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# Modeling IMC growth in leadfree solder joints using the phase-field method coupled with the COST-531 thermodynamic database

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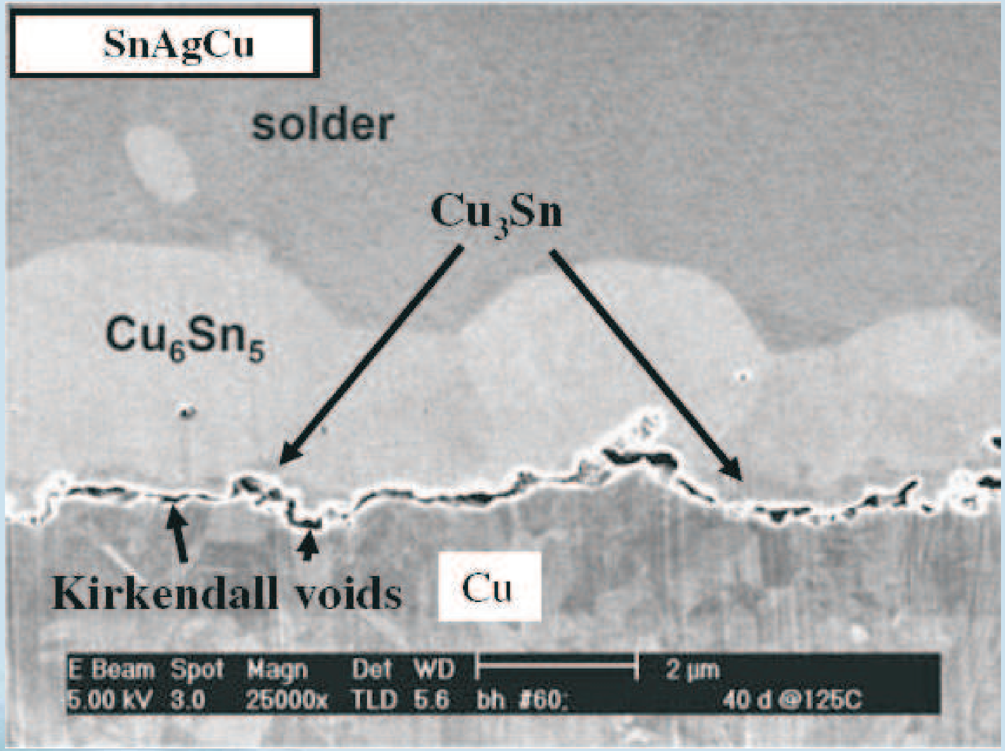
Final COST MP0602 meeting, June 22 - 24, BRNO

# IMC growth and interdiffusion in leadfree solder joints




[J. Mater Sci: Mater. Electron (2007) 18:155 ]

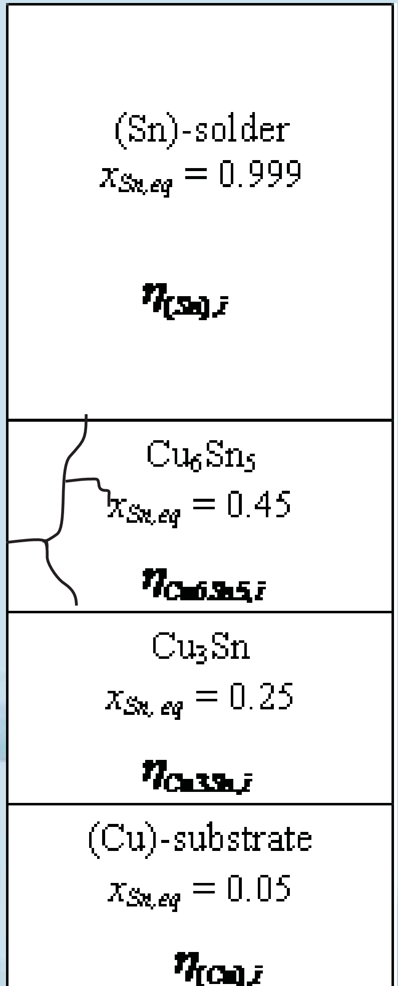
- IMC-layers, IMC precipitates, voids, stresses, cracks . . . during solidification and coarsening

