Phase-field modeling of microstructure evolution in multi-component alloys

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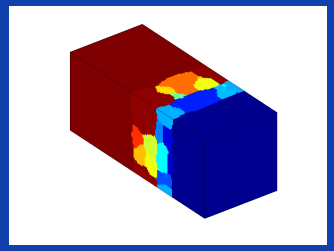
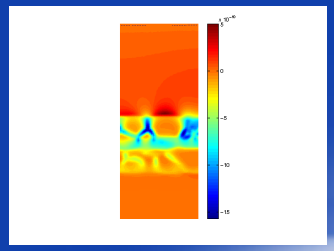




Outline

- Introduction: modeling of microstructure evolution
- Principles of phase field modeling
- Application examples
  - Anisotropic grain growth
  - Precipitates on grain boundaries
  - Lead-free solder joints
  - Solidification
- Summary

Role of microstructures in materials science

Chemical composition
+
Temperature, pressure, cooling rate, deformation, …

↓

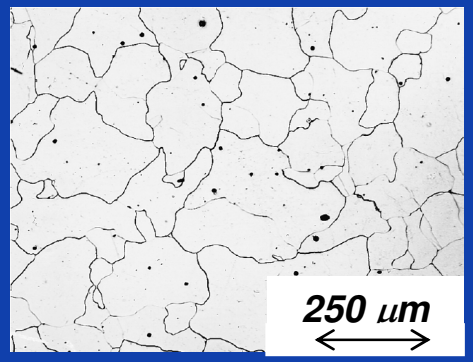
Microstructure

Shape, size and orientation of the grains, mutual distribution of the phases

↓

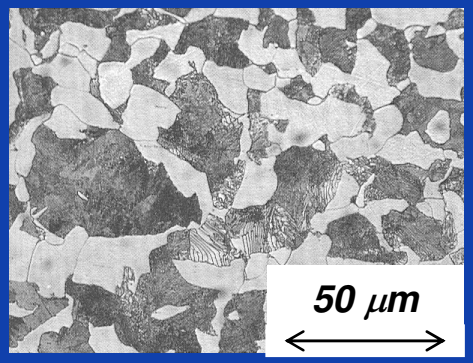
Material properties

Strength, deformability, hardness, toughness, fatigue…



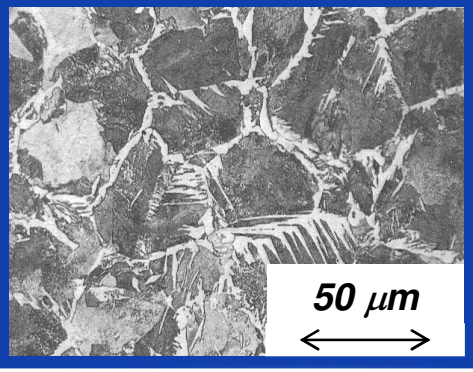
Low-C steel: wt% C < 0.022

Ferrite + small carbides



Steel: wt% C = 0.4, slow cooling rate

Ferrite + cementite



Steel: wt% C = 0.4, fast cooling rate

Ferrite needles+ perlite

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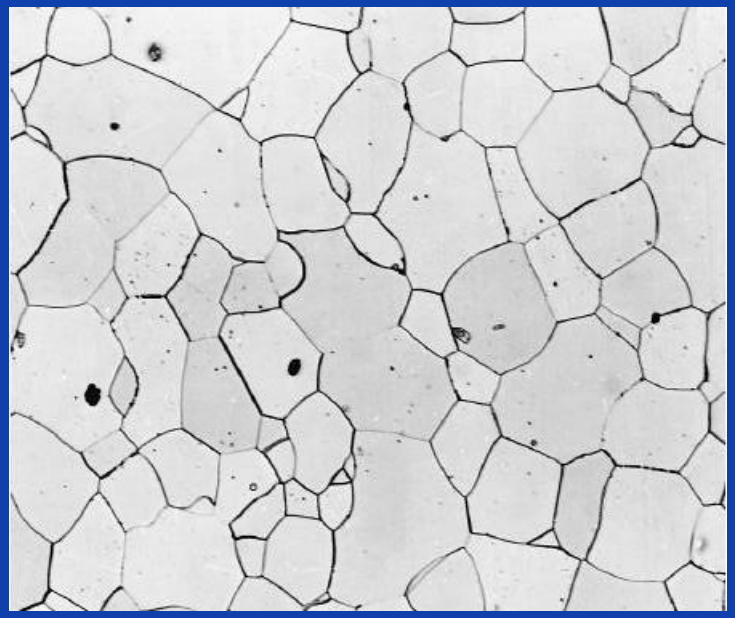
Microstructure evolution in multi-component alloys

- Connected grain structures
- Complex morphologies
- Concurrent processes
  - Solidification - grain growth - Ostwald ripening – diffusion - phase growth
- Materials' properties are largely related to microstructure
  - Material development
  - Reliability



Low C-steel, ferritic grain structure

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Microstructure evolution in multi-component alloys

- **High complexity**
  - **Anisotropy, segregation, solute drag, second-phase precipitates, pipe diffusion, mutual distribution of phases, …**
  - **Many material properties: Crystal structure, Gibbs energy, diffusion coefficient of different phases? Structure, energy, mobility of grain boundaries?**
  - **Evolution connected grain structure ?**
    - **→ Mesoscale simulations**
- **Importance**
  - **Material development: heat treatment, alloying**
  - **Reliability**

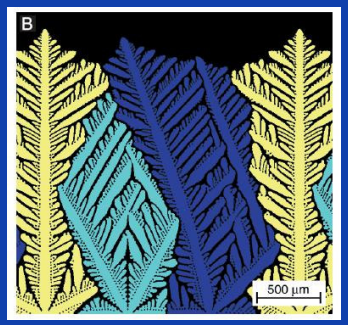
Phase-field modelling

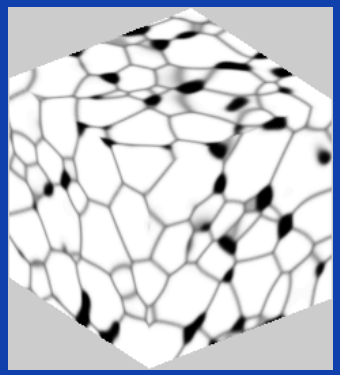
Strength

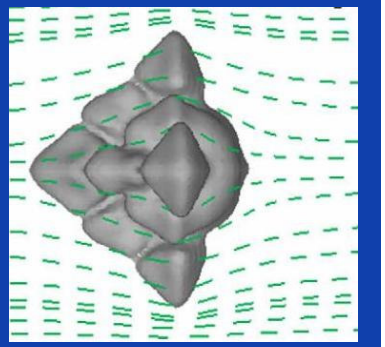
- Complex shapes
- Multi-grain, multi-phase structures
- Thermodynamic driving forces

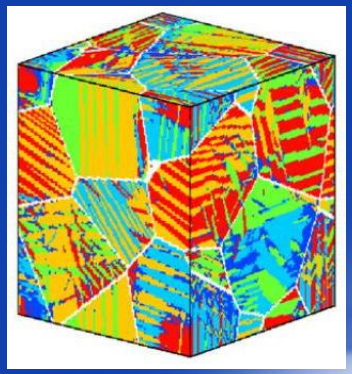
$$F = F_{chem} + F_{int} + F_{elast} + F_{magn} + \ldots$$

- Multi-component
- Transport equations
  - Mass and heat diffusion/convection









Difficulties

- Implementation for realistic length scales
- Parameter choice

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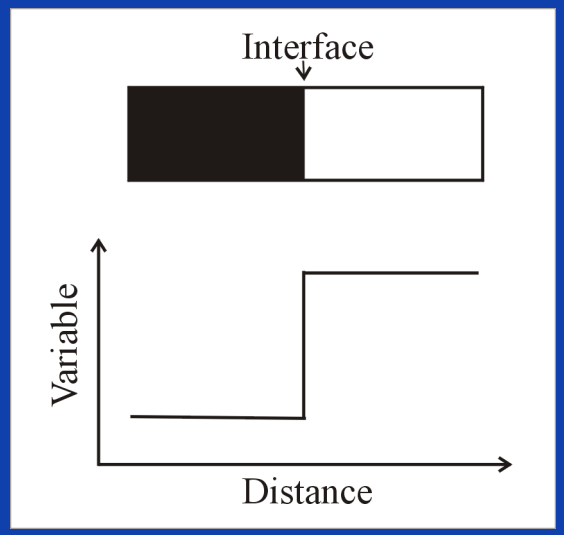
Principles of phase field modeling

- Diffuse interface concept
- Phase field variables
- Thermodynamic free energy functional
- Evolution equations
- Parameter assessment
- Numerical implementation

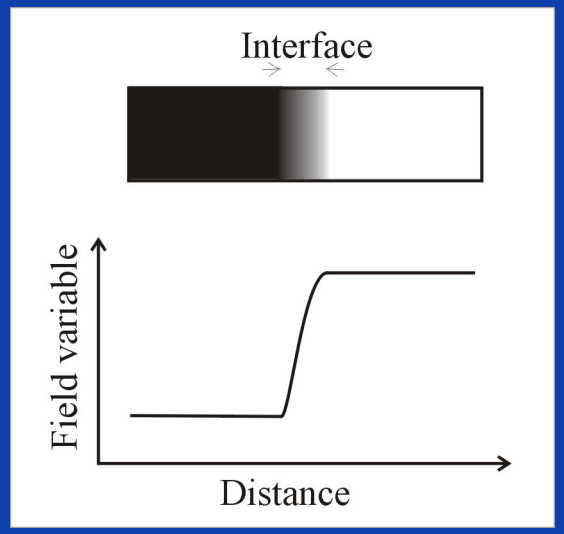
Diffuse-interface description

- **Sharp interface**



  - **Discontinuous variation in properties**
  - **Requires tracking of the interfaces**
  - **Simplified grain morphologies**

- **Diffuse interface**

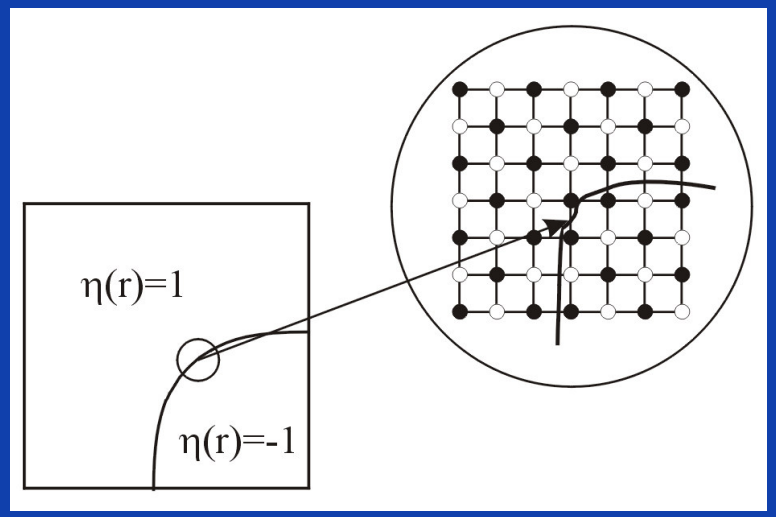


  - **Continuous variation in properties**
  - **Interfaces implicitly given by local variations in phase-field variables**
  - **Complex grain morphologies**

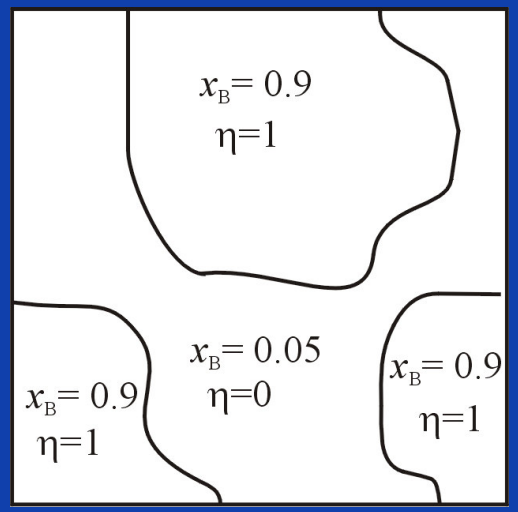
- *Diffuse interface approach (*van der Waals, Cahn-Hilliard (1958), Ginzburg-Landau (1950))
- Microstructure evolution started ± 20 years ago

Representation of microstructures

- **Phase-field variables: continuous functions in space and time**
  - **Local composition** $x_B(\vec{r},t), c_B(\vec{r},t)$
  - **Local structure and orientation** $\eta(\vec{r},t)$ $\phi(\vec{r},t)$



Antiphase boundary



Binary alloy A-B

- *Phase α: η = 0*
- *Phase β: η = 1*

Thermodynamics and kinetics

- **Free energy functional**

$$F = F_{bulk} + F_{surface} = \int_V f_0(x_i, \eta_k, T) + \frac{\kappa}{2}\sum_{k=1}^{p}(\nabla \eta_k)^2 + \frac{\varepsilon}{2}\sum_{i=1}^{C}(\nabla x_i)^2 dV$$

