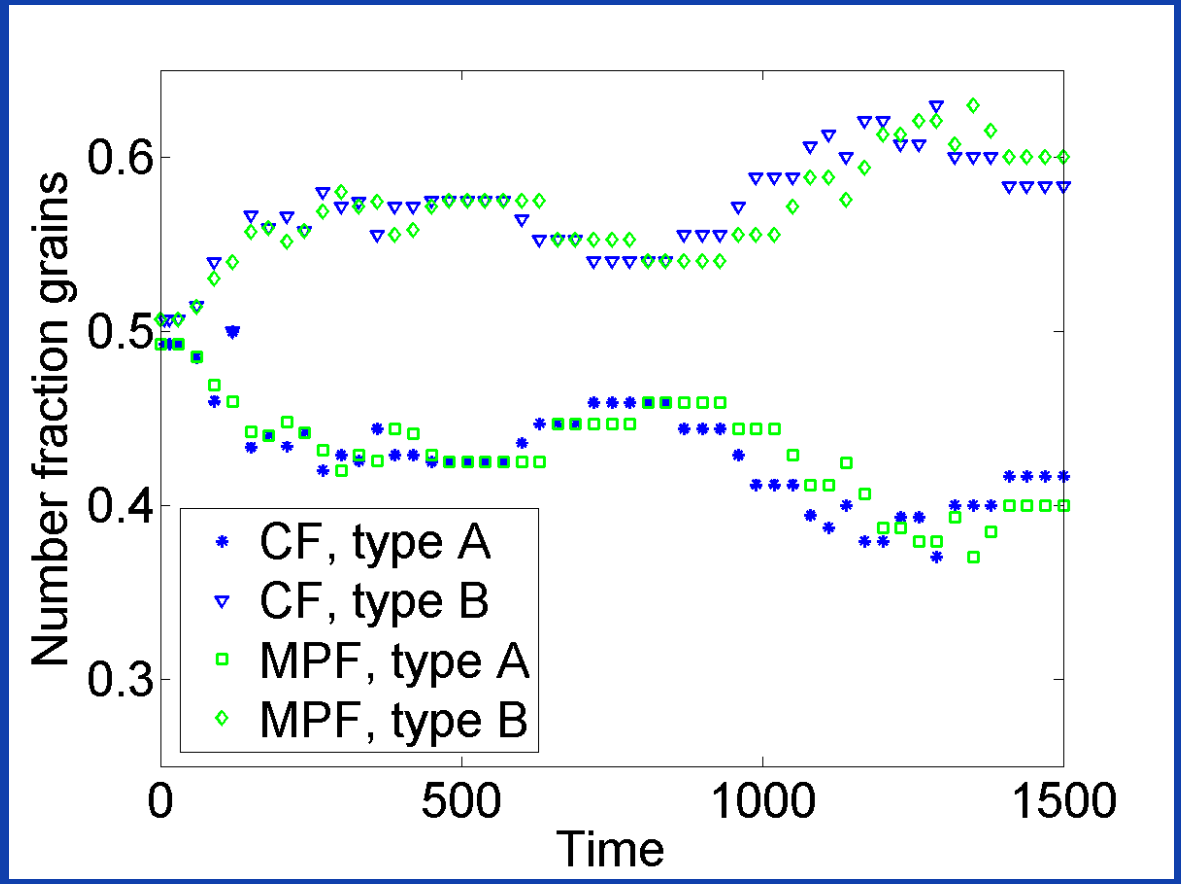


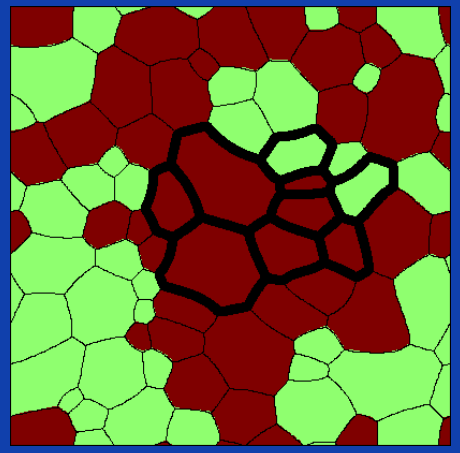
N. Moelans, F. Wendler, B. Nestler, Comp. Mater. Sci. 46 (2009) p479

KATHOLIEKE UNIVERSITEIT LEUVEN

Model comparison : grain assemblies

- 2 orientation variants (2D)

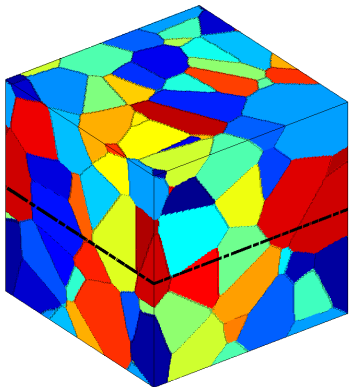


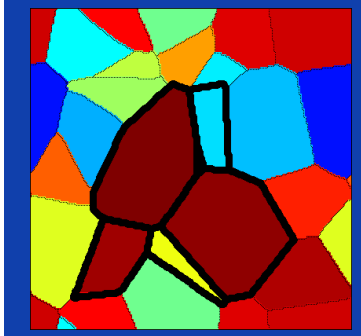


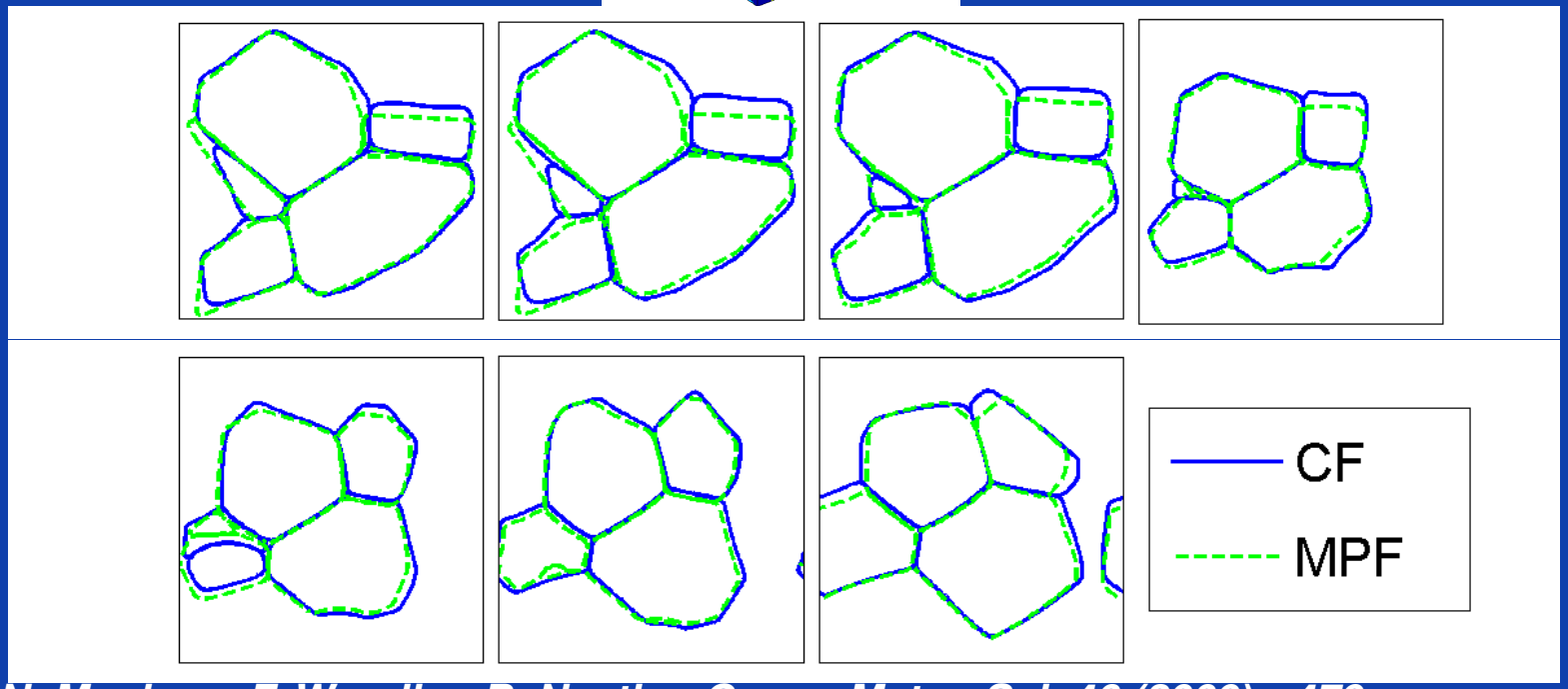
KATHOLIEKE UNIVERSITEIT LEUVEN

Model Comparison : grain assemblies

- Isotropic (3D)