- GP4: Modeling of microstucture evolution in the interdiffusion zone
- Use COST-531 thermodynamic database in phase-field simulations

# Outline

- Phase-field model
- COST - 531 database
- 4 approaches to model phases with low solubility
  - Model I: Stoichiometric
  - Model II: Parabolic composition dependence
  - Model II: Order-disorder model
  - Model IV: Extended sublattice representation
- Concluding remarks

# Phase-Field Model: Variables




- Grains and phases

$$\eta_{bct,1}, \eta_{bct,2}, \ldots, \eta_{bct,i}(\mathrm{x}, \mathrm{y}, \mathrm{z}, t), \ldots$$

$$\eta_{Cu6Sn5,1}, \cdots$$

$$\eta_{Cu3Sn,1}, \cdots$$

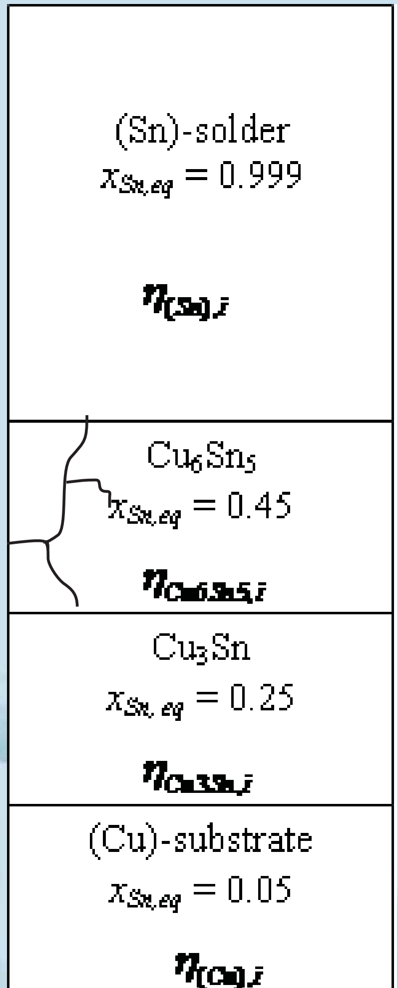
$$\eta_{fcc,1}, \cdots$$

$$\eta_{Ag3Sn,1}, \cdots$$

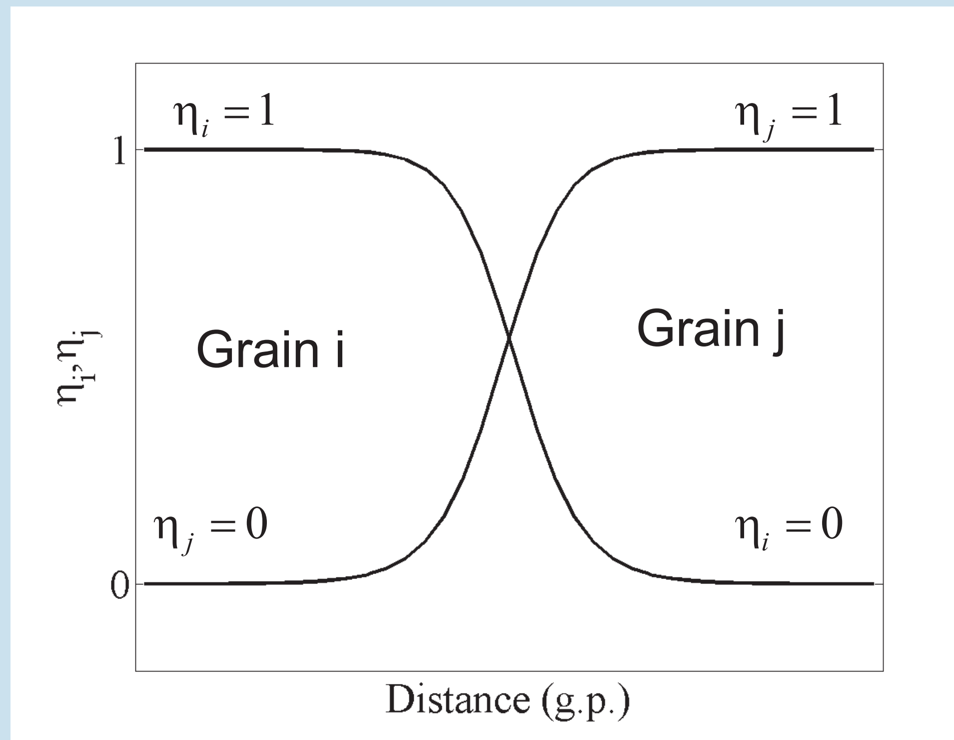
with $(\eta_{bct,1}, \eta_{bct,1}, \ldots, \eta_{\rho,i}, \ldots) = (1, 0, \ldots, 0, \ldots), (0, 1, \ldots, 0, \ldots), \ldots, (0, 0, \ldots, 1, \ldots)$