Homogeneous free energy (chemical, elastic, …)

Gradient free energy (→ diffuse interfaces)

- **Evolution of field variables**
  - **Non-conserved field variables (→ Interface movement)**

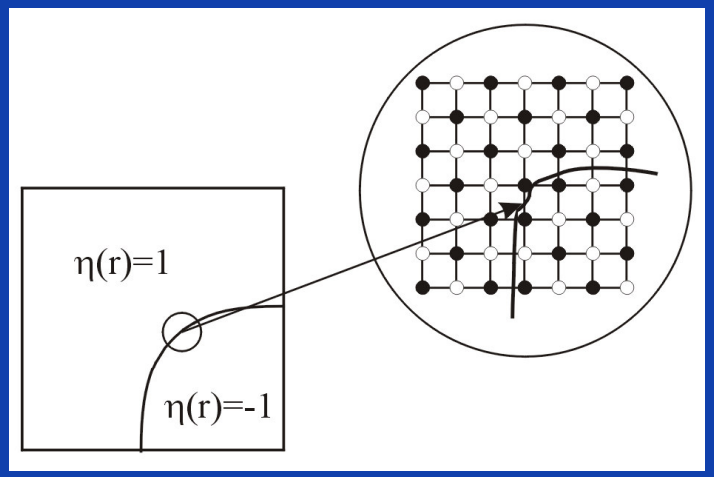
$$\frac{\partial \eta_k(\vec{r},t)}{\partial t} = -L\frac{\partial F(x_1,\ldots,x_C,\eta_1,\ldots,\eta_p)}{\partial \eta_k(\vec{r},t)} \qquad (+\xi(\vec{r},t))$$

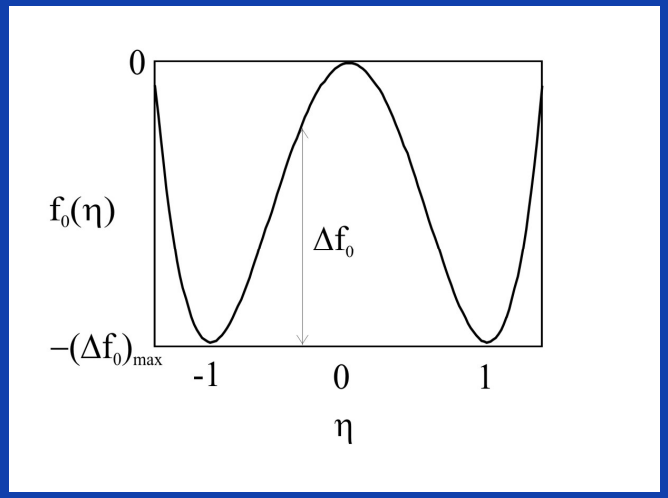
  - **Conserved composition fields (→ Mass diffusion)**

$$\frac{1}{V_m}\frac{\partial x_i(\vec{r},t)}{\partial t} = \vec{\nabla} M \cdot \vec{\nabla}\frac{\partial F(x_1,\ldots,x_C,\eta_1,\ldots,\eta_p)}{\partial x_i(\vec{r},t)} \qquad (+\xi(\vec{r},t))$$

Homogeneous free energy functional

- **Anti-phase boundary**





Boundary energy: $\propto \sqrt{\kappa(\Delta f_0)_{\max}}$

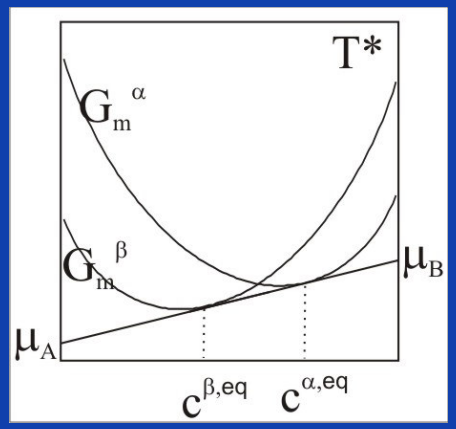
Boundary width: $\propto \sqrt{\dfrac{\kappa}{(\Delta f_0)_{\max}}}$

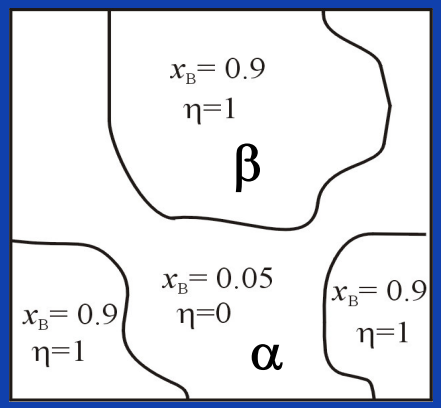
Boundary velocity: $\propto \kappa L$

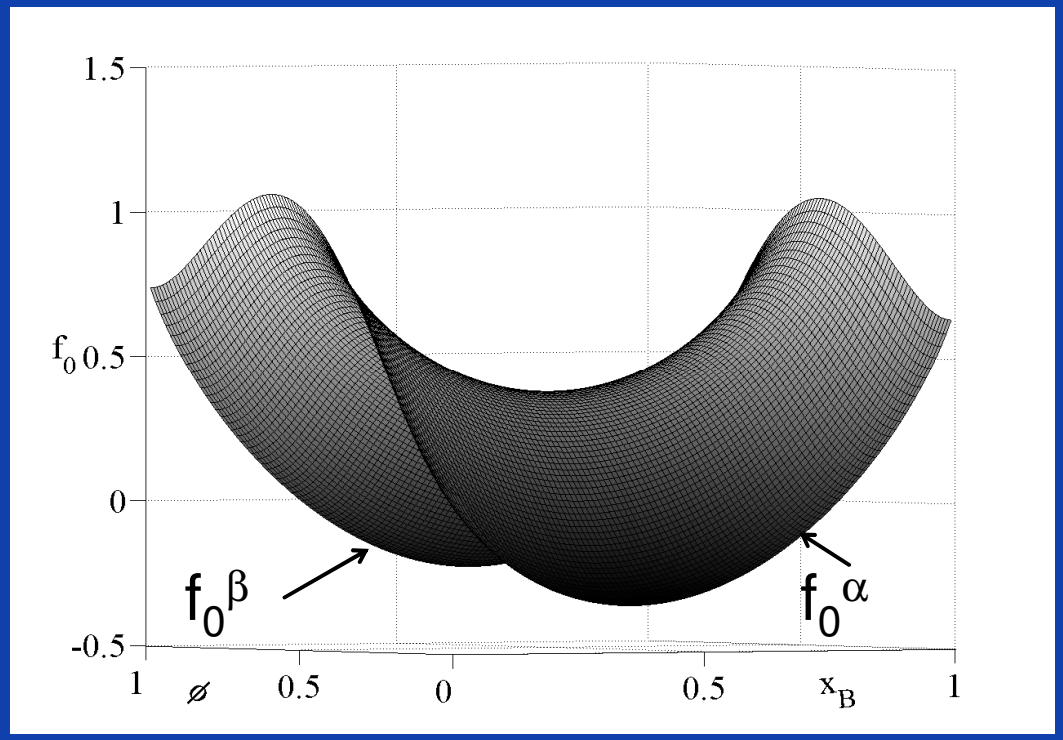
$$f_0 = 4(\Delta f_0)_{\max}\left(\frac{\eta^4}{4} - \frac{\eta^2}{2}\right)$$

Homogeneous free energy

- **Binary two-phase system**





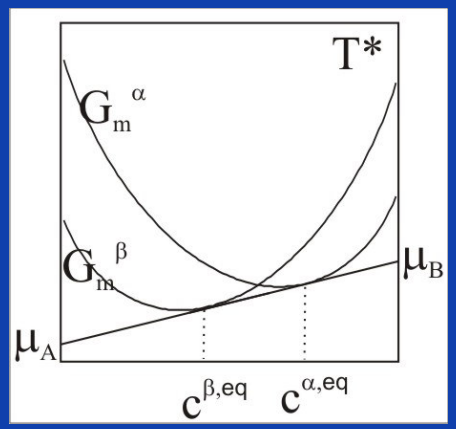


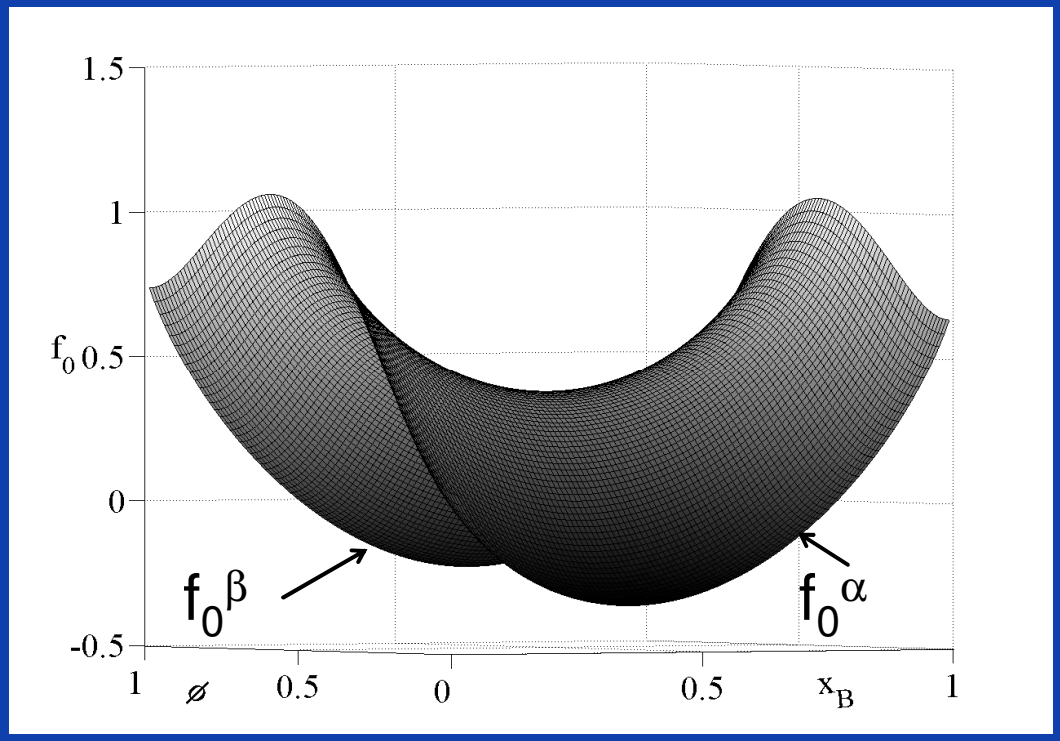
$$f_0 = h(\phi) f^{\beta}(c,T) + \left[1 - h(\phi)\right] f^{\alpha}(c,T) + \omega g(\phi)$$

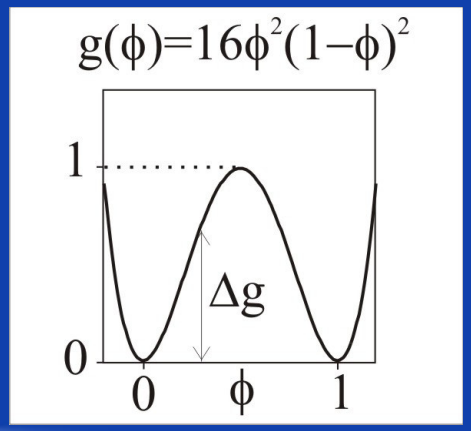
with $f^{\alpha}(c,T) = \dfrac{G_m^{\alpha}}{V_m}, \quad f^{\beta}(c,T) = \dfrac{G_m^{\beta}}{V_m}$ *(CALPHAD)*