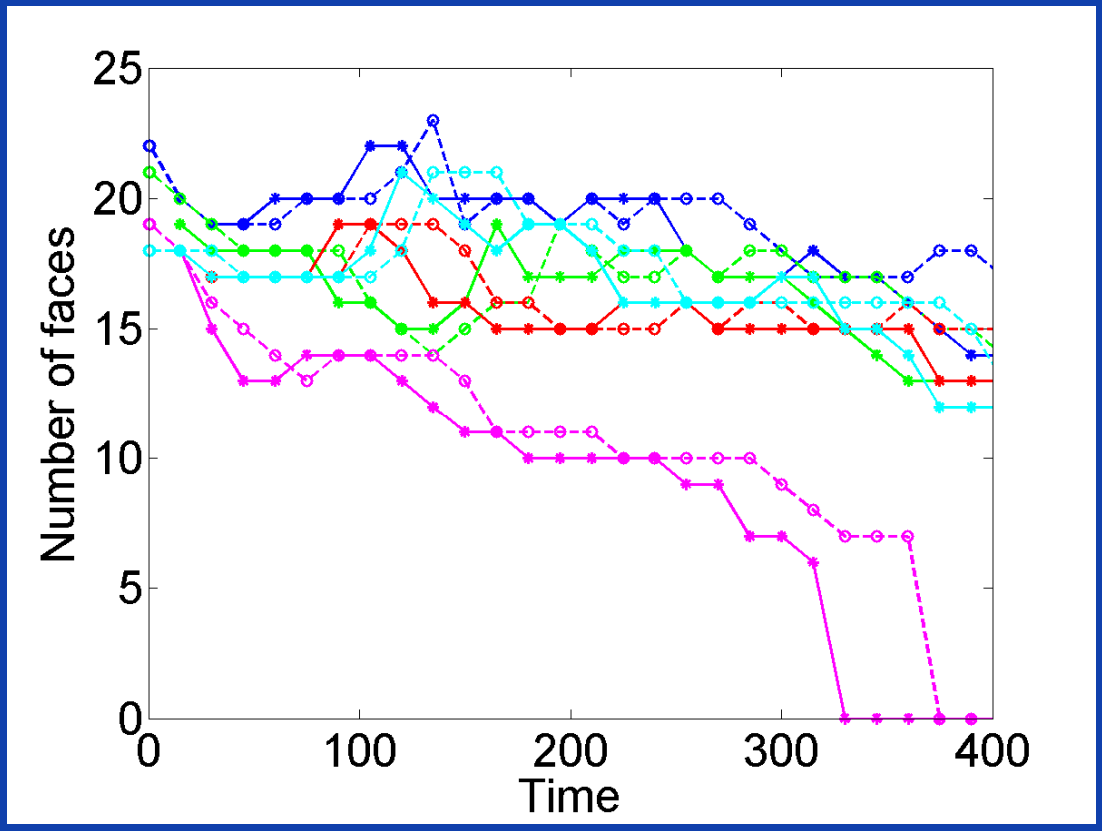


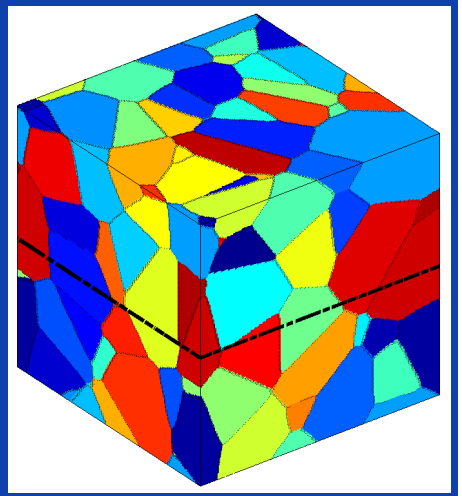
N. Moelans, F. Wendler, B. Nestler, Comp. Mater. Sci. 46 (2009) p479

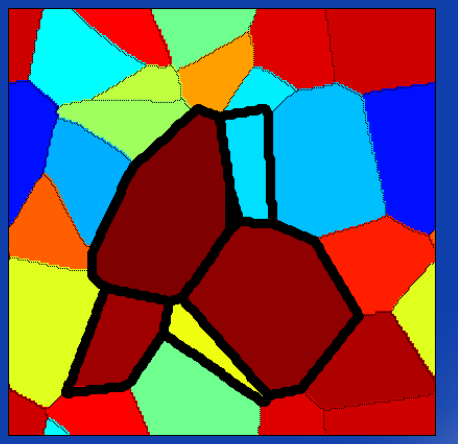
KATHOLIEKE UNIVERSITEIT LEUVEN

Model Comparison : grain assemblies

- **Isotropic (3D)**





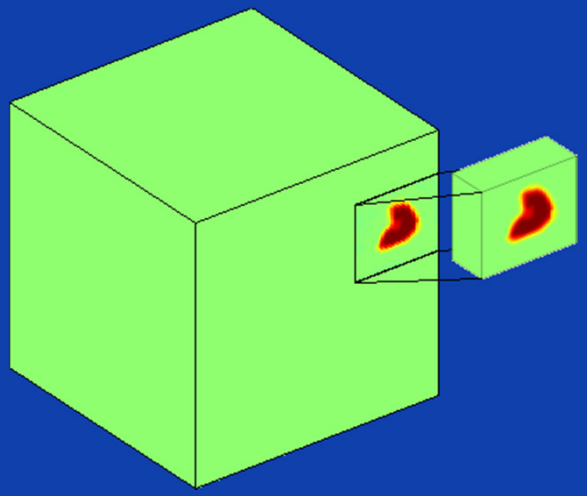


N. Moelans, F. Wendler, B. Nestler, Comp. Mater. Sci. 46 (2009) p479

KATHOLIEKE UNIVERSITEIT LEUVEN

Bounding Box Implementation

- **Basic elements**
  - **A grain is set of connected grid points r where |eta_i(r)| > epsilon**
  - **For each grain, the corresponding bounding box is the smallest cuboid containing the grain**



Algorithm

Solve the equations only locally, inside bounding boxes

Only values inside boxes are kept in memory

Boxes grow or shrink with grain

Object Oriented C++ implementation

Vanherpe et al., PRE, 76, n°056702 (2007)

KATHOLIEKE UNIVERSITEIT
LEUVEN

Solidification & Microstructure Simulation

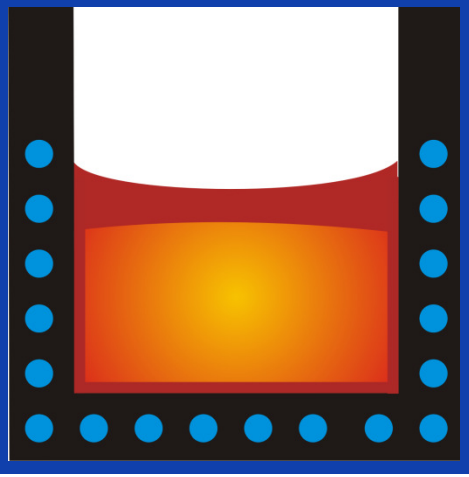
Application example

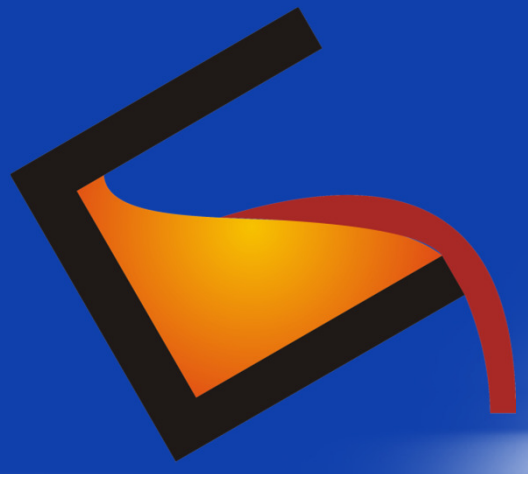
- **Solidification of oxide/silicate melts (slags, lava, magma)**

KATHOLIEKE UNIVERSITEIT LEUVEN

Relevance of slag crystallization

- **Crystallization of slags often occurs in industrial practice**
  1. **Slag in contact with refractory**
     Solid-liquid interaction between liquid and solid oxide material
  2. **Freeze lining due to water-cooled furnace**
     Instantaneously formed layer of crystallized slag
  3. **Tapping and cooling of slag to ambient temperature**
     Crystallization of the slag while cooling down

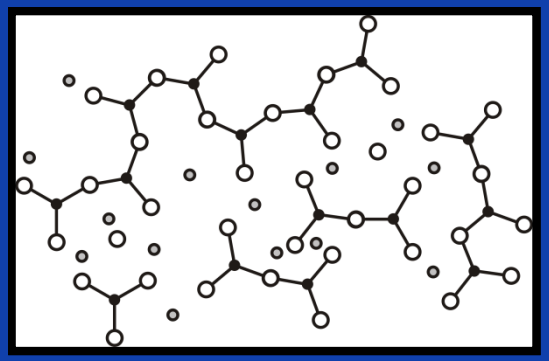




Solidification & Microstructure Simulation

KATHOLIEKE UNIVERSITEIT LEUVEN

Geology and pyrometallurgy



- Oxide melt
- SiO_2, Al_2O_3, CaO, FeO, Fe_2O_3, MgO ...
- High temperature and/or pressure

- Lava (magma)
- Slags

Solidification & Microstructure Simulation

KATHOLIEKE UNIVERSITEIT LEUVEN

Specific to slag solidification

Slag solidification

- Mostly facet growth
- Strong anisotropy
- High interfacial energies
- Partial crystallization
- Glass transition
- Oxides are diffusing
- Possible redox reactions

KATHOLIEKE UNIVERSITEIT LEUVEN

Phase field model for slag crystallization

- Model can treat any number of phases
- Model can treat any number of components
  - CaO, Al_2O_3, FeO, Fe_2O_3, SiO_2, ...
- Model is coupled with thermodynamic database (FACT)
- Stoichiometric solid oxide phases
- Diffusion coefficients are taken from the literature, e.g.

$$D^L = \begin{bmatrix} 8.734 & -2,464 \\ -3,948 & 5.977 \end{bmatrix} 10^{-11}$$

- Dendrites and faceted crystals

J. Heulens et al., Acta Mater. 59 (2011) p2156

Solidification & Microstructure Simulation

KATHOLIEKE UNIVERSITEIT LEUVEN

Equations for microstructure evolution

- System of *p* phases and *c* components
- Phase fields evolve by energy minimization:

$$\frac{\partial \eta_i}{\partial t} = -L(\eta)\frac{\delta}{\delta \eta_i}\left(\int_V \left(mf_0(\eta) + \frac{\kappa(\eta)}{2}\sum_{r=1}^{p}\left|\nabla \eta_r\right|^2 + f_{chem} \right) dV \right)$$

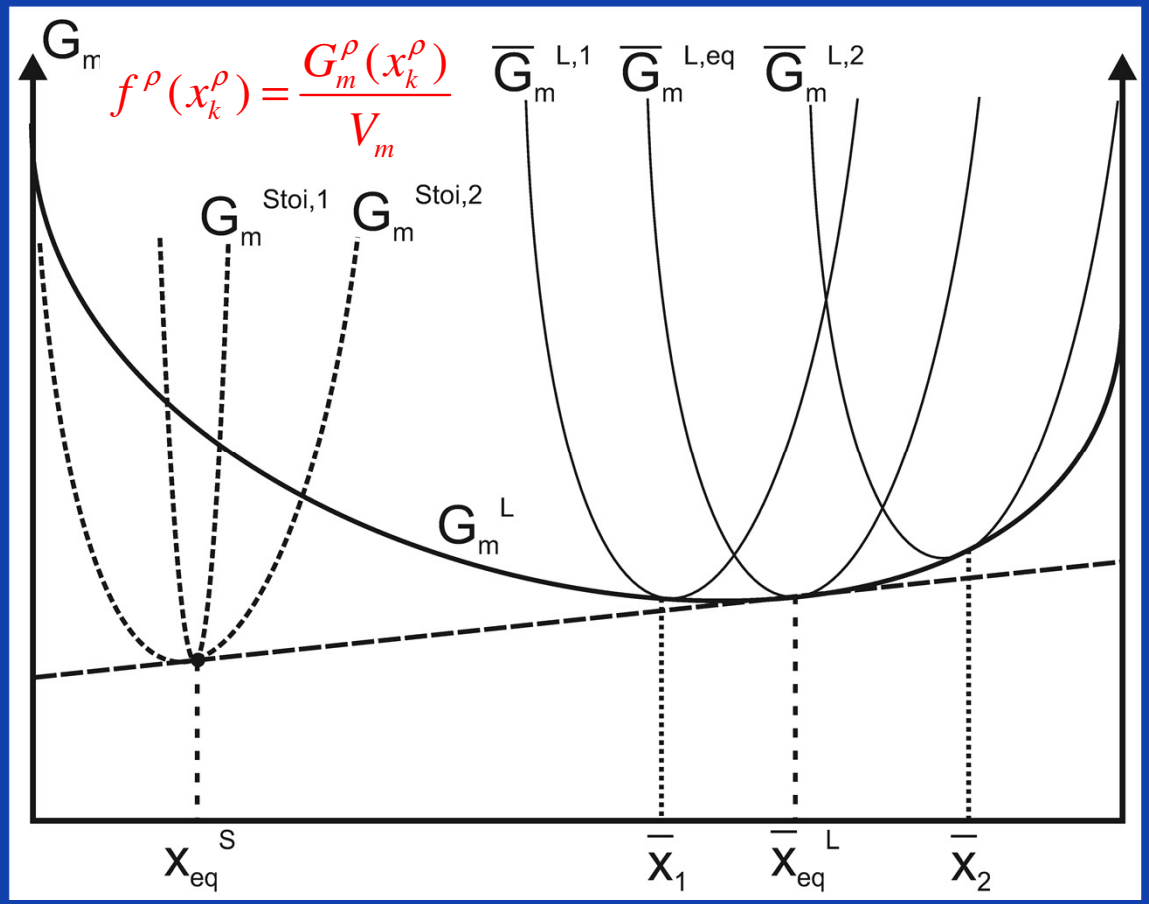
  - Interfacial energy (Double well and gradient term)
  - Chemical energy (Gibbs energies of phases)
- Diffusion equation for every component *k*:

$$\frac{\partial x_k}{\partial t} = \nabla \cdot \left(\sum_{i=1}^{p} \phi_i \sum_{r=1}^{c-1} M^{i}_{rk} \nabla \tilde{\mu}^{i}_{r} \right)$$

$$\tilde{\mu}^{i}_{r} = \mu^{i}_{r} - \mu^{i}_{SiO_2}$$

KATHOLIEKE UNIVERSITEIT LEUVEN

Coupling with FactSage databases



J. Heulens et al., Acta Mater. 59 (2011) p2156

- **KKS approach**

$$f_{chem} = \sum_{\rho=1}^{p} \varphi_\rho f^{\rho}\left(x_k^{\rho}\right)$$

  - **Solve x_k^{ρ} from**

$$\begin{cases} \dfrac{\partial f^{\alpha}(x_k^{\alpha})}{\partial x_k^{\alpha}} = \dfrac{\partial f^{\beta}(x_k^{\beta})}{\partial x_k^{\beta}} \\ \ldots = \dfrac{\partial f^{\rho}(x_k^{\rho})}{\partial x_k^{\rho}} = \tilde{\mu}_k \\ x_k = \sum_{\rho} \phi_\rho x_k^{\rho} \end{cases}$$

- **At discrete compositions Gibbs energy approximated with parabola**

KATHOLIEKE UNIVERSITEIT LEUVEN

Coupling with FactSage databases

- At discrete x_k Gibbs energy of phase *i* approximated by

$$\hat{f}^i = \sum_{k=1}^{c-1}\left(\frac{A^i_{kk}}{2}\left(x^i_k - \hat{x}^i_k\right)^2 + \sum_{l\neq k}^{c-1} A^i_{kl}\left(x^i_k - \hat{x}^i_k\right)\left(x^i_l - \hat{x}^i_l\right) + B^i_k\left(x^i_k - \hat{x}^i_k\right)\right) + C^i$$

$$A^i_{kl} = \frac{\partial^2 f^i}{\partial x^i_k \partial x^i_l} \qquad B^i_k = \frac{\partial f^i}{\partial x^i_k} = \tilde{\mu}^i_k \qquad C^i = f^i$$

- A, B and C are retrieved by ChemApp and stored in an array to load in the phase field code before start simulation

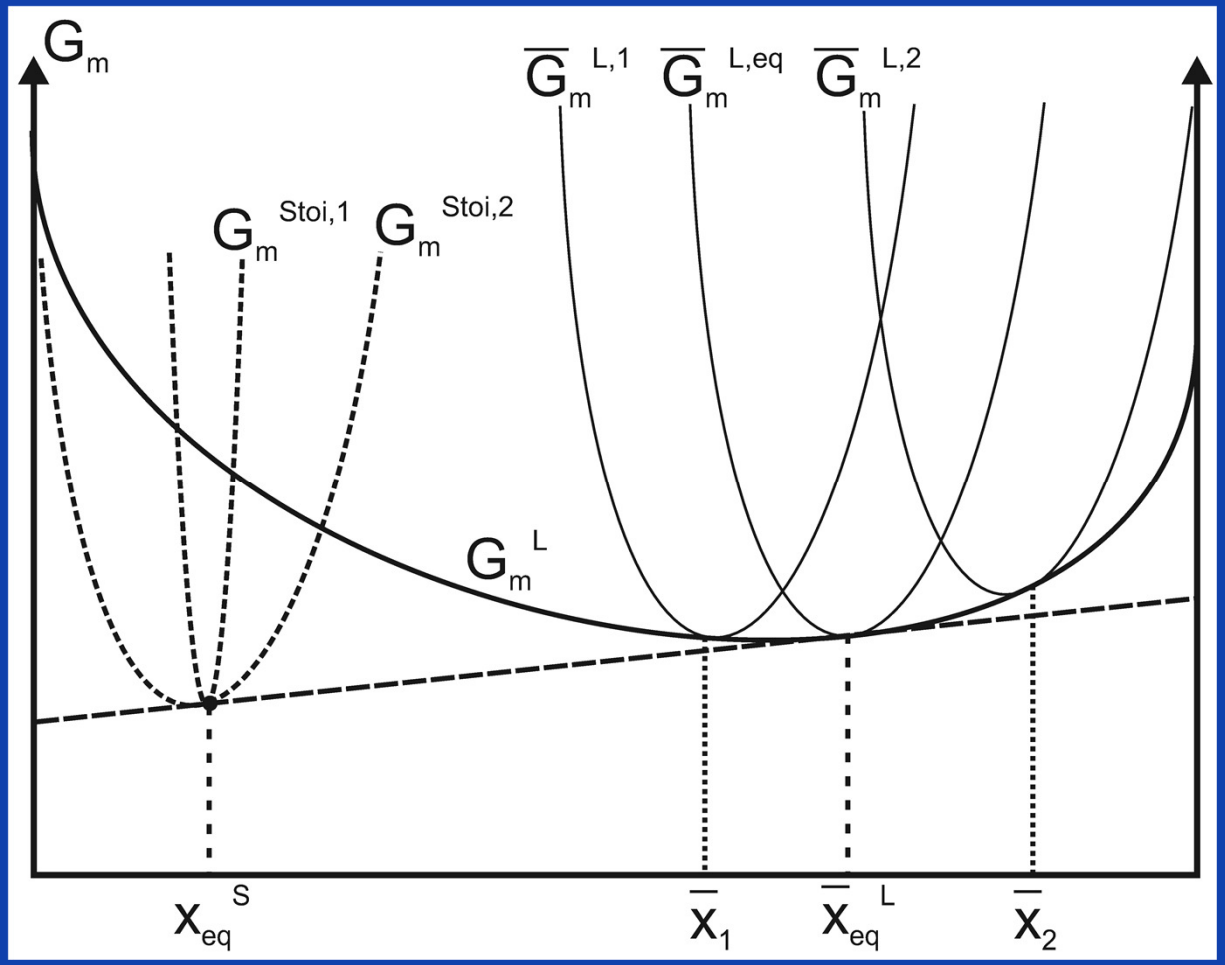
- Diffusion potentials are linear in concentrations, which greatly reduces computational effort

J. Heulens et al., Acta Mater. 59 (2011) p2156

Solidification & Microstructure Simulation

KATHOLIEKE UNIVERSITEIT LEUVEN

Stoichiometric phases



- **Parabola for Gibbs energy of stoichiometric phase**

KATHOLIEKE UNIVERSITEIT LEUVEN

Anisotropic interfaces

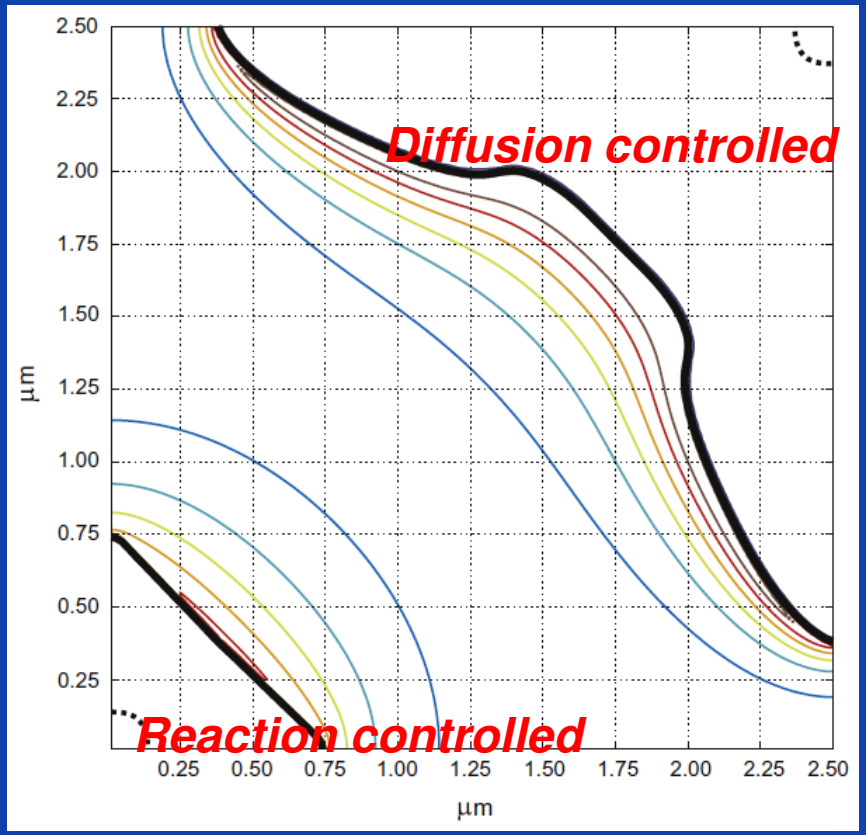
- **Dendrites -- Diffusion controlled**
  - **Anisotropic energy**

$$\sigma_{i,j} = \bar{\sigma}_{i,j}\left(1+\delta_{i,j}\cos\left(a_{i,j}\theta_{i,j}\right)\right)$$

- **Facets –reaction controlled**
  - **Anisotropic kinetics**

$$L_{i,j} = \bar{L}_{i,j}\left(1-\beta_{i,j}+2\beta_{i,j}tanh\left(\frac{r_{i,j}}{\left|\tan\left(0.5a_{i,j}\theta_{i,j}\right)\right|}\right)\right)$$