- Composition: $x_{Cu}, x_{Sn}, (x_{Ag} = 1 - x_{Cu} - x_{Sn})$

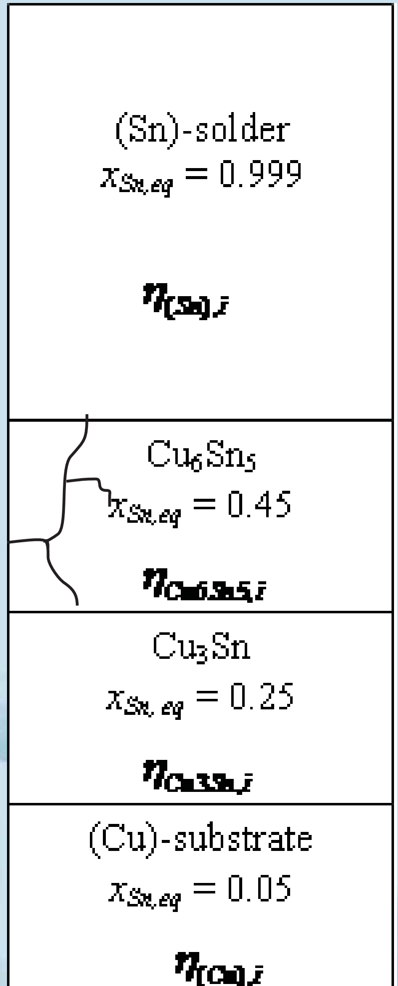
# Phase-Field Model: Diffuse interface



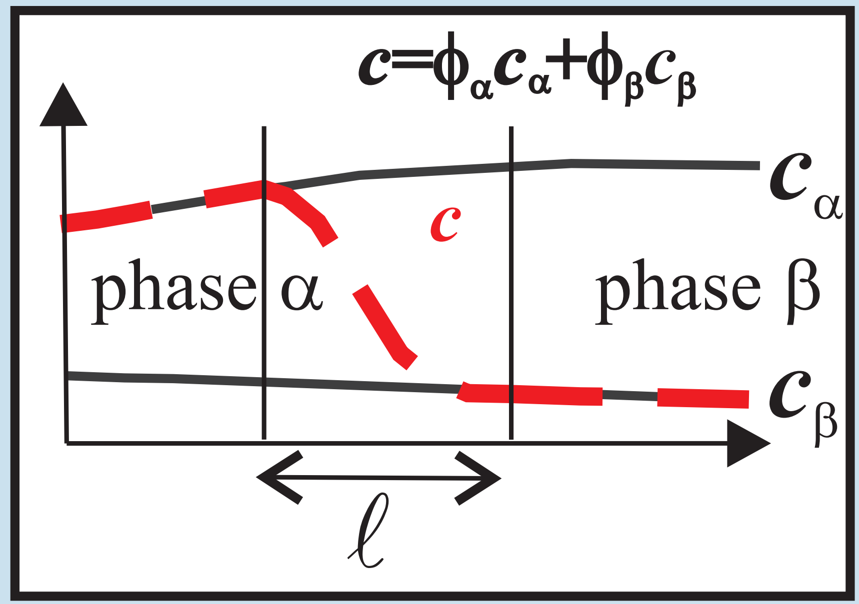

- $\eta_{bct,i}$, $\eta_{Cu6Sn5,i}$, $\eta_{Cu3Sn,i}$, $\eta_{fcc,i}$, $\eta_{Ag3Sn,i}$