Homogeneous free energy

- **Binary two-phase system**





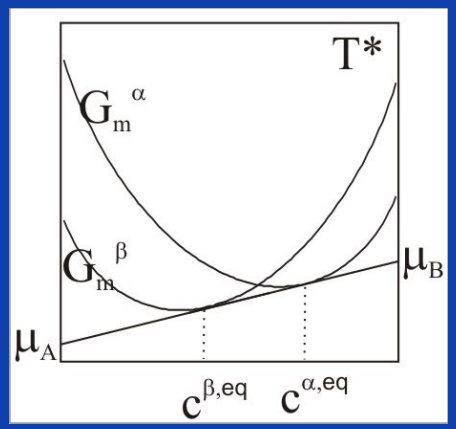


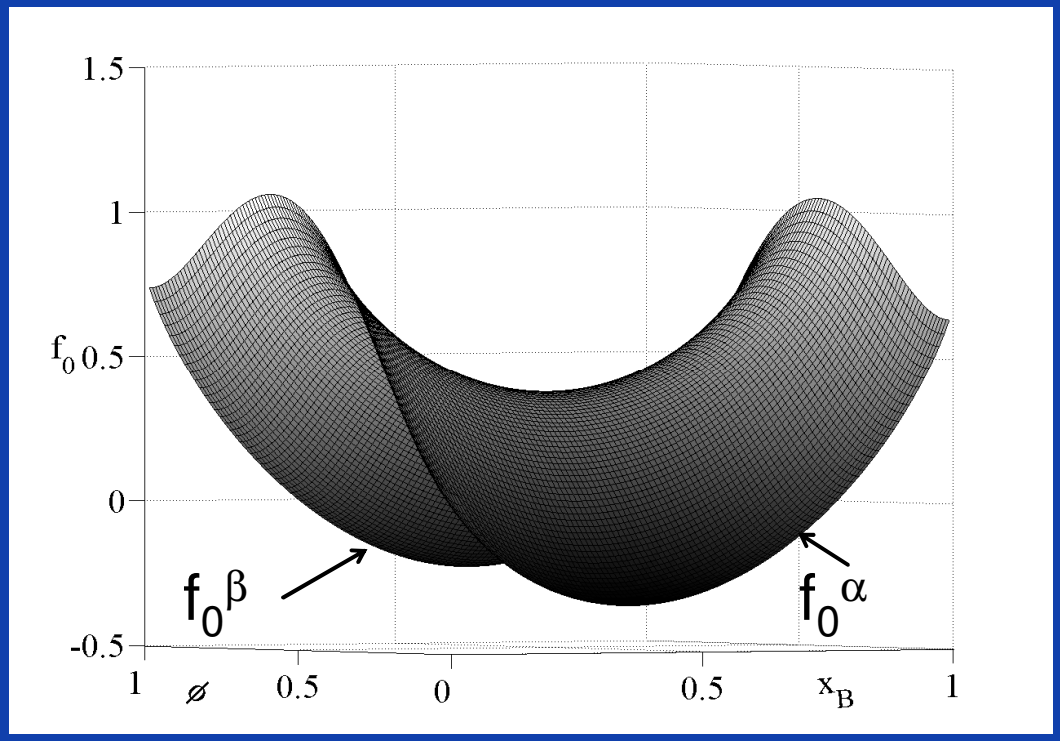
$$f_0 = h(\phi) f^{\beta}(c,T) + \left[1 - h(\phi)\right] f^{\alpha}(c,T) + \omega g(\phi)$$

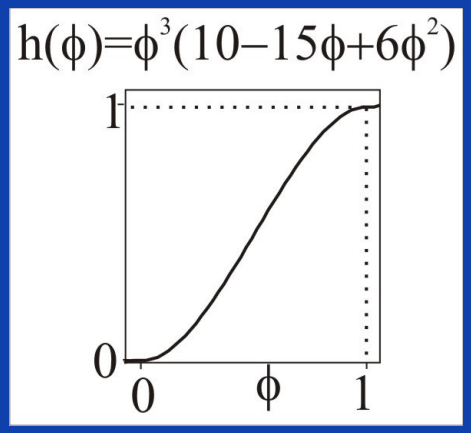
Double well function

Homogeneous free energy

- **Binary two-phase system**





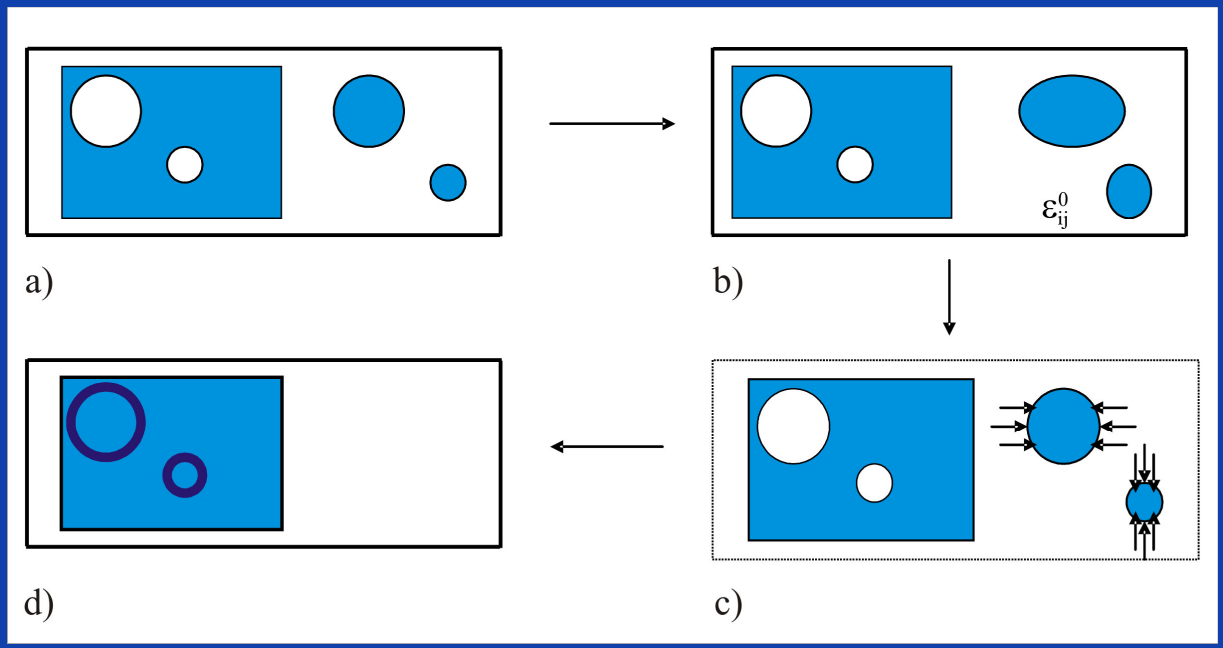


$$f_0 = h(\phi) f^{\beta}(c,T) + \left[1 - h(\phi)\right] f^{\alpha}(c,T) + \omega g(\phi)$$

Interpolation function

Effect of elastic stresses and strain

- Coupling with micro-elasticity theory → $F = F_{chem} + F_{int} + F_{elast}$
  - Effect of transformation and thermal strains, applied stress/strain
  - Martensitic transformation, precipitate growth



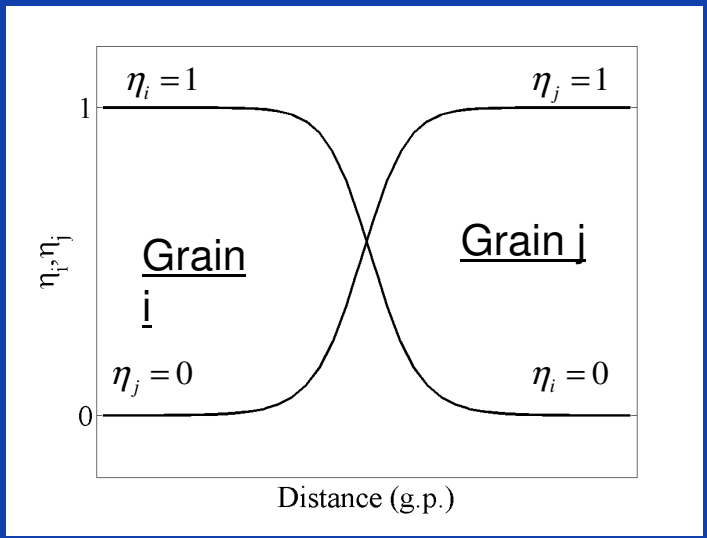
Polycrystalline structures

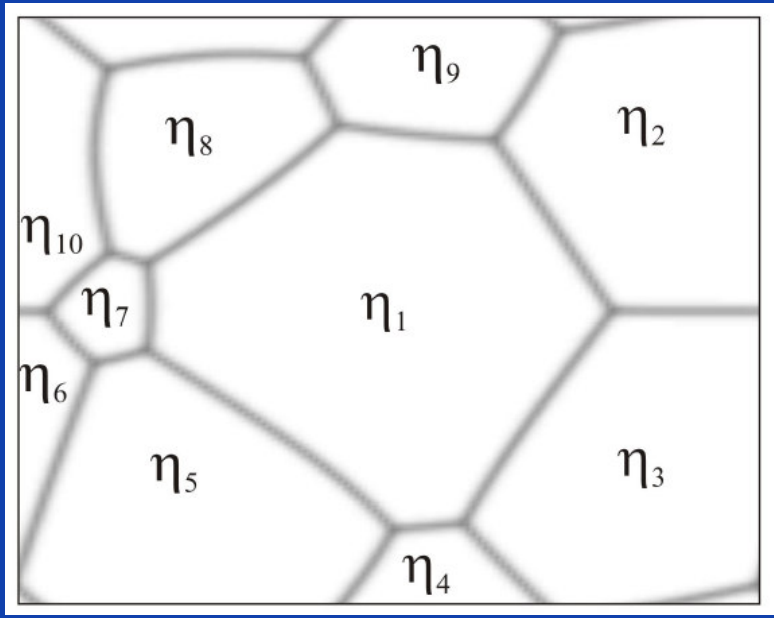
- **Polycrystalline microstructure**

$$\eta_1, \eta_2, \ldots, \eta_i(\vec{r}, t), \ldots, \eta_p$$

- **Grain i of matrix-phase**

$$(\eta_1, \eta_2, \ldots, \eta_i, \ldots, \eta_p) = (0, 0, \ldots, 1, \ldots, 0)$$





- **Free energy functional**

$$F = F_{surface} = \int_V f_0(\eta_1, \eta_2, \ldots \eta_p) + \frac{\kappa}{2} \sum_{k=1}^{p} (\nabla \eta_k)^2 dV$$

Multi-phase and multi-component alloys

- **Phase field variables:**
  - **Grains**

$$\eta_{\alpha 1}, \eta_{\alpha 2}, \ldots, \eta_{\alpha i}(\vec{r}, t), \ldots,$$

$$\eta_{\beta 1}, \eta_{\beta 2}, \ldots \eta_{p}$$

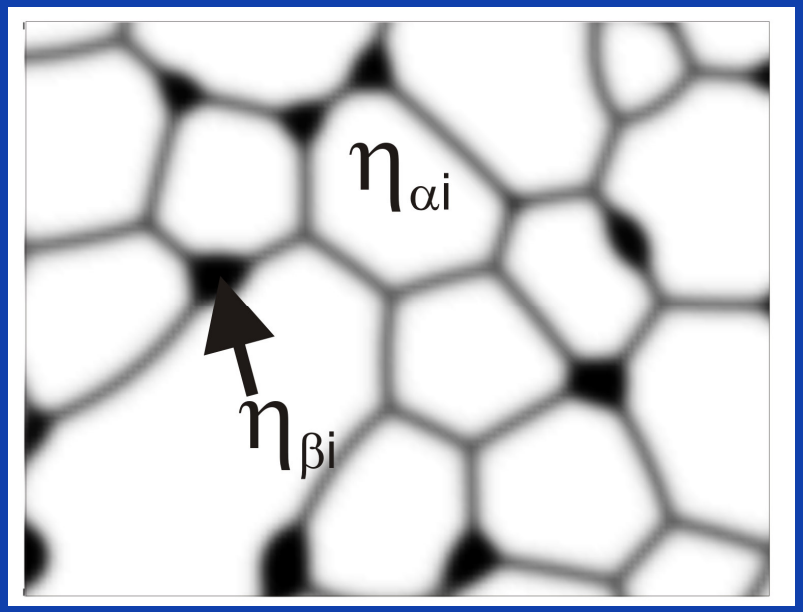
  - **Composition**

$$x_A, x_B(\vec{r}, t), \ldots, x_{C-1}$$

- **Free energy functional**

$$f_{bulk}(x_k, \eta_{\rho i}) = \sum_{\rho} h_{\rho}(\eta_{\rho i}) f^{\rho}(x_k^{\rho})$$