T. Uehara and RF Sekerka, J. Cryst. Growth (2003) 254, p251.

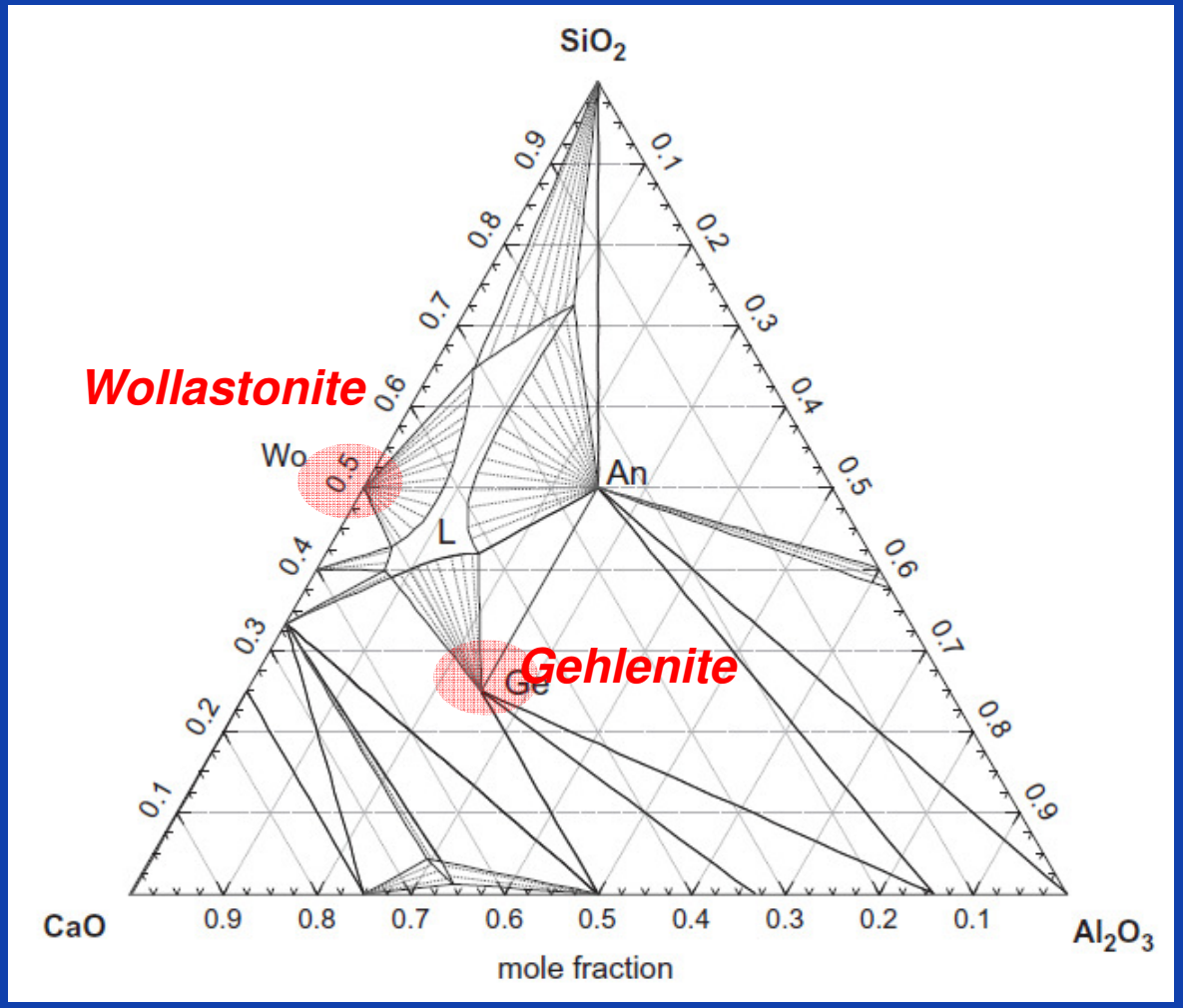


Interface orientation $\theta_{i,j} = \arctan\left|\frac{\nabla_y\eta_i - \nabla_y\eta_j}{\nabla_x\eta_i - \nabla_x\eta_j}\right|$

J. Heulens et al., Acta Mater. 59 (2011) p2156

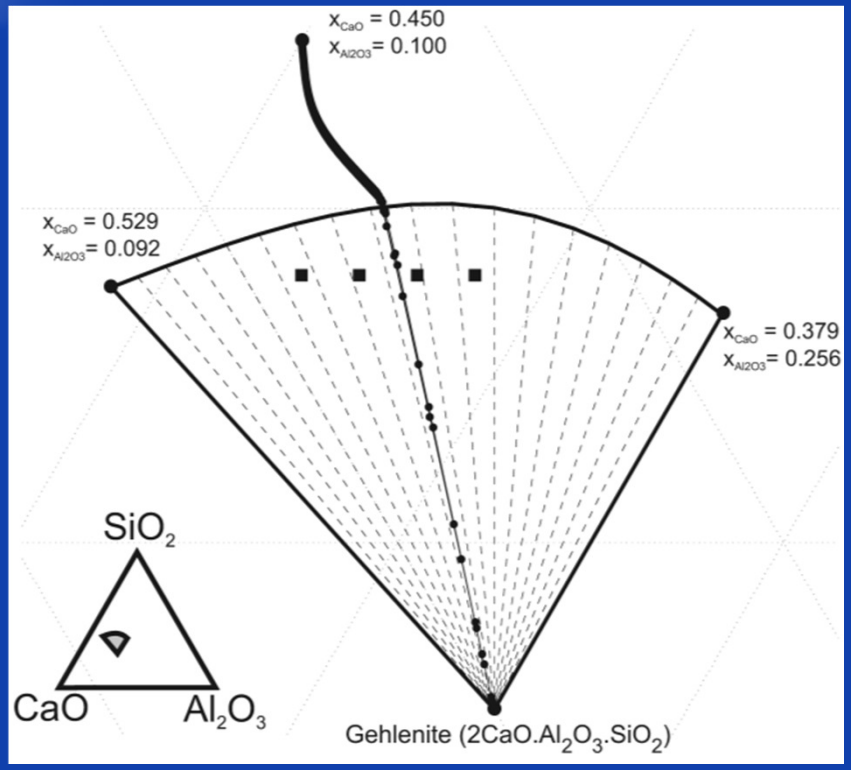
KATHOLIEKE UNIVERSITEIT LEUVEN

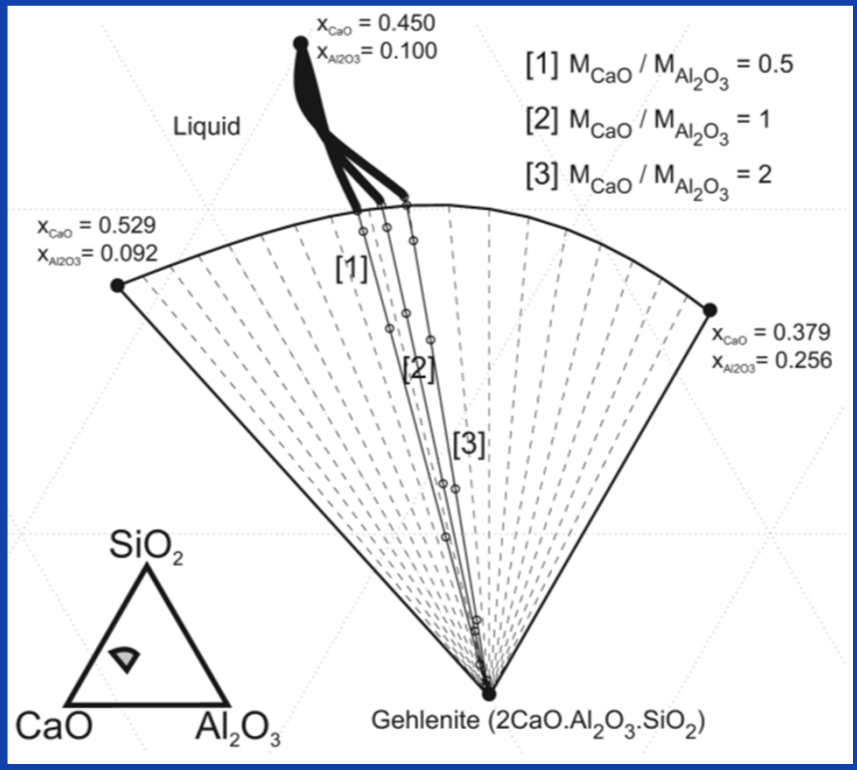
CaO-Al2O3-SiO2



KATHOLIEKE UNIVERSITEIT LEUVEN

Dissolution of Gehlenite





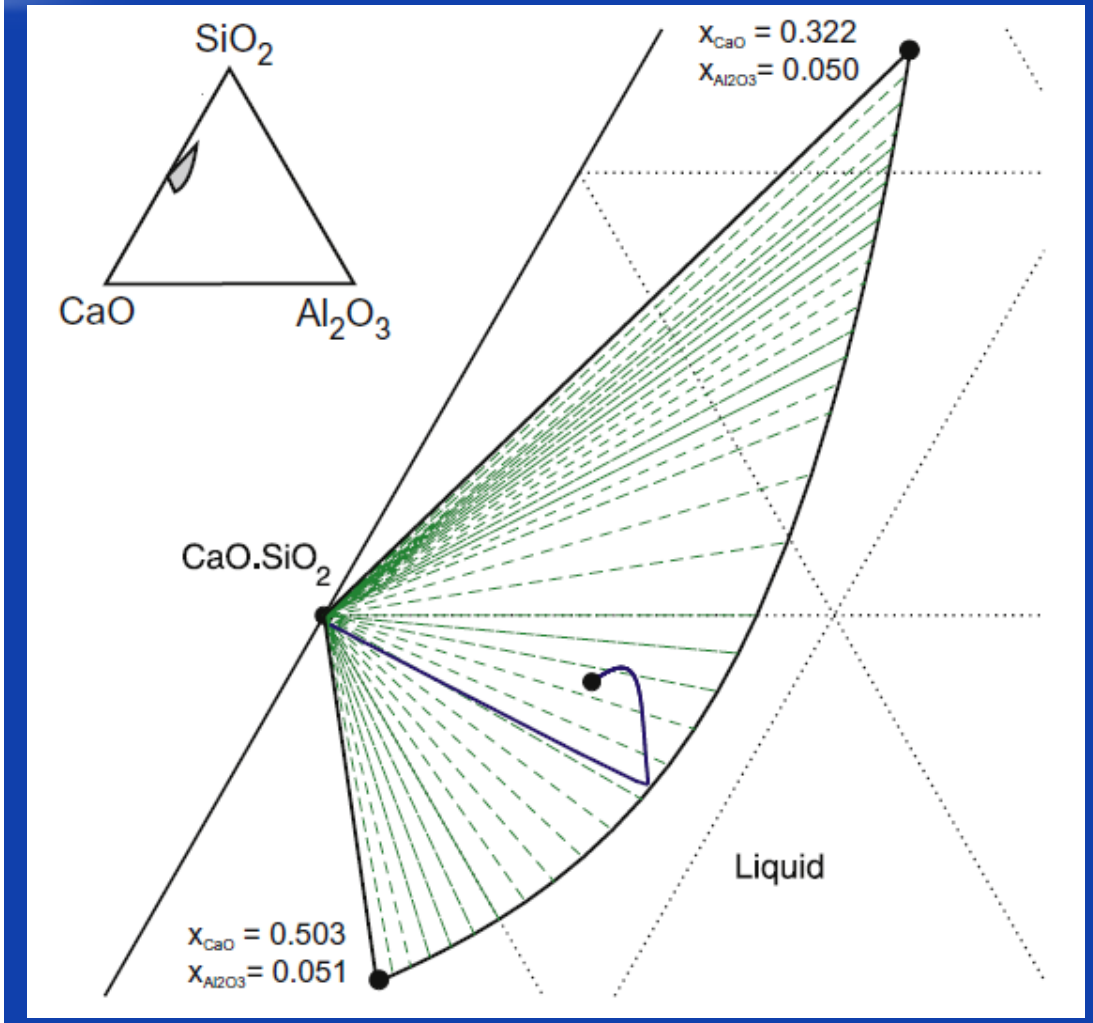
Parabola construction with minimal influence on results