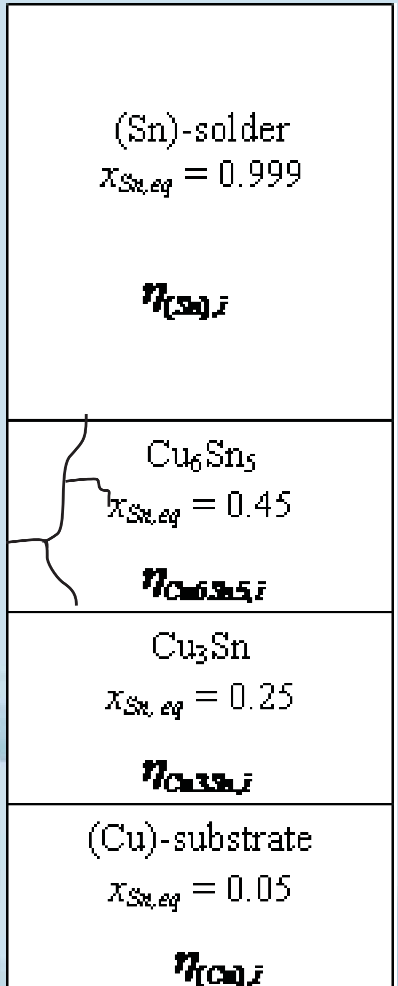
# Phase-Field Model: Diffuse interface



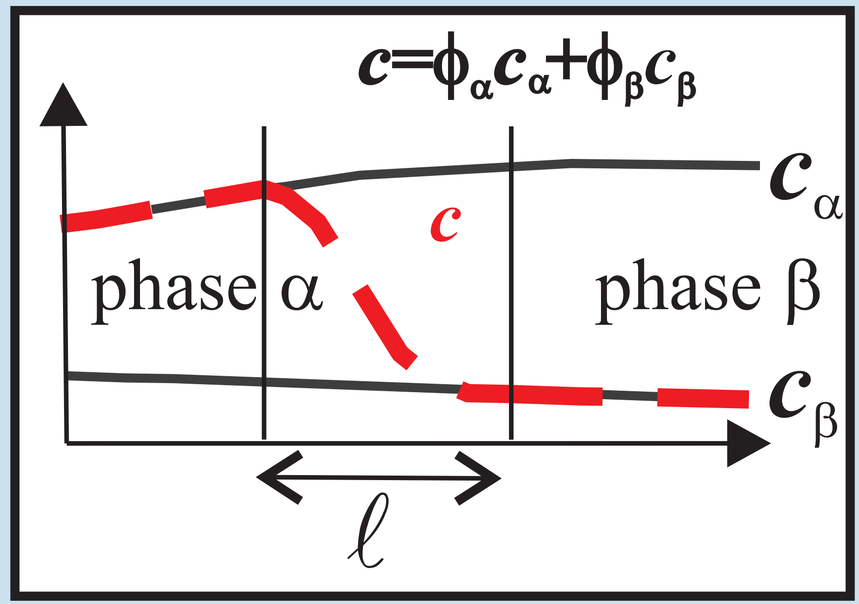

- Interface : Mixture of 2 phases



# Phase-Field Model: Diffuse interface

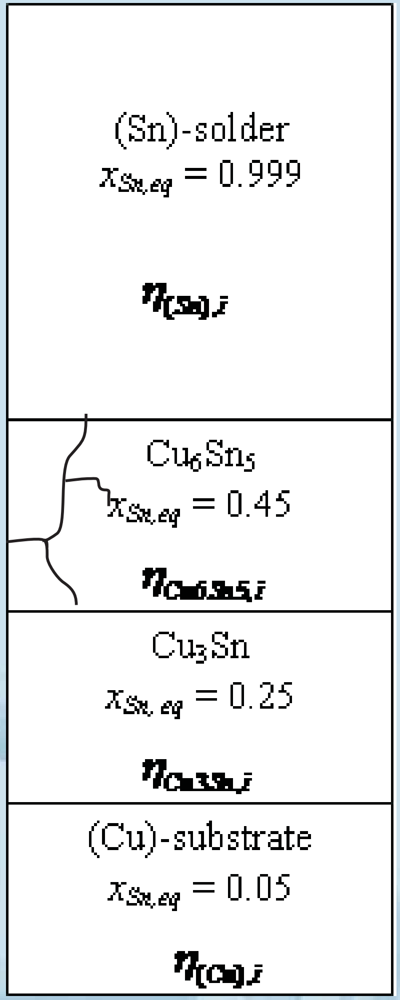



- Interface : Mixture of 2 phases



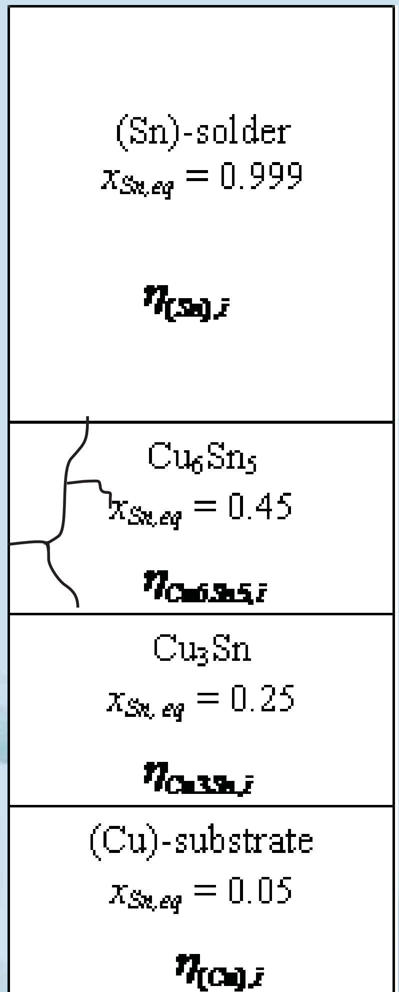

- Phase fractions $\phi_\rho = \frac{\sum_i \eta_{\rho,i}}{\sum_\sigma \sum_i \eta_{\sigma,i}}$
- Phase compositions $x_k^\rho(x_k, \phi_\rho)$