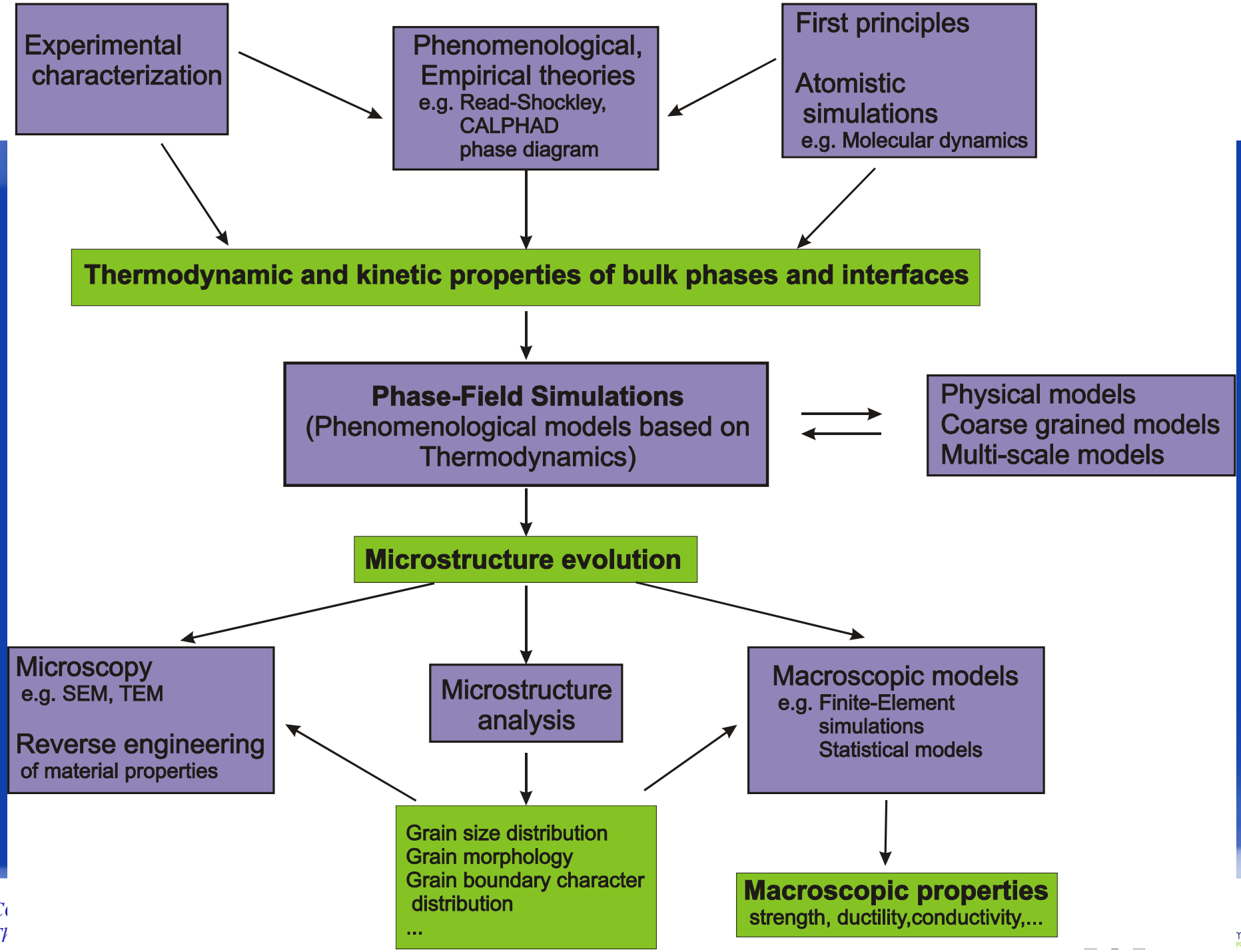
$$= \sum_{\rho} h_{\rho}(\eta_{\rho i}) \frac{G_m^{\rho}(x_k^{\rho})}{V_m}$$



2 phase polycrystalline structure

Parameter assessment

- Different kinds of input data (calculated and/or measured)
  - Phase stabilities, phase diagram information
    - CALPHAD ← (ab-initio, experiments)
  - Interfacial energy and mobility
    - ab-initio, (MD, MC ← ab-initio), experimental
  - Elastic properties, crystal structure, lattice parameters
    - ab-initio, experimental
  - Atomic diffusion mobilities
    - CALPHAD ← ((MC ← ab-initio), experimental)
- Orientation and composition dependence
  - Anisotropy, segregation, solute drag


Experimental characterization
Phenomenological, Empirical theories
e.g. Read-Shockley, CALPHAD phase diagram
First principles
Atomistic simulations
e.g. Molecular dynamics
Thermodynamic and kinetic properties of bulk phases and interfaces
Phase-Field Simulations
(Phenomenological models based on Thermodynamics)
Physical models
Coarse grained models
Multi-scale models
Microstructure evolution
Microscopy
e.g. SEM, TEM
Reverse engineering
of material properties
Microstructure analysis
Macroscopic models
e.g. Finite-Element simulations
Statistical models
Grain size distribution
Grain morphology
Grain boundary character distribution
...
Macroscopic properties
strength, ductility,conductivity,...

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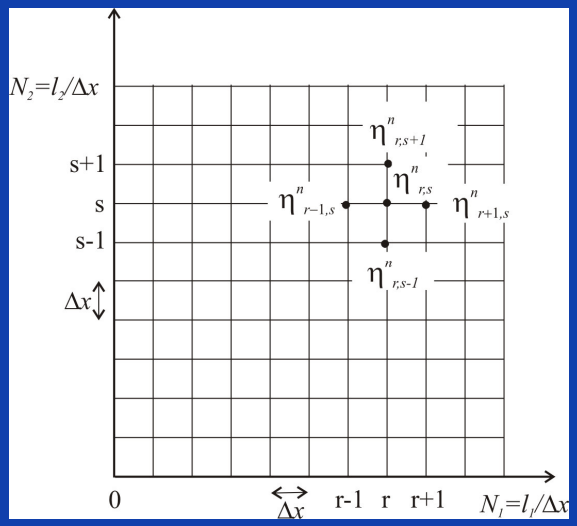
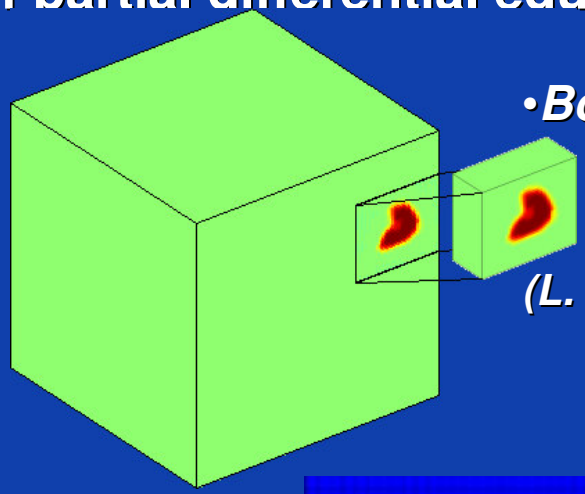
Quantitative aspects

- Numerical solution of partial differential equations

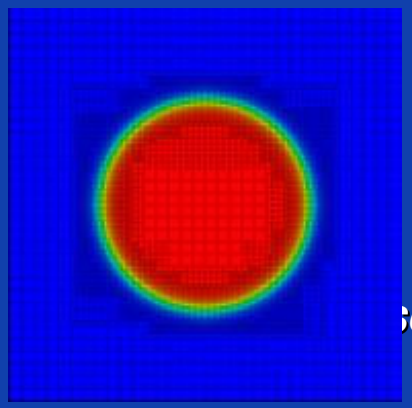


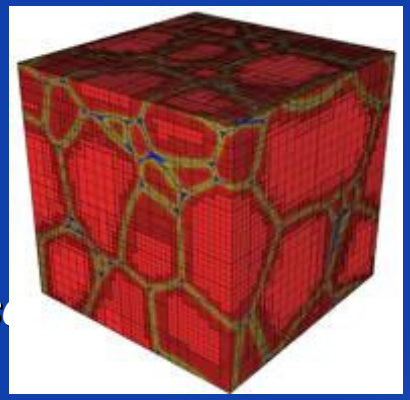


- *Bounding box algortihm*
  - *Sparse data structure*
  - *Object oriented C++*

(L. Vanherpe et al., K.U.Leuven)

- *Discretization (Finite differences, finite elements, Fourier-spectral method*





MICRESS, commercial software forphase-field coupled with CALPHAD

- *Adaptive meshing (M. Dorr et al. AMPE, LLNL)*

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Examples of applications

- Anisotropic grain growth
- Precipitates on grain boundaries
- Lead-free solder systems
- Solidification

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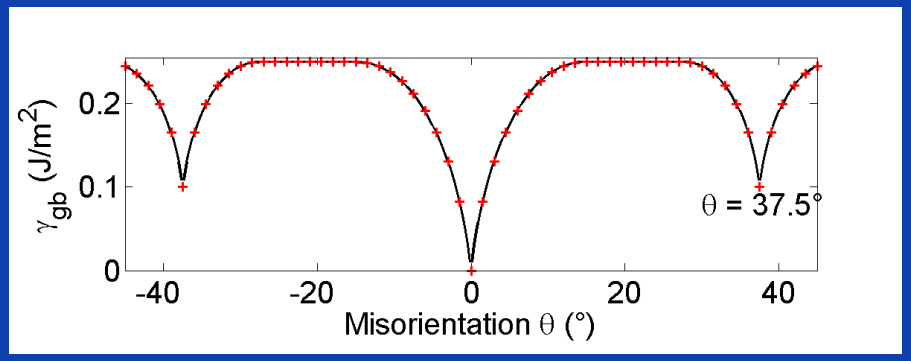
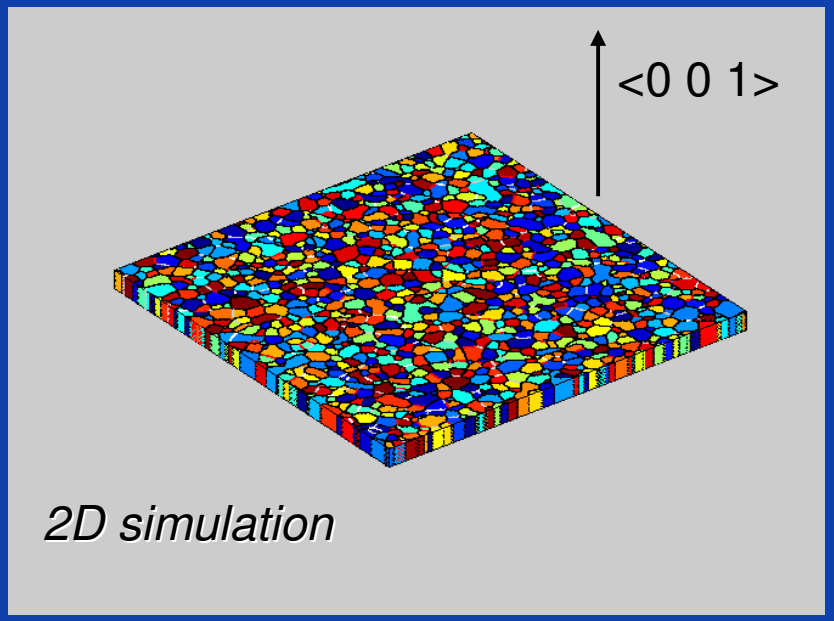
Columnar films with fiber texture

- **Grain boundary energy:**
  - **Fourfold symmetry**
  - **Extra cusp at θ = 37.5°**
  - **Read-shockley**





- **Discrete orientations**

$$\eta_1, \eta_2, \ldots, \eta_i(\vec{r}, t), \ldots, \eta_{60} \Rightarrow \Delta\theta = 1.5°$$

- **Constant mobility**
- **Initially random grain orientation and grain boundary type distributions**

White: $\theta = 1.5$
Gray: $\theta = 3$
Red: $\theta = 37{,}5$
Black: $\theta > 3$, $\theta \neq 37.5$

In collaboration with F. Spaepen, School of Engineering and Applied Sciences, Harvard University

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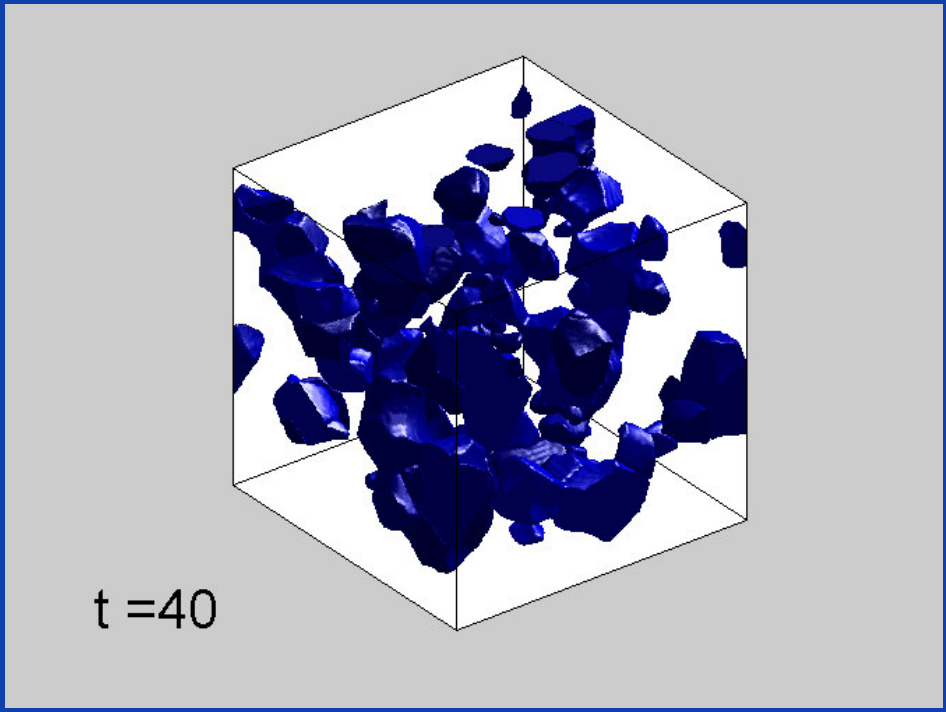
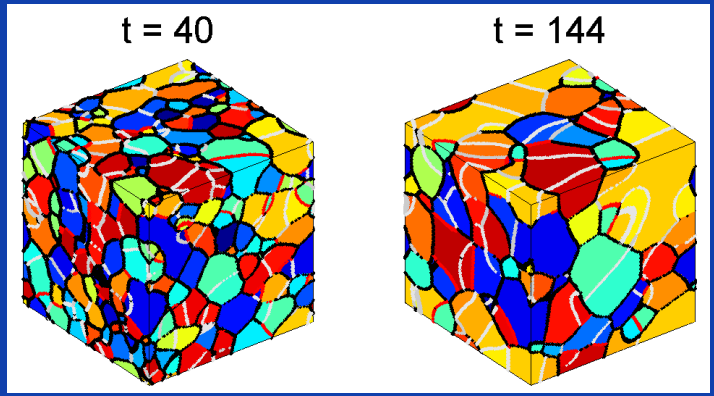
3D simulations for wires with fiber texture