Tie-line selection depending on diffusion kinetics in liquid

J. Heulens et al., Acta Mater. 59 (2011) p2156

KATHOLIEKE UNIVERSITEIT LEUVEN

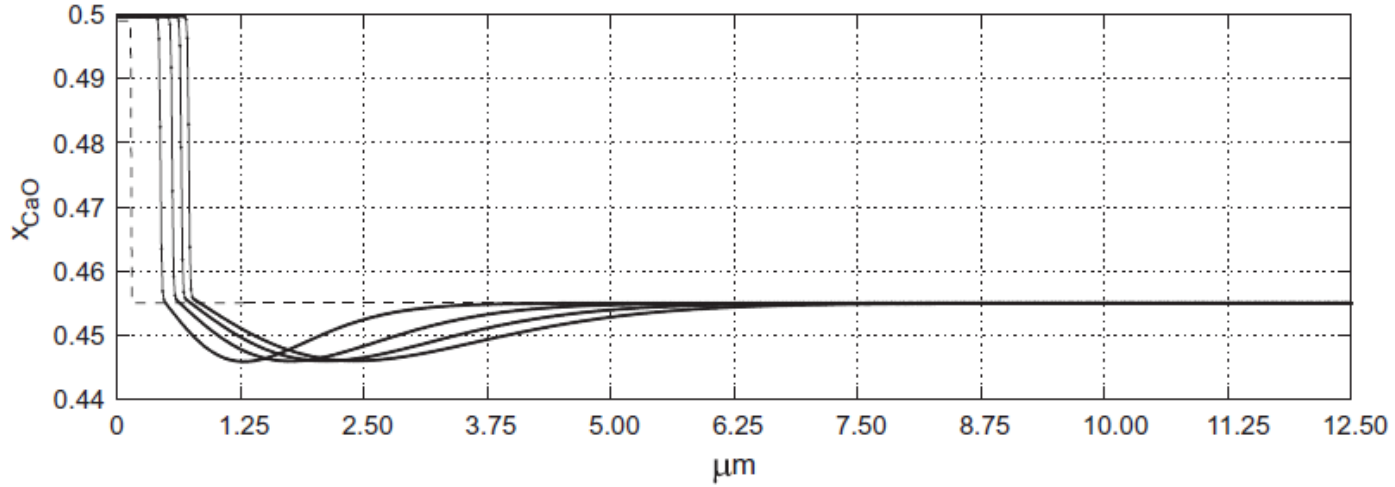
Crystallization Wollastonite (1D)

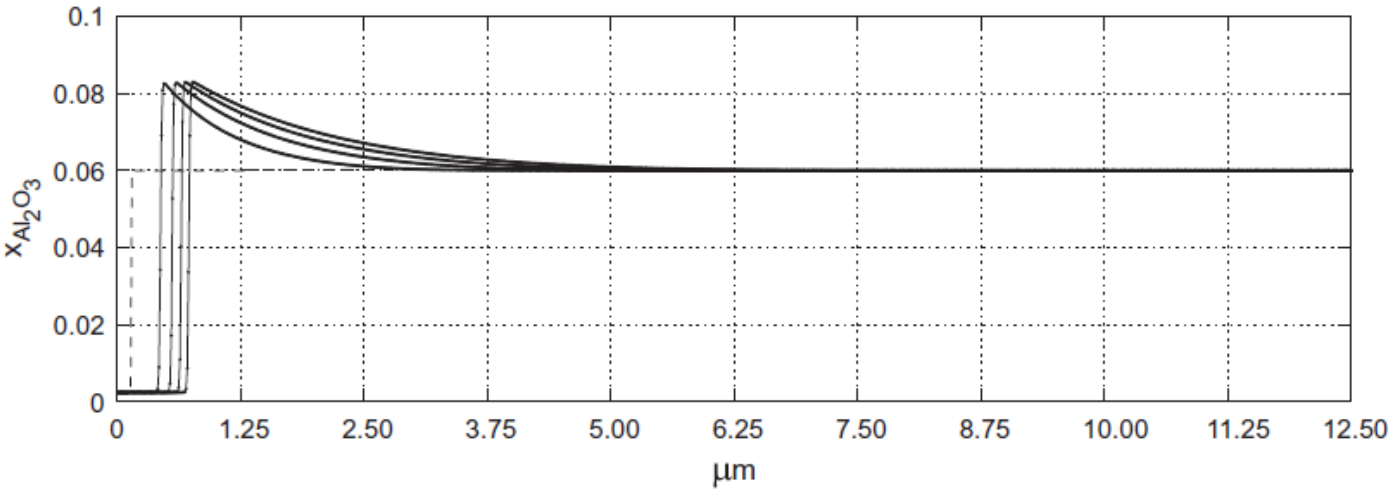


- Uphill diffusion
- Automatic tie-line selection

KATHOLIEKE UNIVERSITEIT LEUVEN

Crystallization Wollastonite (1D)



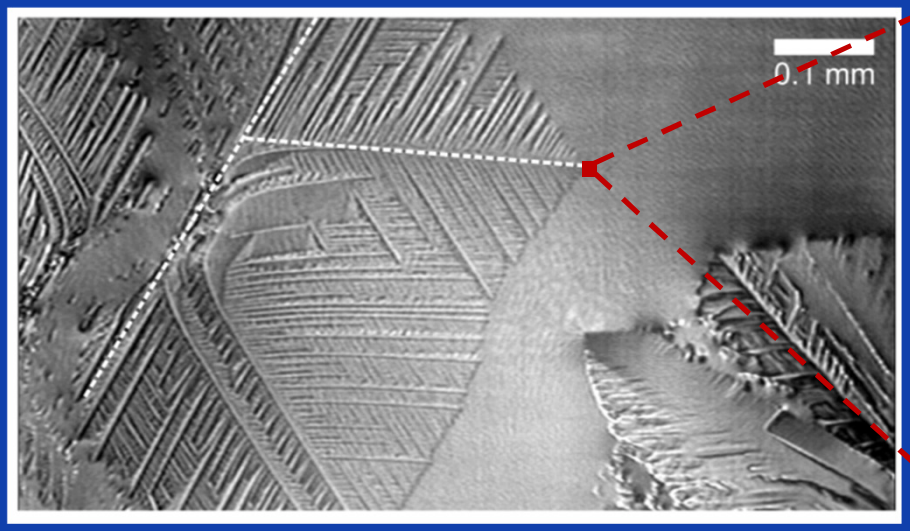


- Uphill diffusion
- Automatic tie-line selection

KATHOLIEKE UNIVERSITEIT LEUVEN

Crystallization Wollastonite (2D)

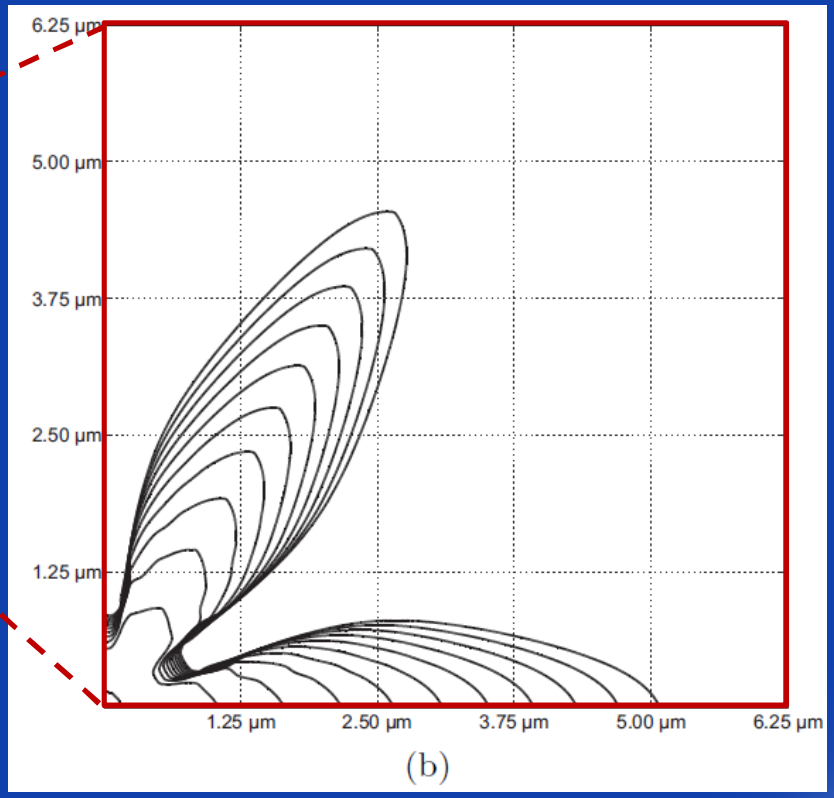
Experiment



Growth of wollastonite in 42CaO-10Al_2O_3-48SiO_2 at 1320 °C

Confocal laser microscope

Simulation

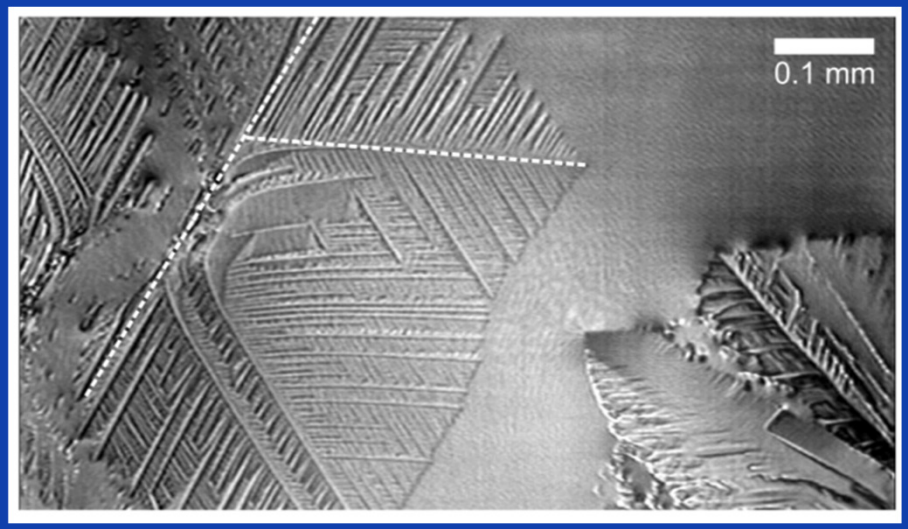


Computer cluster (100 cpu)