# Phase-Field Model: Free energy functional




$$F_{total} = \int_V f_{int}(\eta_{\rho,i}, \nabla\eta_{\rho,i})\mathrm{d}V + \int_V f_{bulk}(\eta_{\rho,i}, x_k)\mathrm{d}V$$

# Phase-Field Model: Free energy functional

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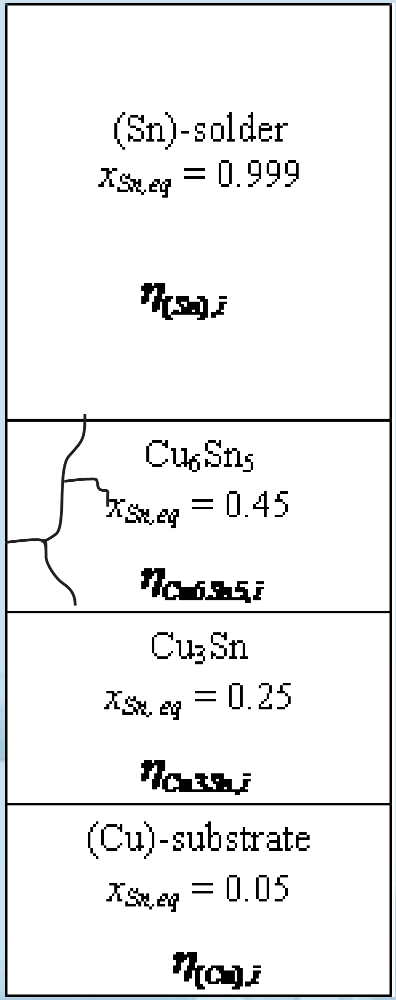
- Bulk contribution

$$f_{bulk} = \sum_\rho \phi_\rho f^\rho(x_k^\rho) = \sum_\rho \phi_\rho \frac{G_m^\rho(x_k^\rho)}{V_m}$$