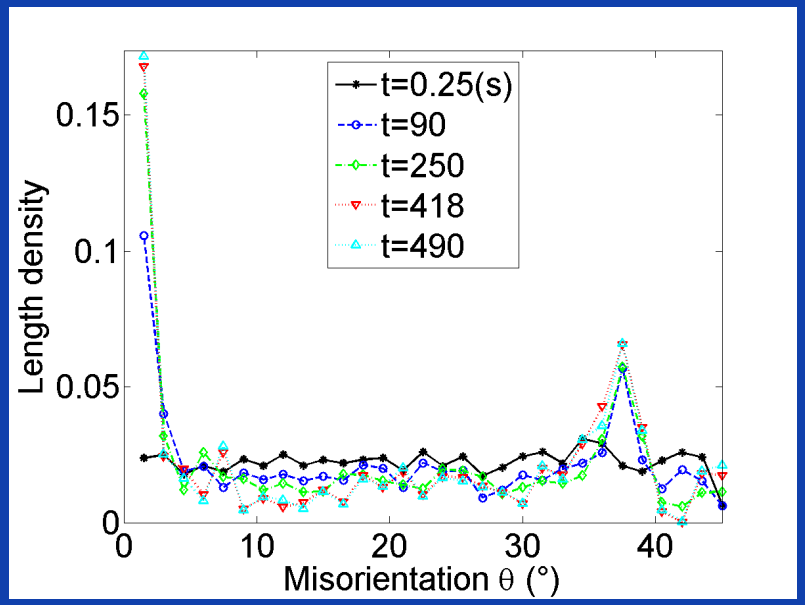


$\vartheta < 6°$

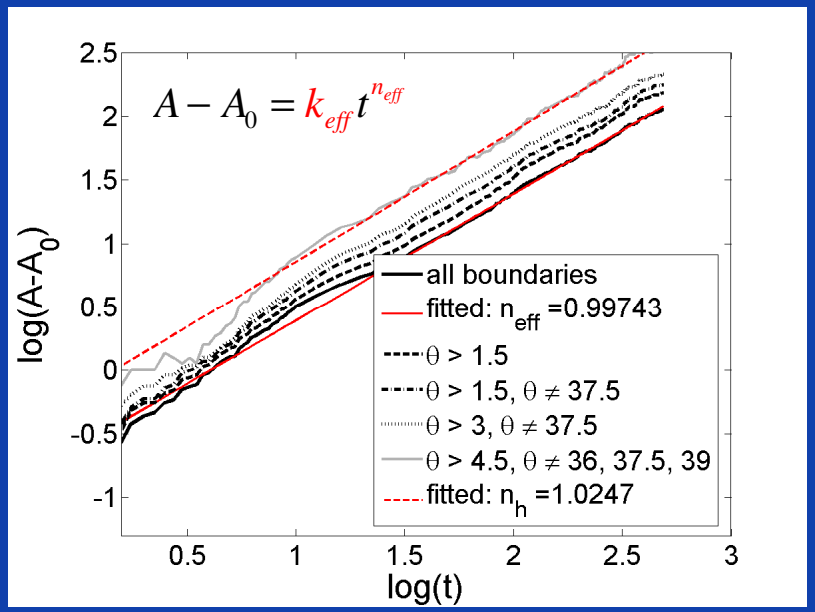


Microstructure analysis: films

- **Misorientation distribution function (MDF)**



- **Evolution mean grain area**



$$n_{eff} = \frac{kt}{A_h(0) + kt} \rightarrow 1, t \rightarrow \infty$$

$$k_{eff} = \frac{dA_{eff}}{dt} = \frac{k}{1 + N'/N}$$

- **Evolution towards stead-state regime**
  → Simple mean field models

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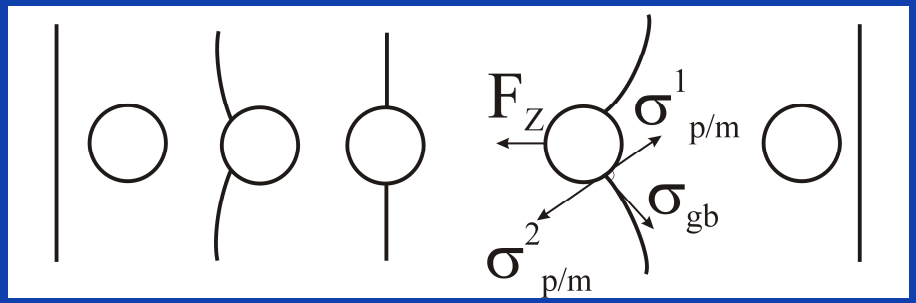
Examples of applications

- Anisotropic grain growth
- Precipitates on grain boundaries
- Lead-free solder systems
- Solidification

Zener pinning

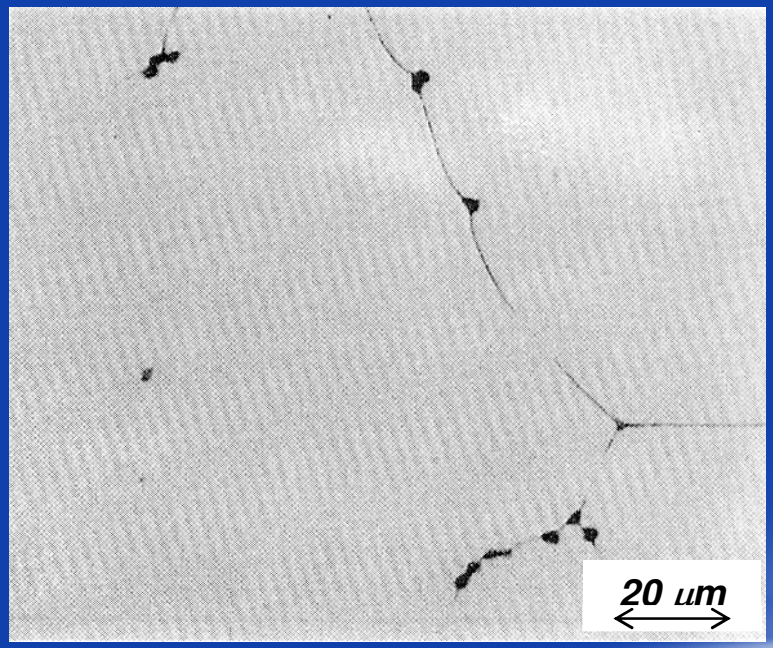
- **Mechanism for controlling grain size**
  - **E.g. *NbC, AlN, TiN,... in HSLA-steels***
  - **Nano-grain structures**



- **Zener relation for limiting grain size**

$$\frac{\overline{R}_{\lim}}{\overline{r}} = K \frac{1}{f_V^b}$$

- **Influence of**
  - **Shape of the particle**
  - **Interfacial properties of particles**
  - **Initial distribution**
  - **Evolution particles**



Fe-0.09 to 0.53 w% C-0.02 w% P with Ce2O3 inclusions (PhD. M. Guo)

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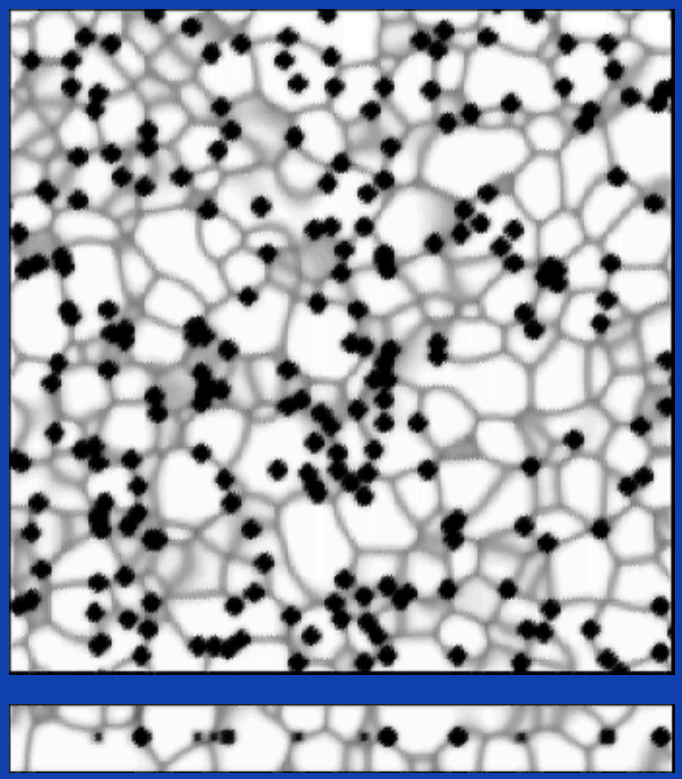
Simulation results: Al thin films

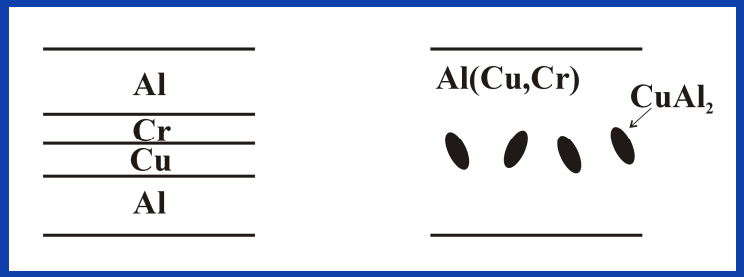
- **Thin films with $CuAl_2$ - precipitates**