KATHOLIEKE UNIVERSITEIT LEUVEN

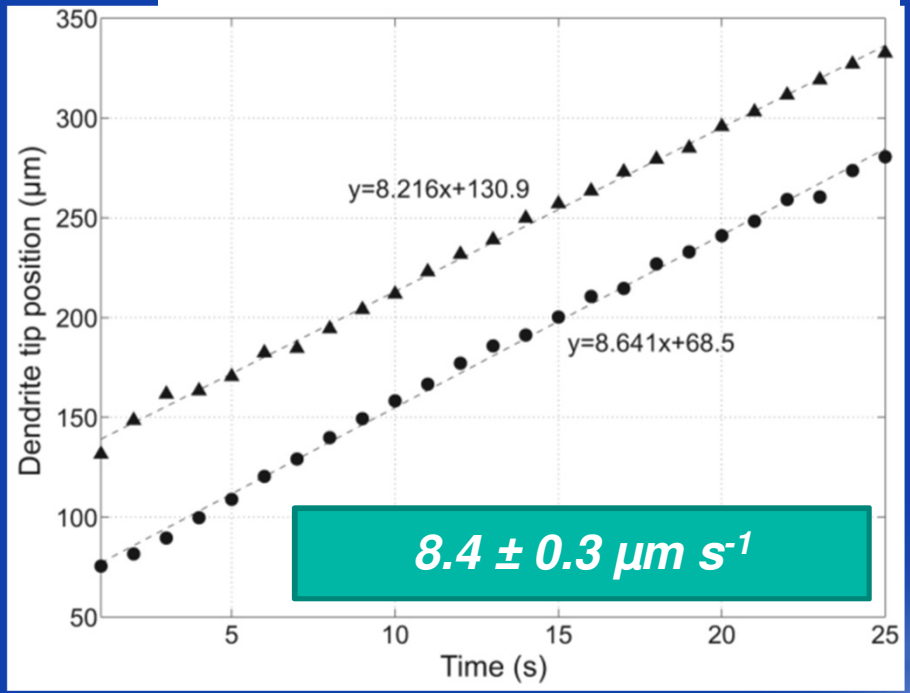
In situ observation

- Confocal Laser Scanning Microscope (CLSM)
- At low undercooling (1370℃) → faceted growth
- At high undercooling (1320℃) → dendrite growth with 6-fold anisotropy



Hexagonal dendrites of $CaSiO_3$ in $CaO-Al_2O_3-SiO_2$ @1320℃

Linear growth at steady-state

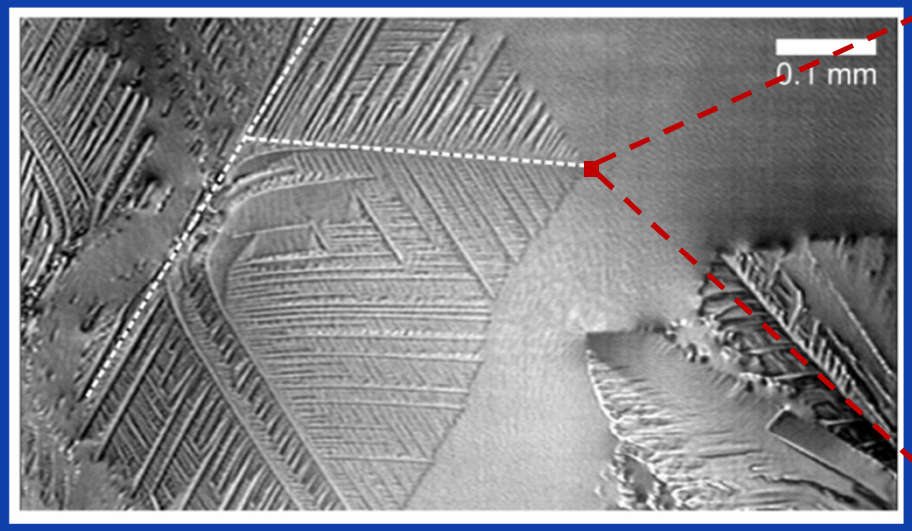


J. Heulens et al., J. Eur. Cer. Soc. 31 (2011) p1873

KATHOLIEKE UNIVERSITEIT LEUVEN

Crystallization Wollastonite (2D)

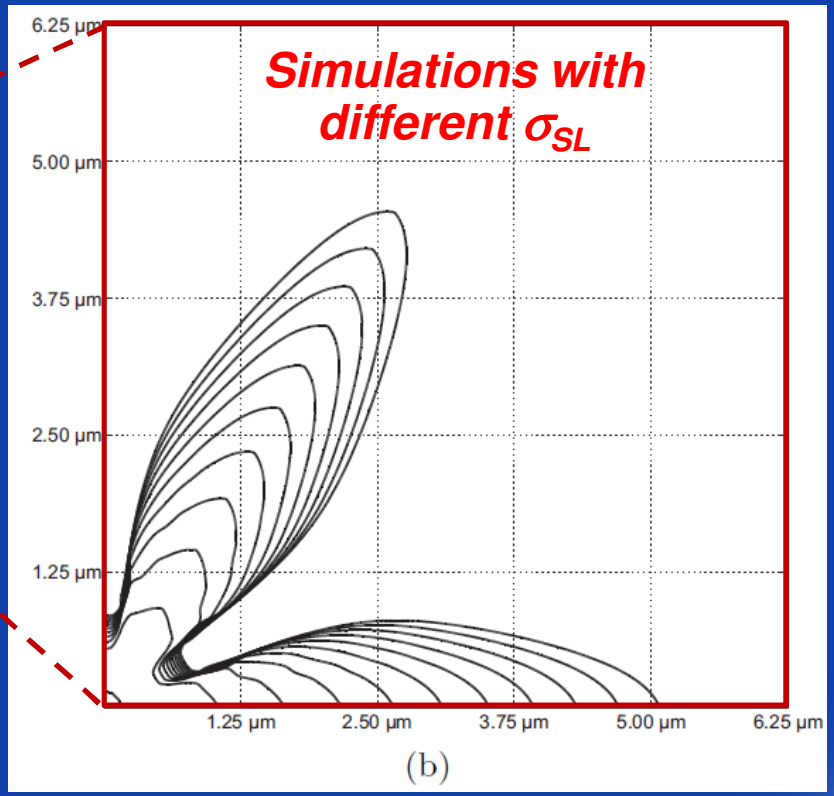
Experiment



Growth of wollastonite in 42CaO-10Al_2O_3-48SiO_2 at 1320 °C

Confocal laser microscope

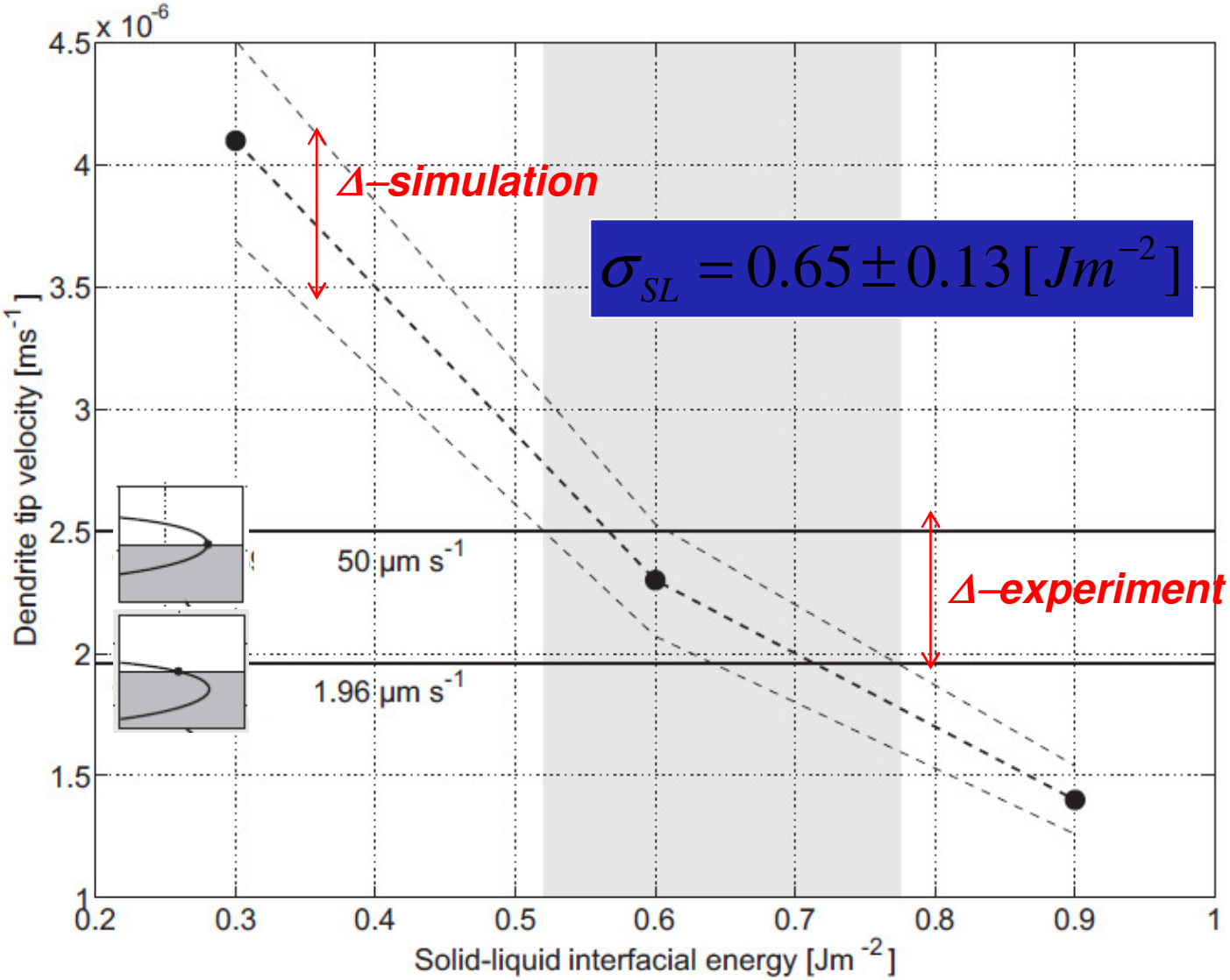
Simulation



Computer cluster (100 cpu)