# Phase-Field Model: Free energy functional

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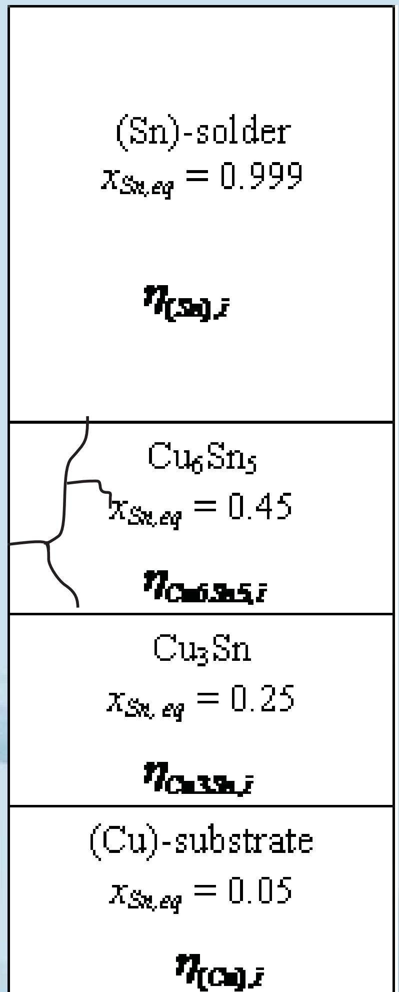
  - Phase fractions $\phi_\rho = \frac{\sum_i \eta_{\rho,i}}{\sum_\sigma \sum_i \eta_{\sigma,i}}$

# Phase-Field Model: Free energy functional




$$F_{total} = \int_V f_{int}(\eta_{\rho,i}, \nabla \eta_{\rho,i}) \mathrm{d}V + \int_V f_{bulk}(\eta_{\rho,i}, x_k) \mathrm{d}V$$

- Bulk contribution

$$f_{bulk} = \sum_\rho \phi_\rho f^\rho(x_k^\rho) = \sum_\rho \phi_\rho \frac{G_m^\rho(x_k^\rho)}{V_m}$$

  - Phase fractions $\phi_\rho = \frac{\sum_i \eta_{\rho,i}}{\sum_\sigma \sum_i \eta_{\sigma,i}}$
  - Phase compositions $x_k^\rho(x_k, \phi_\rho)$

# Phase field model: Evolution equations



- Diffusion

$$\frac{\partial x_k}{\partial t} = \nabla \cdot \left[ \sum_l \left[ \left( \sum_\rho \phi_\rho M_{kl}^\rho \right) \nabla \left( \frac{\partial f^\rho}{\partial x_l^\rho} \right) \right] \right]$$

  - Within each phase: $\frac{\partial x_k}{\partial t} = \nabla \cdot \left[ \sum_l \left[ \left( \frac{M_{kl}^\rho}{V_m} \right) \nabla \left( \mu_l - \mu_{Ag} \right) \right] \right]$
  - Link with atomic mobilities $\beta^\rho$:

$$M_{kk}^\rho = x_k^\rho (1 - x_k^\rho) \beta^\rho, \quad M_{kl,k \neq l}^\rho = -x_k^\rho x_l^\rho \beta^\rho$$

  - Link with interdiffusion coefficients: $M_{kl}^\rho = \frac{D_{kl}^\rho}{\frac{\partial^2 f^\rho}{\partial x_k^\rho x_l^\rho}} = \frac{V_m D_{kl}^\rho}{\frac{\partial^2 G^\rho}{\partial x_k^\rho x_l^\rho}}$