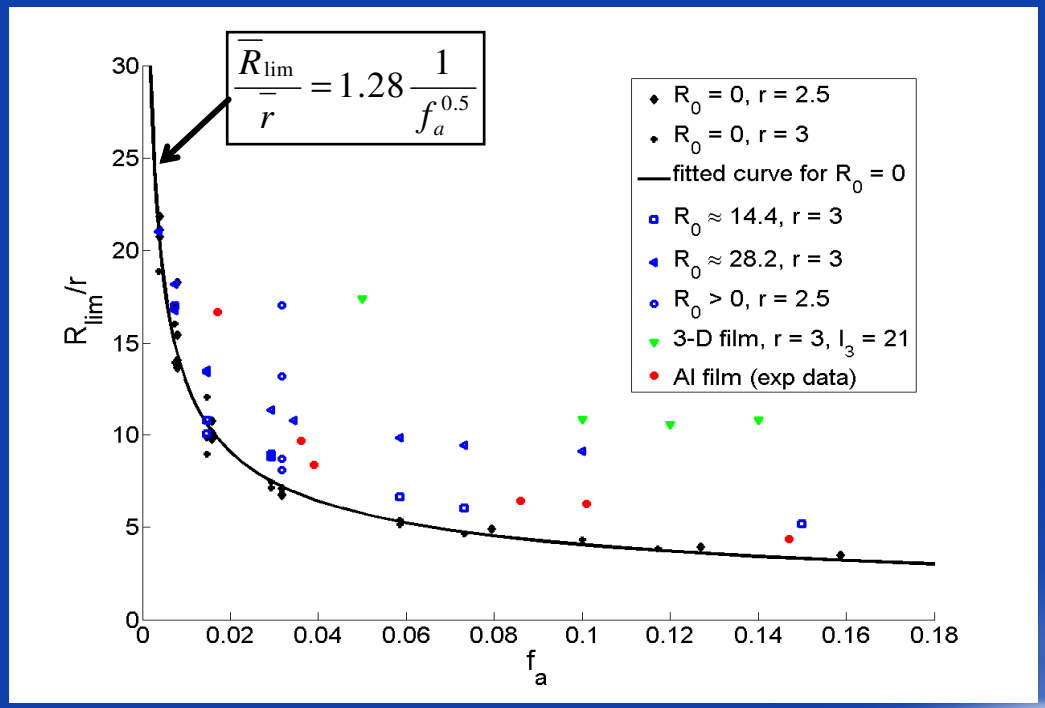


$$r = 3, f_a = 0.12, l_3 = 21$$

(exp from H.P. Longworth and C.V. Thompson*)*

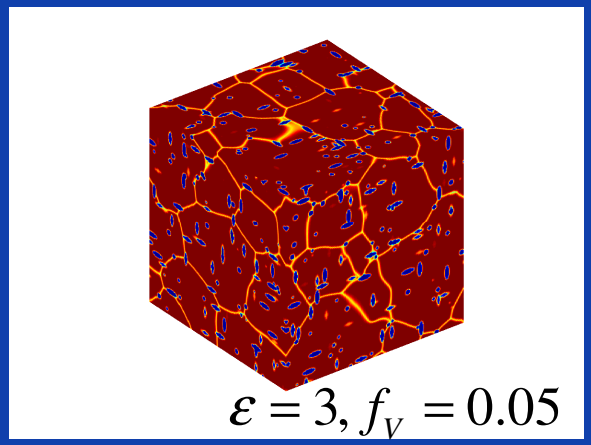
Film preparation

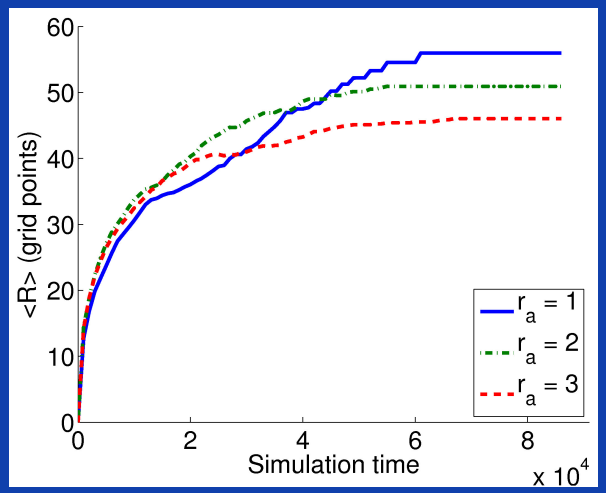




Simulation results: effect of particle shape and coarsening

- **Ellipsoid particles**





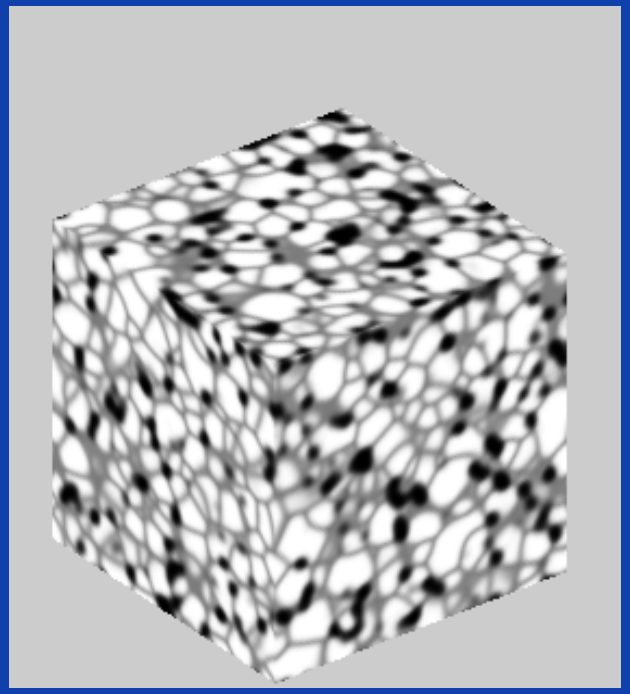
Modified Zener relation

$$\frac{\overline{R}_{\lim}}{s} = K \frac{r_a}{1 + a r_a} \frac{1}{f_V^b}$$

$$K = 3.7, b = 1, a = 3.1$$

L. Vanherpe, K.U. Leuven

- **Evolving particles**



f_V=0.12, L=10M

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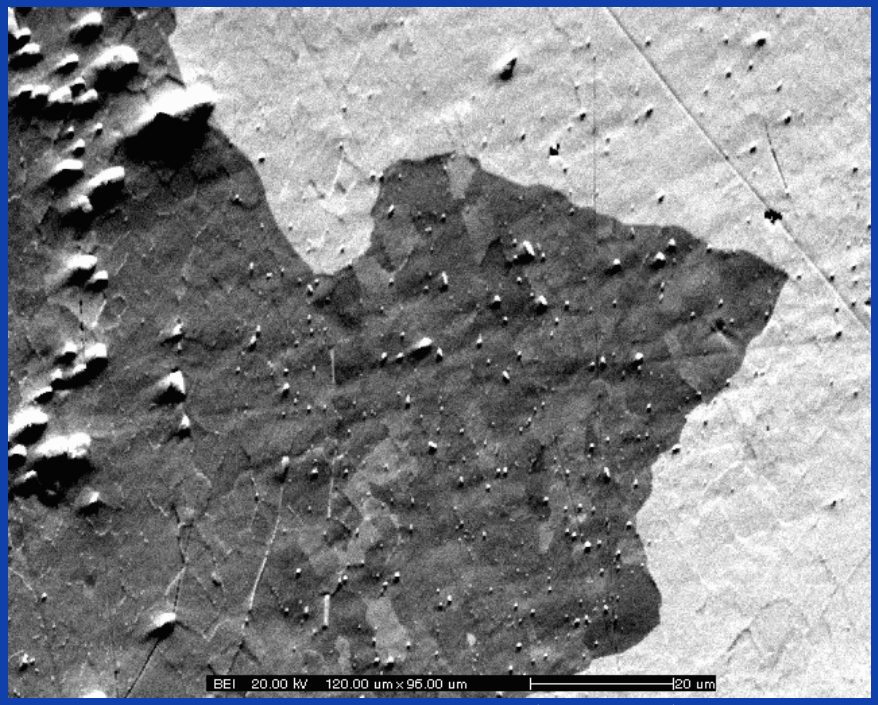
Jerky motion during recrystallization in Al-Mn alloy

- **In-situ EBSD observation of recrystallization in AA3103 at 400 ℃**
  - **CamScan X500 Crystal Probe FEGSEM**
- **Jerky grain boundary motion**
  - **Stopping time: 15-25 s**
  - **Pinning by second-phase precipitates**
    - **$Al_6(Fe,Mn)$, α-$Al_{12}(Fe,Mn)_3Si$**
- **Added to phase field model**
  - **Grain boundary diffusion**
  - **Driving force for recrystallization**



20μm

In collaboration with A. Miroux, E. Anselmino, S. van der Zwaag, T. U. Delft

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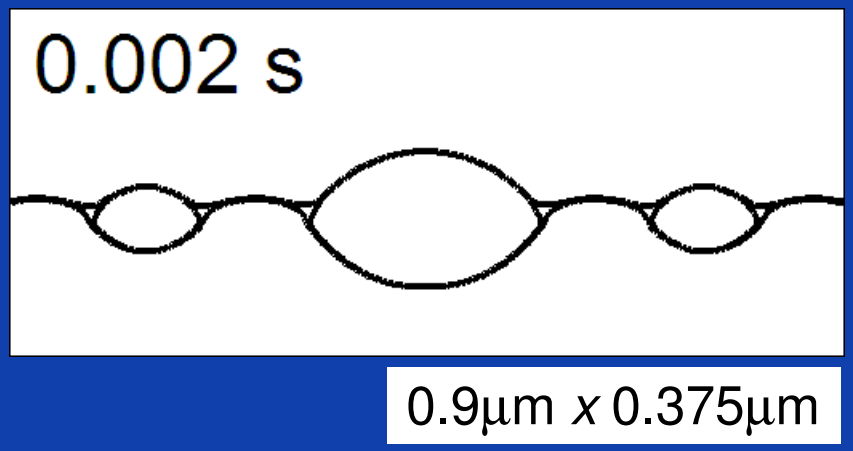
Material properties at 723K

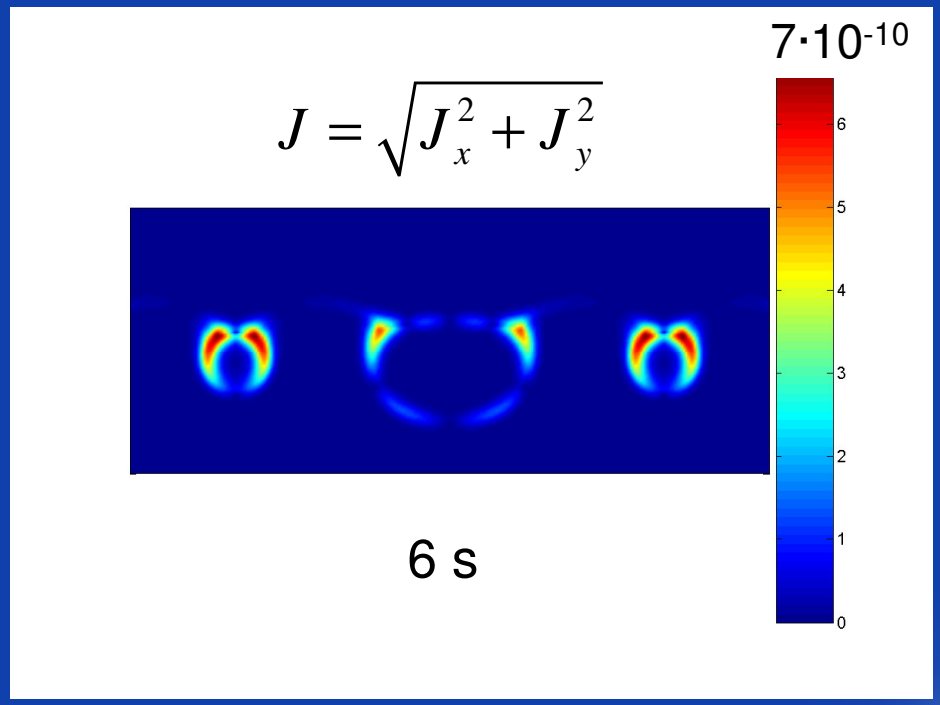
Grain boundary energy high angle	$\gamma_h = 0.324$ J/m^2
Interfacial energy Al_6Mn precipitates	$\gamma_{pr} = 0.3$ J/m^2
Mobility high angle grain boundary At solute content 0.3w% Mn	$M_h = 2.94 \cdot 10^{-11}$ m^{2}s/kg (Miroux et al.,Mater. Sci. Forum,467-470,393(2004))
Equilibrium composition of matrix	$c_{Mn,eq} = 0.0524$ w% (0.02456 at%) (PhD thesis Lok 2005)
Actual composition of matrix (supersaturated)	$c_{Mn} = 0.3$ w% (0.1474 at%) (PhD thesis Lok 2005)
Mn diffusion in fcc Al	$D_{0,bulk} = 10^{-2}$ m^2/s, $Q_{bulk} = 211$ kJ/mol $\rightarrow D_{bulk} = 5.5973 \cdot 10^{-18}$ m^2/s
Pipe diffusion high angle boundaries, precipitate/matrix interface	$D_{0,p} = D_{0,bulk}$, $Q_p = 0.65 Q_{bulk}$ $\rightarrow D_p = 1.2195 \cdot 10^{-12}$ m^2/s
Bulk energy density: $f^\rho = A^\rho (x - x^\rho_0)^2$	$A^m = 6 \cdot 10^{11}$; $x^m_0 = 0.000258$ $A^\rho = 6 \cdot 10^{12}$; $x^\rho_0 = 0.1429$

Precipitate coarsening and unpinning

- $P_D < P_{ZS}$ ($P_D \approx P_{ZS}$)
  - Pinning: P_{ZS}=3.6 MPa
  - Rex: P_D=3.1 MPa

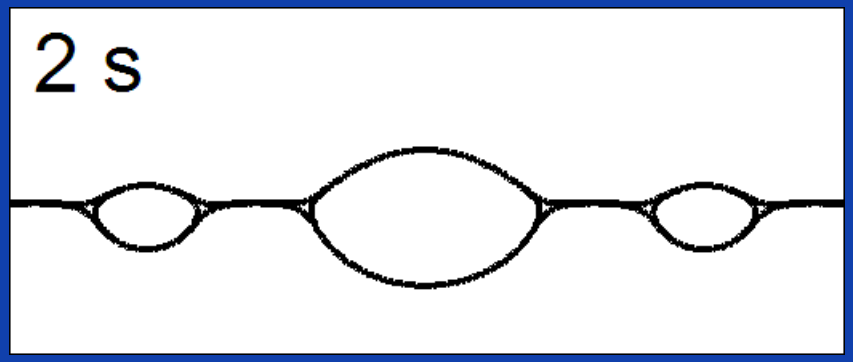


- Unpinning mainly through surface diffusion around precipitates



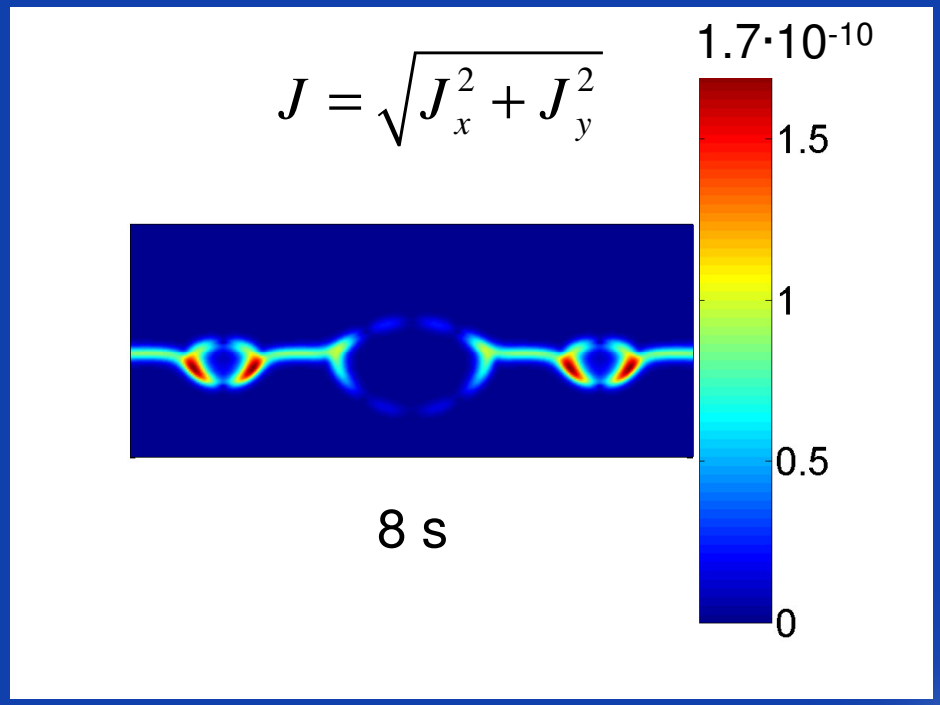
Precipitate coarsening and unpinning

- $P_D <<< P_{ZS}$
  - Pinning: P_{ZS} = 3.6 MPa
  - Rex: P_D = 1.1 MPa



0.9µm *x* 0.375µm

- Unpinning through grain boundary diffusion



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Examples of applications

- Anisotropic grain growth
- Precipitates on grain boundaries
- Lead-free solder systems
- Solidification