KATHOLIEKE UNIVERSITEIT LEUVEN

Estimation of the S-L interfacial energy



$$\sigma_{SL} = 0.65 \pm 0.13\,[Jm^{-2}]$$

KATHOLIEKE UNIVERSITEIT LEUVEN

Oxidation state dependent crystallization

- System : $FeO\text{-}Fe_2O_3\text{-}SiO_2$ @ 1400°C
  - Crystallization of magnetite ($FeO.Fe_2O_3$)
  - Local oxidation state in liquid
  - Open system in contact with O_2 atmosphere (fixed p_{O2})

J. Heulens et al., Chem. Geology, 290 (2011) p156

Solidification & Microstructure Simulation

KATHOLIEKE UNIVERSITEIT LEUVEN

Oxidation state dependent crystallization

- System : $FeO\text{-}Fe_2O_3\text{-}SiO_2$ @ 1400°C
  - Crystallization of magnetite ($FeO.Fe_2O_3$)
  - Local oxidation state in liquid
  - Open system in contact with O_2 atmosphere (fixed p_{O2})
- Redox reactions
  - Redox reactions in local equilibrium
  - Fe^{3+} / Fe^{2+} direct measure for local oxygen potential (true within limited composition and p_{O2} range)
  - O_2 diffusion by changing the Fe^{3+} / Fe^{2+} ratio -> diffusion of FeO and Fe_2O_3 is considered

Solidification & Microstructure Simulation

KATHOLIEKE UNIVERSITEIT LEUVEN

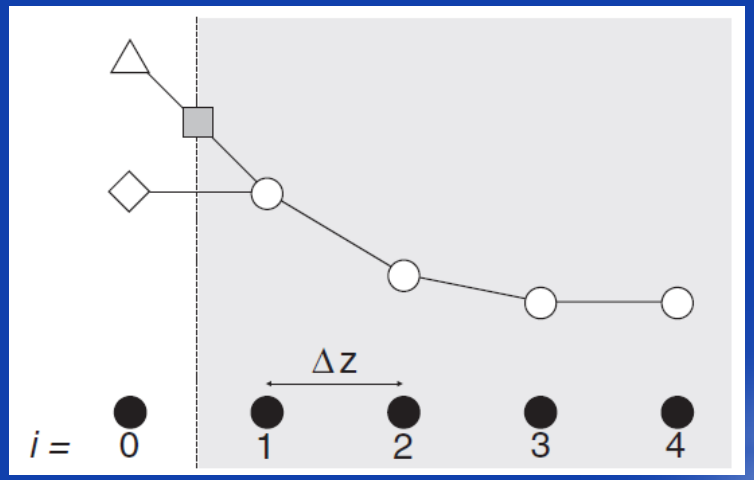
Oxidation state dependent crystallization

- System : $FeO\text{-}Fe_2O_3\text{-}SiO_2$ @ 1400°C
  - Crystallization of magnetite ($FeO.Fe_2O_3$)
  - Local oxidation state in liquid
- Open system in contact with O_2 atmosphere (fixed p_{O2})
  - Special boundary condition to preserve Fe but not O
    - Mass balance Fe

$$x_{FeO}^{i=0} + 2x_{Fe2O3}^{i=0} = x_{FeO}^{i=1} + 2x_{Fe2O3}^{i=1}$$

    - Fixed p_{O2}

$$\frac{x_{FeO}^{i=0.5}}{x_{Fe2O3}^{i=0.5}} = cte\left(p_{O2,atm}\right)$$

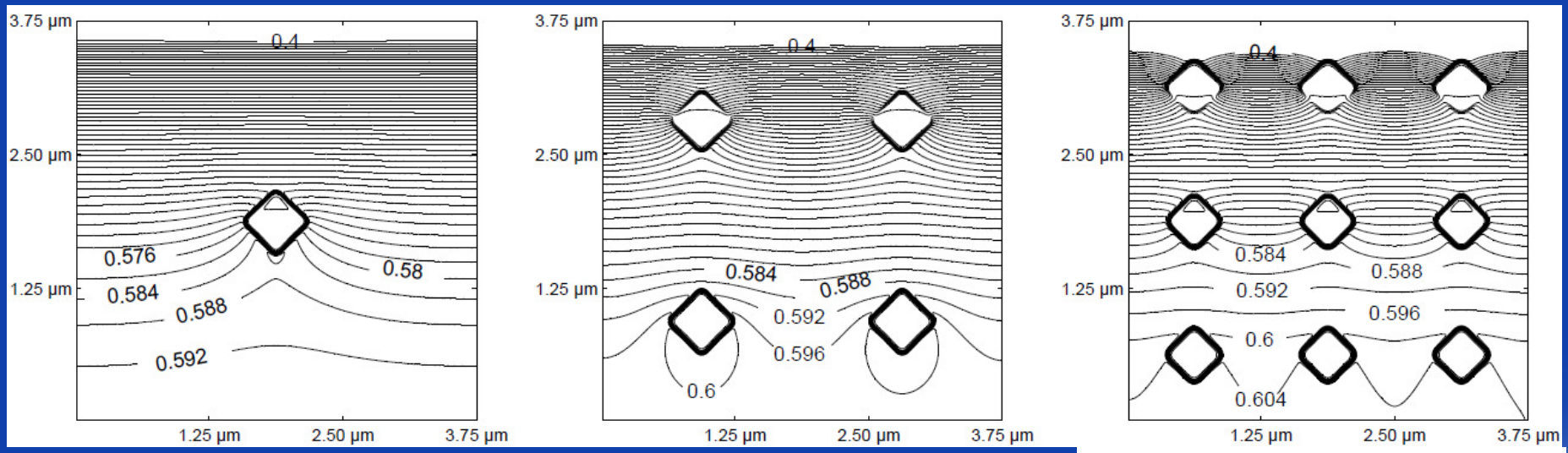


J. Heulens et al., Chem. Geology, 290 (2011) p156

KATHOLIEKE UNIVERSITEIT LEUVEN

Crystallization of magnetite

- Atmosphere: $p_{O2}=1.5x10^{-3}$; Initial melt: $a_{O2}= 2.4x10^{-5}$
  - Oxidation from atmosphere
  - Reduction from growth of Fe_3O_4
- Faceted reaction controlled growth



Contour plots x_{FeO}

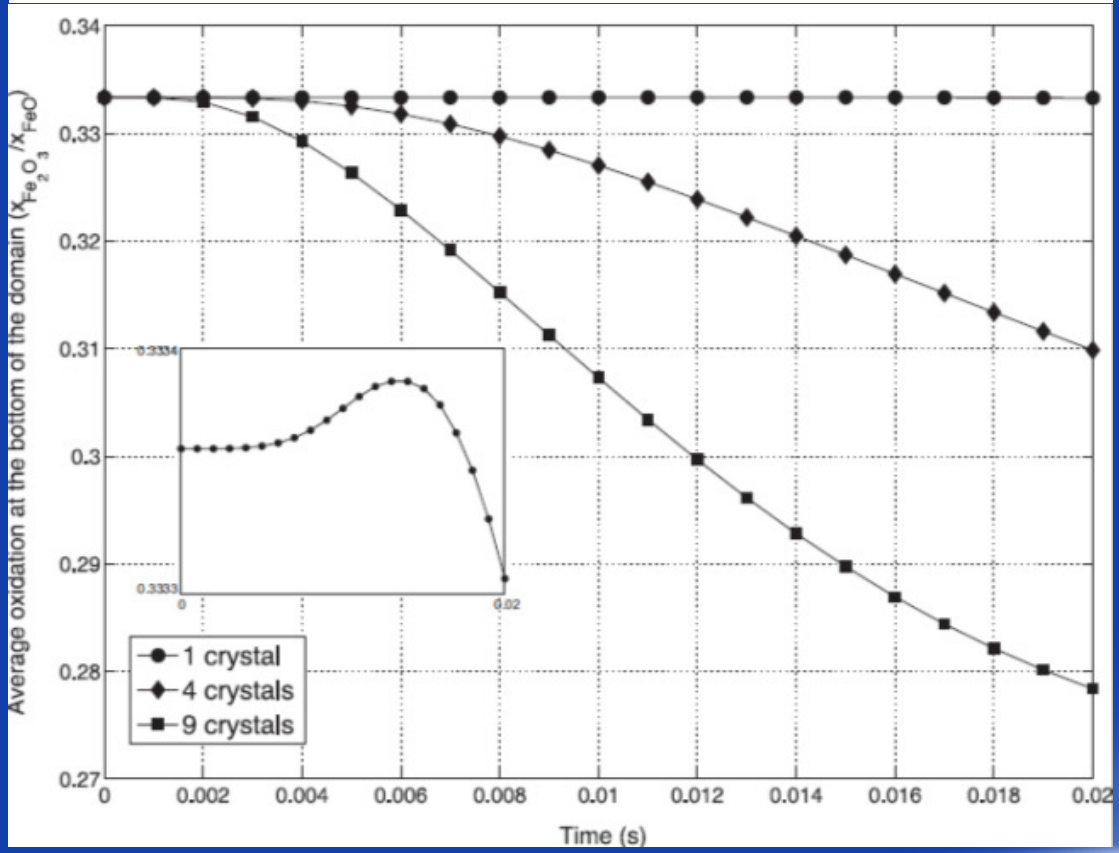
J. Heulens et al., Chem. Geology, 290 (2011) p156

KATHOLIEKE UNIVERSITEIT LEUVEN

Crystallization of magnetite

- Melt is reduced
  - Faster for higher crystal density
  - Some oxidation initially for low crystal density
- Limited effect of p_{O2} atmosphere on a_{O2} melt due to crystallization
  - e.g. rhyolite lavas in Yellowstone Park
- p_{O2} atmosphere affects crystal growth

Average oxidation state at bottom of simulation domain



KATHOLIEKE UNIVERSITEIT LEUVEN

Conclusions

- What do we need further to improve the quantitative accuracy for polycrystalline and multi-phase systems ?
  - Accurate representation of triple-junction angles outside [100°-140°] ↔ equal interface width
  - General solution for chemical potential jump accros interface
  - (CALPHAD) Gibbs/free energies over full composition domain (stoichiometric phases, metastable regions)
  - Composition and orientation dependent expressions for diffusion and interfacial properties
  - Elastic and plastic effects

Solidification & Microstructure Simulation

KATHOLIEKE UNIVERSITEIT LEUVEN

Acknowledgements

- OT/07/040 (Quantitative phase field modelling of coarsening in lead-free solder joints)
- IUAP Program DISCO (Dynamical Systems, Control, and Optimization
- IWT grant SB-73163 (Phase-Field Modelling of the Solidification of Oxidic Systems)
- Research Foundation - Flanders (FWO-Vlaanderen)
- Simulations were performed on the Flemisch Super Computer (VSC)

- More information on *http//nele.studentenweb.org* and *https://www.mtm.kuleuven.be/Onderzoek/Semper/SolMicS/*

Solidification & Microstructure Simulation

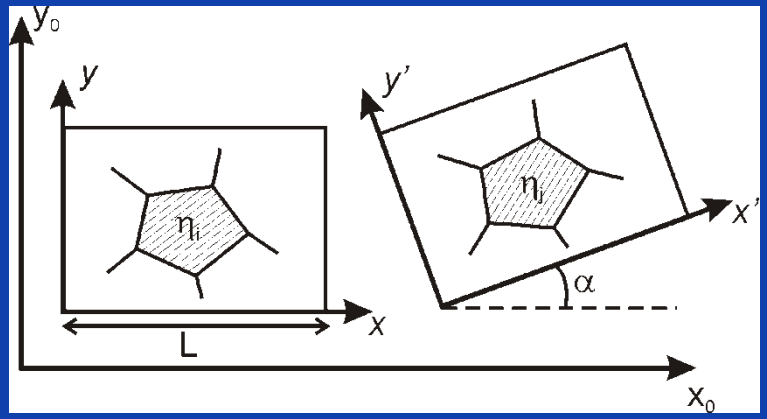
End

- Thank you for your attention !! Questions ?