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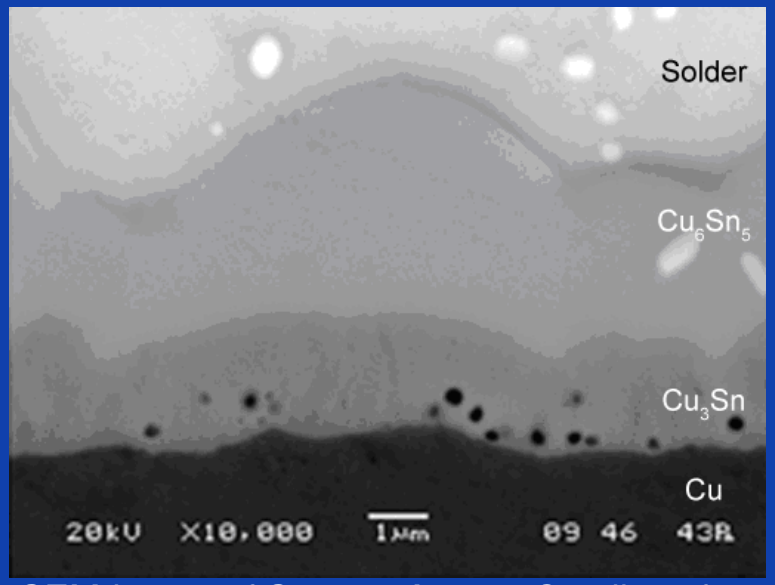
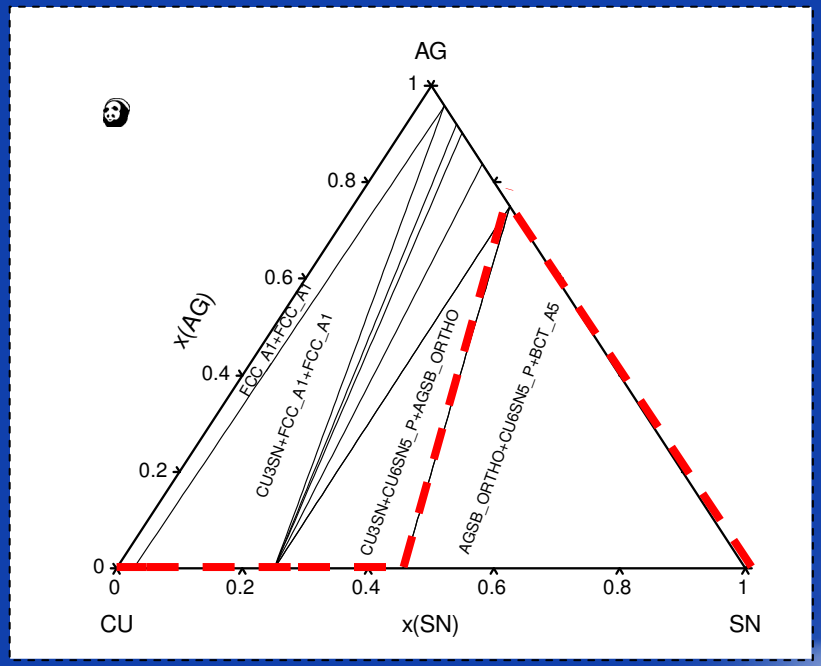
Coarsening in Sn(-Ag)-Cu solder joints

- **COST MP-0602 (Advanced Solder Materials for High Temperature Application)**
  - **IMC formation and growth – precipitate growth – Kirkendal voids – stresses – grain boundary diffusion**
    - **CALPHAD description**
    - **Diffusion coefficients, growth coefficient for IMC-layers**

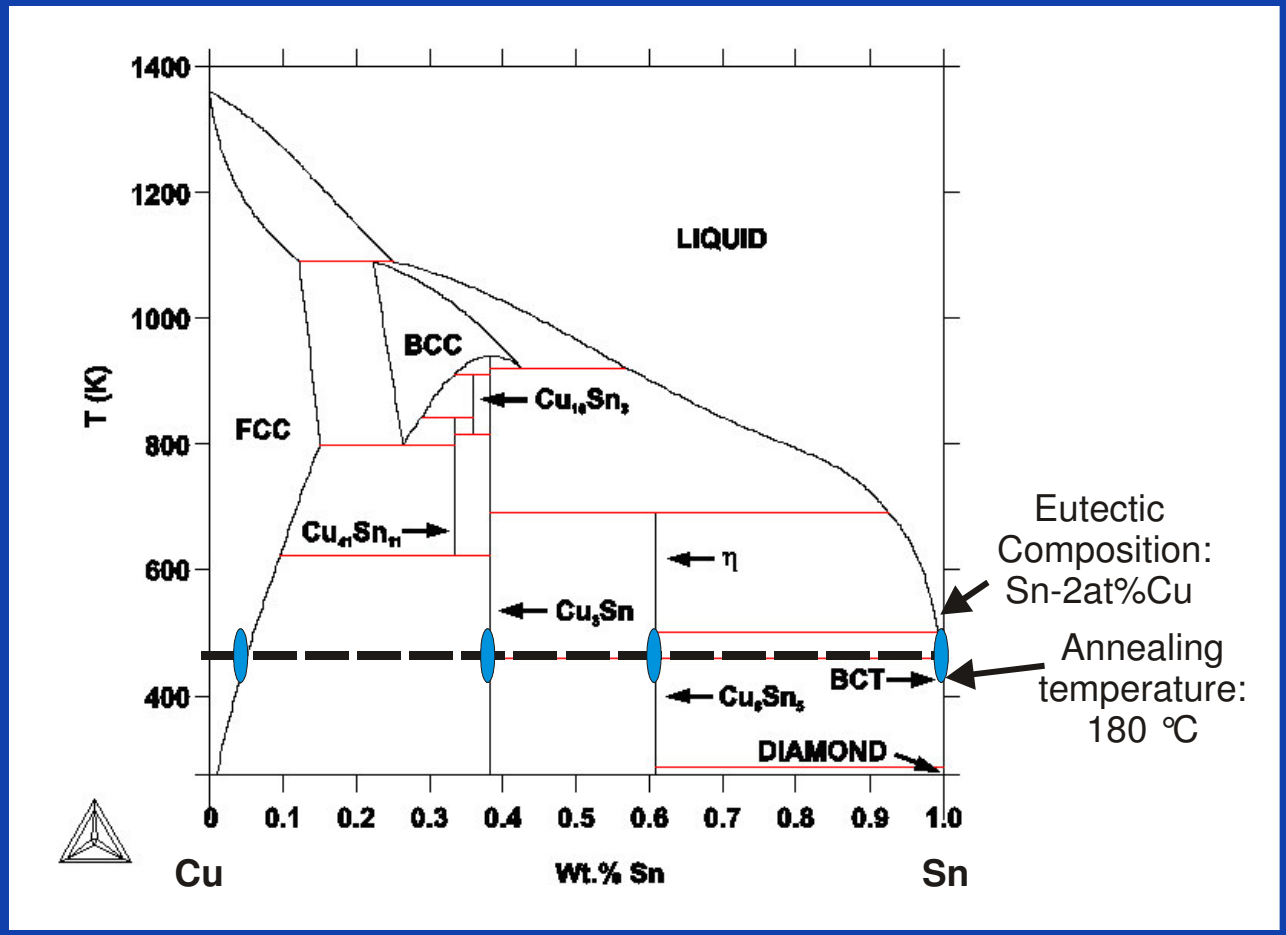


SEM-image of Sn – 3.8Ag–0.7 Cu alloy after annealing for 200h at 150 °C



Cu-Sn system

- **Equilibrium compositions**



- **Interdiffusion coeffcients**

$$D_{Sn}^{(Cu)} = 10^{-25}$$

$$D_{Sn}^{Cu3Sn} = 5 \cdot 10^{-16}\,\mathrm{m^2/s}$$

$$D_{Sn}^{Cu6Sn5} = 10^{-15}\,\mathrm{m^2/s}$$

$$D_{Sn}^{(Sn)} = 10^{-12}\,\mathrm{m^2/s}$$

- **Interfacial energy**

$$\sigma_{gb} = 0.35 \quad \mathrm{J/m^2}$$

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Effect of precipitates in Sn-2at%Cu

- **Interdiffusion coefficients:**

$$D_{Sn}^{(Cu)} = 10^{-25}, 10^{-12}\,\mathrm{m^2/s}$$

$$D_{Sn}^{Cu6Sn5} = 10^{-16}, 10^{-13}, 10^{-12}\,\mathrm{m^2/s}$$

$$D_{Sn}^{(Sn)} = 10^{-12}\,\mathrm{m^2/s}$$

- **Interfacial energies:**

$$0.35\,\mathrm{J/m^2}$$

- **Initial volume fraction precipitates:**

$$f_V = 0.04$$

- **Interfacial reactions are diffusion controlled**

- ***Initial compositions***

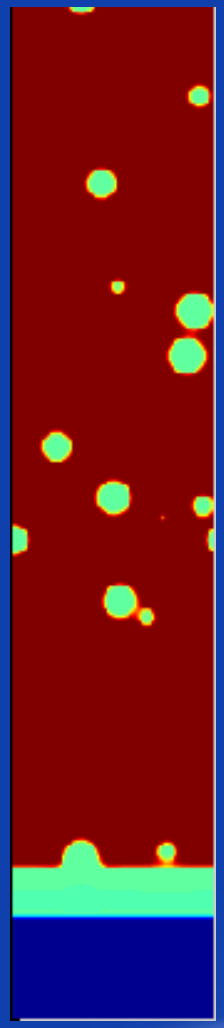
Solder:
$x_{Sn,0} = 0.98$

(Sn)-matrix
$x_{Sn} = 0.999$

Cu_6Sn_5-precipitates
$x_{Sn} = 0.4545$

IMC layer
Cu_6Sn_5
$x_{Sn} = 0.4545$

(Cu)-substrate
$x_{Sn} = 0.001$



- **System size: 0.1μmx0.5μm**

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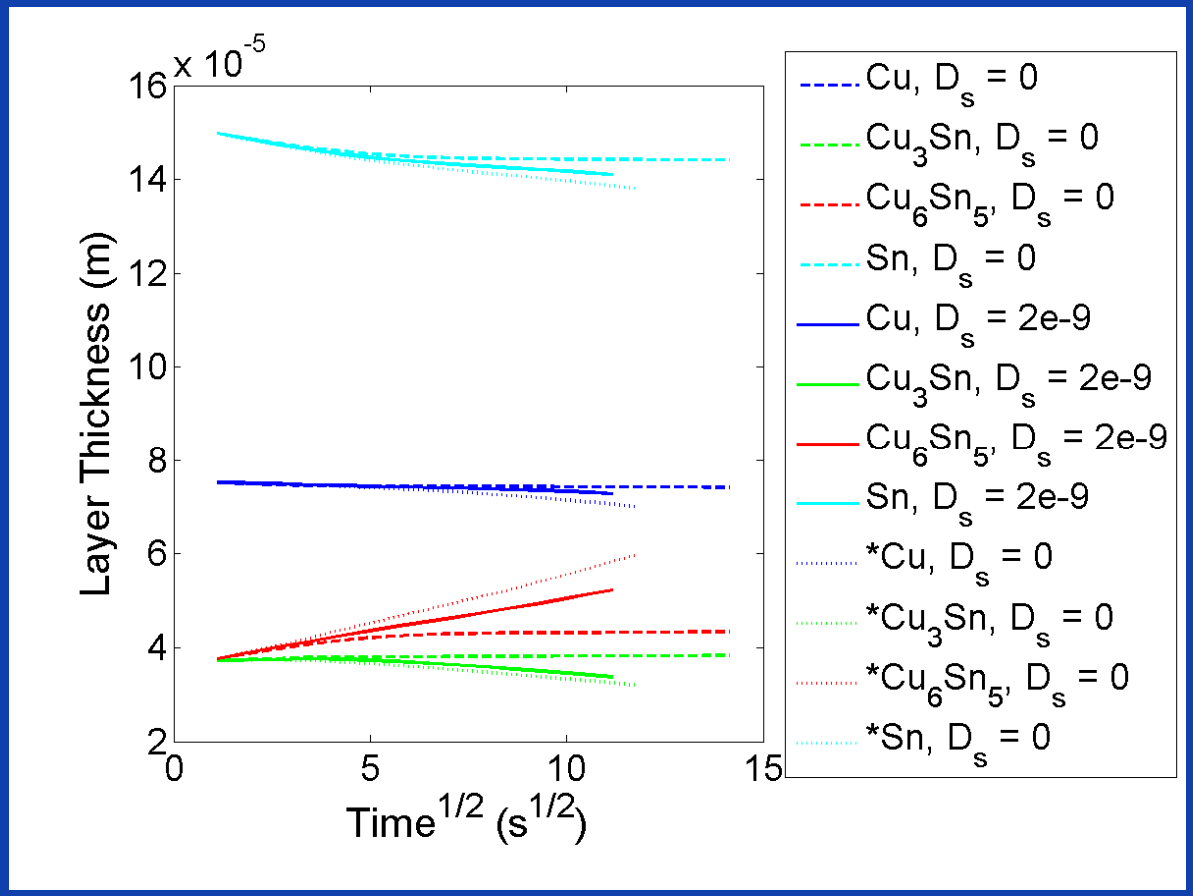
Effect of grain boundary diffusion