KATHOLIEKE UNIVERSITEIT LEUVEN

Rotation invariance of the model

- **Mathematically, the model equations are invariant to rotation, but …**
- **the order parameters represent orientations in a fixed reference frame.**



grid spacing Δh

physical width of domain L

rotational symmetry n

- **The precision of α depends on the numerical setup,**

$$\Delta\alpha \approx \frac{1}{\cos\alpha}\frac{\Delta h}{L}$$

- **For the model to be rotational invariant in practice, lower limit of amount of order parameters *p*:**

$$p > \frac{\sqrt{2}\pi L}{n\Delta h}$$

J. Heulens and N. Moelans, Scripta Mat. (2010)

Thin interface models

Principles of the matched asymptotic expansion

Expansion inner region:

$$\eta(n/\varepsilon, t_1, t_2) = \eta_0(n/\varepsilon, t_1, t_2) + \varepsilon\eta_1(n/\varepsilon, t_1, t_2) + \ldots$$
$$c(n/\varepsilon, t_1, t_2) = c_0(n/\varepsilon, t_1, t_2) + \varepsilon c_1(n/\varepsilon, t_1, t_2) + \ldots$$

Expansion outer regions:

$$\eta^*(n, t_1, t_2) = \eta_0^*(n, t_1, t_2) + \varepsilon\eta_1^*(n, t_1, t_2) + \ldots$$
$$c^*(n, t_1, t_2) = c_0^*(n, t_1, t_2) + \varepsilon c_1^*(n, t_1, t_2) + \ldots$$

Match inner and outer region:

$$\lim_{n/\varepsilon\to\pm\infty} \eta_0(n/\varepsilon) = \left[\eta_0^*\right]^{\pm}, \quad \lim_{n/\varepsilon\to\pm\infty} \eta_j(n/\varepsilon) = \ldots$$

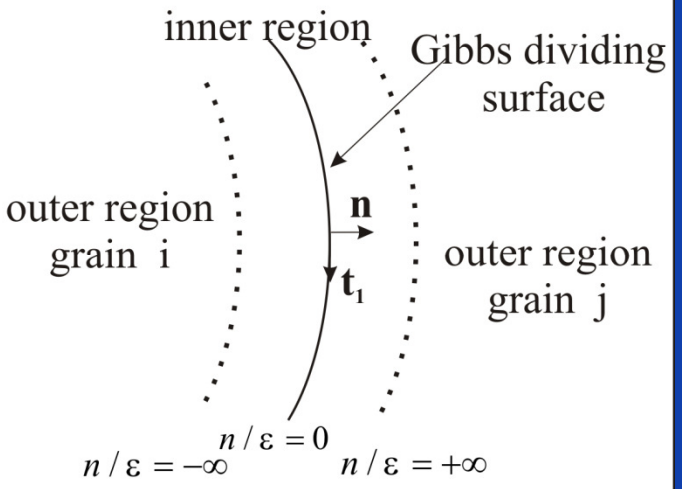
$$\lim_{n/\varepsilon\to\pm\infty} c_0(n/\varepsilon) = \left[c_0^*(0)\right]^{\pm}, \quad \lim_{n/\varepsilon\to\pm\infty} c_j(n/\varepsilon) = \ldots$$

gives sharp-interface model with corrections

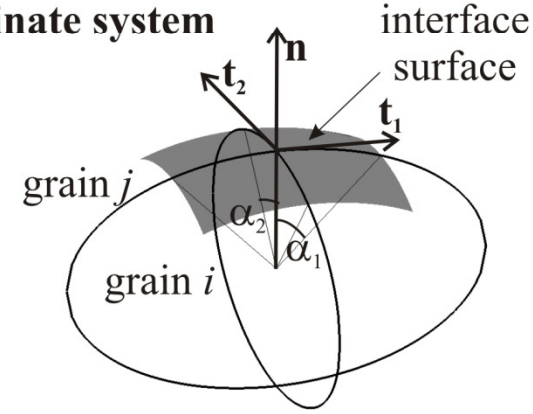
Gibbs Thomson $\dfrac{c_\alpha^i}{c_\alpha^{eq}} = 1 - (1-k)d_0\mathrm{K} - (1-k)\beta v_n + corr(O(\varepsilon^\nu))$

with $k = \dfrac{c_\beta^i}{c_\alpha^i}$

Conservation $(c_\alpha^i - c_\beta^i)v_n = \left[D\partial_n c\right]_+ + corr(O(\varepsilon^\nu))$



3D curvilinear coordinate system



KATHOLIEKE UNIVERSITEIT LEUVEN

Multi-grain and multi-phase models

- **Multi-phase-field model**
  - **Phase fields** $\varphi_1, \varphi_2, \varphi_3, \ldots \varphi_p, \quad \sum_{i=1}^{p} \varphi_i = 1$
  - **Interfacial energy** $f_{\text{int}} = \sum_{i \neq j} \frac{4\sigma_{i,j}}{\eta_{i,j}} \left\{ \frac{\eta_{i,j}^2}{\pi^2} \left| \nabla \phi_i \cdot \nabla \phi_j \right| + \phi_i \phi_j \right\}$ $\quad 0 < \phi_{i,j} < 1$

Steinbach et al.

MICRESS phase-field code

H. Garcke, B.Nestler, B. Stoth, SIAM J. Appl. Math. 60 (1999) p 295.

Solidification & Microstructure Simulation

KATHOLIEKE UNIVERSITEIT LEUVEN

Multi-grain and multi-phase models

- **Multi-phase-field model**

- **Multi-order parameter models**

$$\eta_1, \eta_2, \ldots, \eta_i(\vec{r}, t), \ldots, \eta_p, \quad \left(\sum_{i=1}^{p} \eta_i \neq 1 \right)$$

L.-Q. Chen and W. Yang, PRB, 50 (1994) p15752

  - **Order parameters**

$$f_{\text{int}} = m \left(\sum_{i=1}^{p} \left(\frac{\eta_i^4}{4} - \frac{\eta_i^2}{2} \right) + \sum_{i=1}^{p} \sum_{j<i}^{p} \gamma_{i,j} \eta_i^2 \eta_j^2 + \frac{1}{4} \right) + \frac{\kappa(\eta)}{2} \sum_{i=1}^{p} (\vec{\nabla} \eta_i)^2$$

  - **Interfacial energy**

$$\kappa(\eta) = \sum_{i=1}^{p} \sum_{j<i}^{p} \kappa_{i,j} \eta_i^2 \eta_j^2 \Big/ \sum_{i=1}^{p} \sum_{j<i}^{p} \eta_i^2 \eta_j^2$$

A. Kazaryan et al., PRB, 61 (2000) p14275

Solidification & Microstructure Simulation

KATHOLIEKE UNIVERSITEIT LEUVEN

Multi-grain and multi-phase models

- **Multi-phase-field model**
  - **Phase fields** $\varphi_1, \varphi_2, \varphi_3, \ldots \varphi_p, \quad \sum_{i=1}^{p} \varphi_i = 1$
  - **Interfacial energy** $f_{\text{int}} = \sum_{i \neq j} \frac{4\sigma_{i,j}}{\eta_{i,j}} \left\{ \frac{\eta_{i,j}^2}{\pi^2} \left| \nabla \phi_i \cdot \nabla \phi_j \right| + \phi_i \phi_j \right\}$ $\quad 0 < \phi_{i,j} < 1$

Steinbach et al.

MICRESS phase-field code

H. Garcke, B.Nestler, B. Stoth, SIAM J. Appl. Math. 60 (1999) p 295.

- **Multi-order parameter models**
  - **Order parameters** $\eta_1, \eta_2, \ldots, \eta_i(\vec{r}, t), \ldots, \eta_p, \quad \left(\sum_{i=1}^{p} \eta_i \neq 1 \right)$
  - **Interfacial energy** $f_{\text{int}} = m \left(\sum_{i=1}^{p} \left(\frac{\eta_i^4}{4} - \frac{\eta_i^2}{2} \right) + \sum_{i=1}^{p} \sum_{j<i}^{p} \gamma_{i,j} \eta_i^2 \eta_j^2 + \frac{1}{4} \right) + \frac{\kappa(\eta)}{2} \sum_{i=1}^{p} (\vec{\nabla} \eta_i)^2$

$$\kappa(\eta) = \sum_{i=1}^{p} \sum_{j<i}^{p} \kappa_{i,j} \eta_i^2 \eta_j^2 \Big/ \sum_{i=1}^{p} \sum_{j<i}^{p} \eta_i^2 \eta_j^2$$

L.-Q. Chen and W. Yang, PRB, 50 (1994) p15752

A. Kazaryan et al., PRB, 61 (2000) p14275

Solidification & Microstructure Simulation

KATHOLIEKE UNIVERSITEIT LEUVEN

Multi-phase and multi-phase models

- **Vector valued model**
  - **Orientation field (θ) and phase field (ϕ)**
  - **Free energy** $f_{\text{int}} = f(\phi, |\nabla\phi|, |\nabla\theta|)$

R. Kobayashi, J.A. Warren, W.C. Carter, Physica D, 119 (1998) p415

- **2-phase solidification**
  - **Phase fields** $\varphi_1, \varphi_2, \varphi_3, \quad \sum_{i=1}^{3} \varphi_i = 1$
  - **Free energy** $f_{\text{int}} = f(\phi_1, \phi_2, \phi_3) + \frac{\kappa}{2} \sum_{i=1}^{3} (\nabla\phi_i)^2$
    - **No third-phase contributions**
    - **Bulk energy interpolation function with 0-slope**

R. Folch and M. Plapp, PRE, 72 (2005) n° 011602

Solidification & Microstructure Simulation