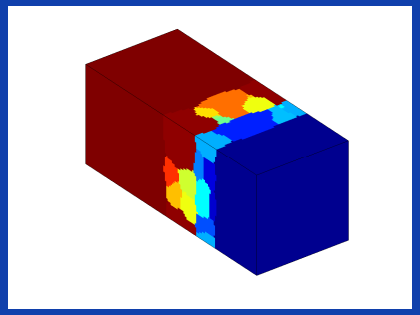


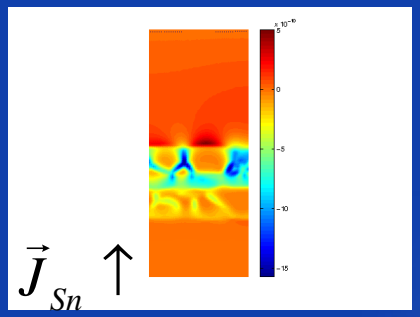
$$D_{Sn}^{(Cu)} = 2\cdot 10^{-25}, *2\cdot 10^{-25}\,\mathrm{m}^2/\mathrm{s}$$

$$D_{Sn}^{Cu3Sn} = 2\cdot 10^{-15}, *2\cdot 10^{-13}\,\mathrm{m}^2/\mathrm{s}$$

$$D_{Sn}^{Cu6Sn5} = 2\cdot 10^{-15}, *2\cdot 10^{-13}\,\mathrm{m}^2/\mathrm{s}$$

$$D_{Sn}^{(Sn)} = 2\cdot 10^{-12}, *2\cdot 10^{-12}\,\mathrm{m}^2/\mathrm{s}$$





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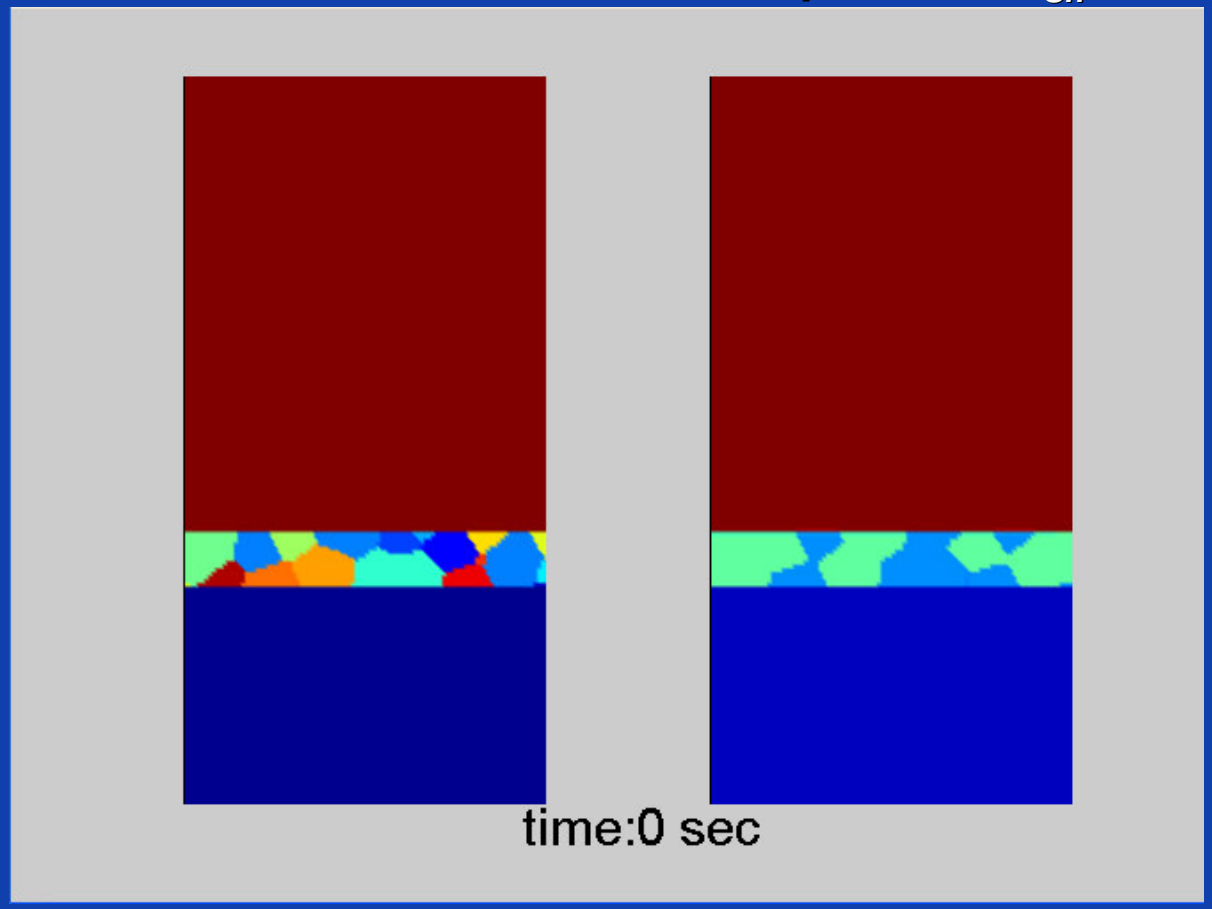
Growth behavior Cu_3Sn ?

Grain structure **Composition: x_{Sn}**



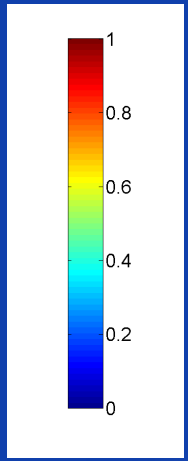
$$D_{Sn}^{(Cu)} = 2 \cdot 10^{-25}\,\mathrm{m}^2/\mathrm{s}$$

$$D_{Sn}^{Cu3Sn} = 2 \cdot 10^{-15}\,\mathrm{m}^2/\mathrm{s}$$

$$D_{Sn}^{Cu6Sn5} = 2 \cdot 10^{-15}\,\mathrm{m}^2/\mathrm{s}$$

$$D_{Sn}^{(Sn)} = 2 \cdot 10^{-12}\,\mathrm{m}^2/\mathrm{s}$$

$$\mathrm{D}_{Sn}^{surf} = 2 \cdot 10^{-12}\,\mathrm{m}^2/\mathrm{s}$$



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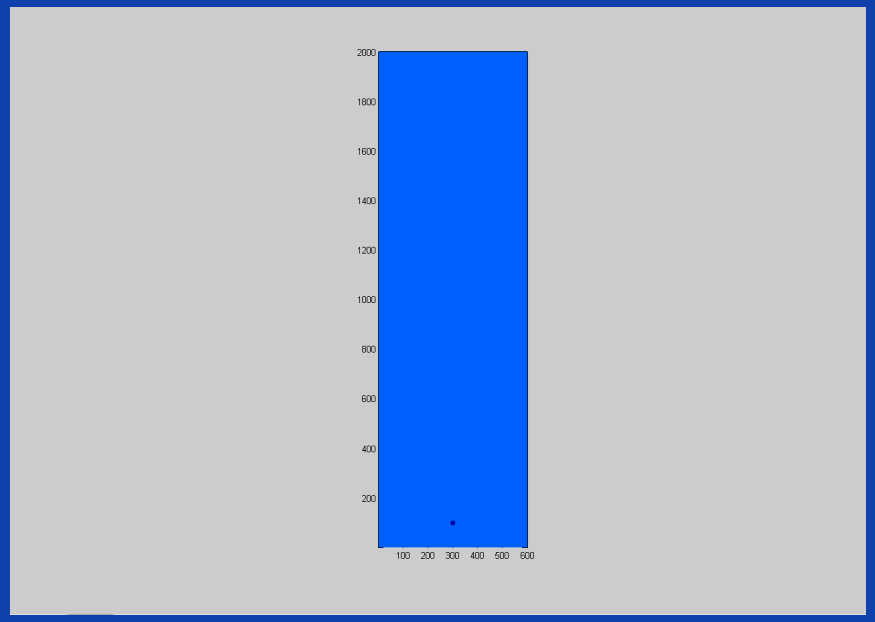
Examples of applications

- Anisotropic grain growth
- Zener pinning
- Coarsening of precipitates on grain boundaries
- Lead-free solder systems
- Solidification

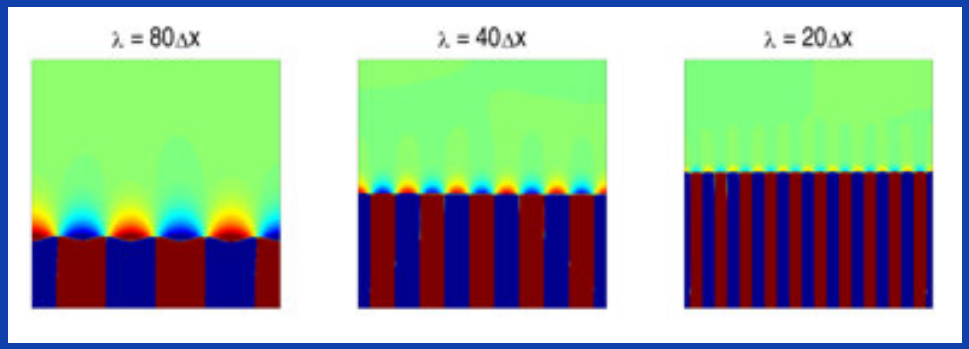
Solidification

- **Dendritic growth**

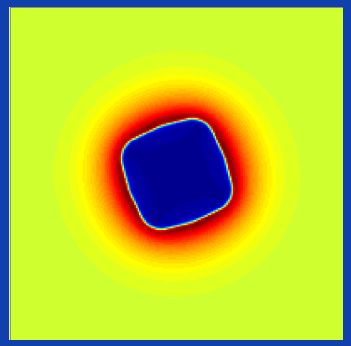


4-fold weak anisotropy in interface energy, Cu-Ni

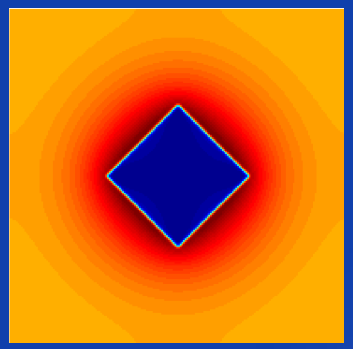
- **Eutectic growth**



- **Faceted growth (strong anisotropy)**



4-fold anisotropy in interface energy



4-fold anisotropy in interface mobility

J. Heulens, K.U. Leuven

Summary

- Understanding microstructure evolution is important for material science, but processes can be very complex
  - Phase-field technique + other models and experimental input
- Principles phase-field modeling
  - Diffuse interface concept, conserved and non-conserved field variables
  - Evolution equations derived from a free energy functional
  - Quantitative aspects: Parameter choice + advanced implementation techniques
- Applications
  - Grain growth, recrystallization, coarsening, solidification, growth intermetallic phases, …

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Thank you for your attention ! Questions ?

- **Acknowledgements**
  - **Research Foundation - Flanders (FWO-Vlaanderen)**
  - **Flemish Supercomputing Center (VSC)**

- **More information on *http//nele.studentenweb.org***