# Phase field model: Evolution equations



- Diffusion

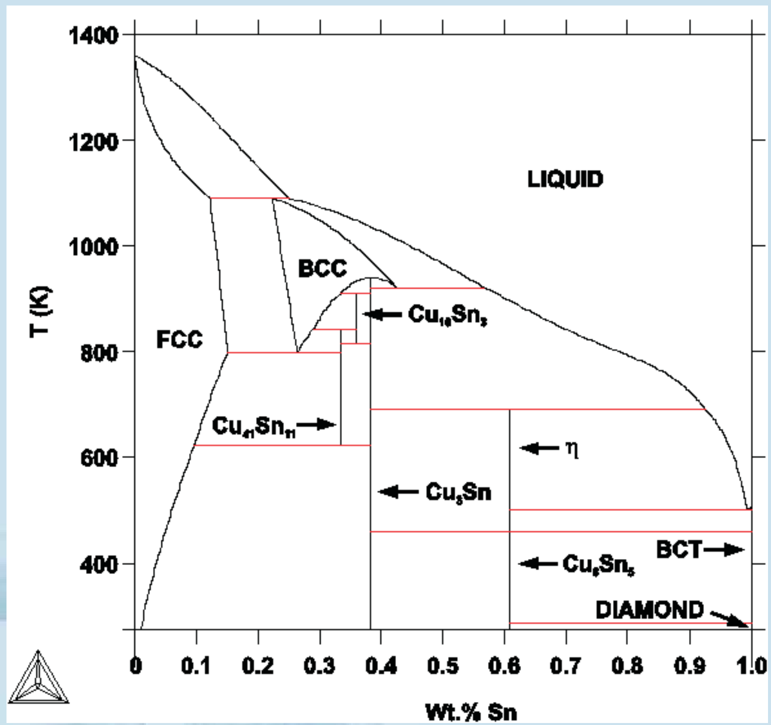
$$\frac{\partial x_k}{\partial t} = \nabla \cdot \left[ \sum_l \left[ \left( \sum_\rho \phi_\rho M_{kl}^\rho \right) \nabla \left( \frac{\partial f^\rho}{\partial x_l^\rho} \right) \right] \right]$$

- Interface movement

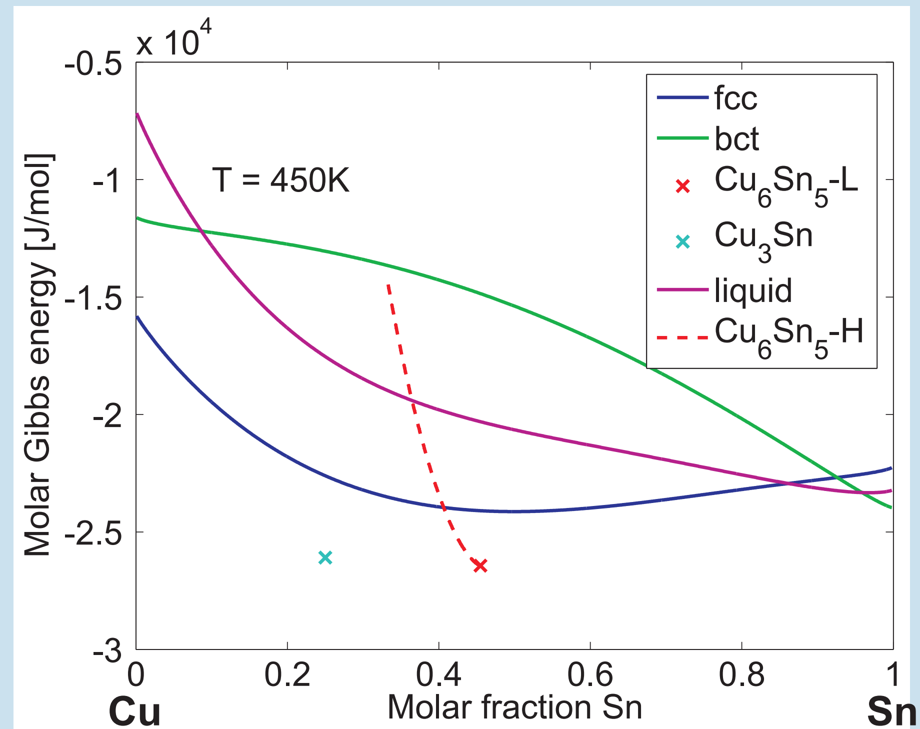
$$\frac{\partial \eta_{\rho,i}}{\partial t} = -L \frac{\delta F(\eta_{\sigma,j}, x_k)}{\delta \eta_\rho}$$

# COST-531 tdb: Cu-Sn

- Phase diagram



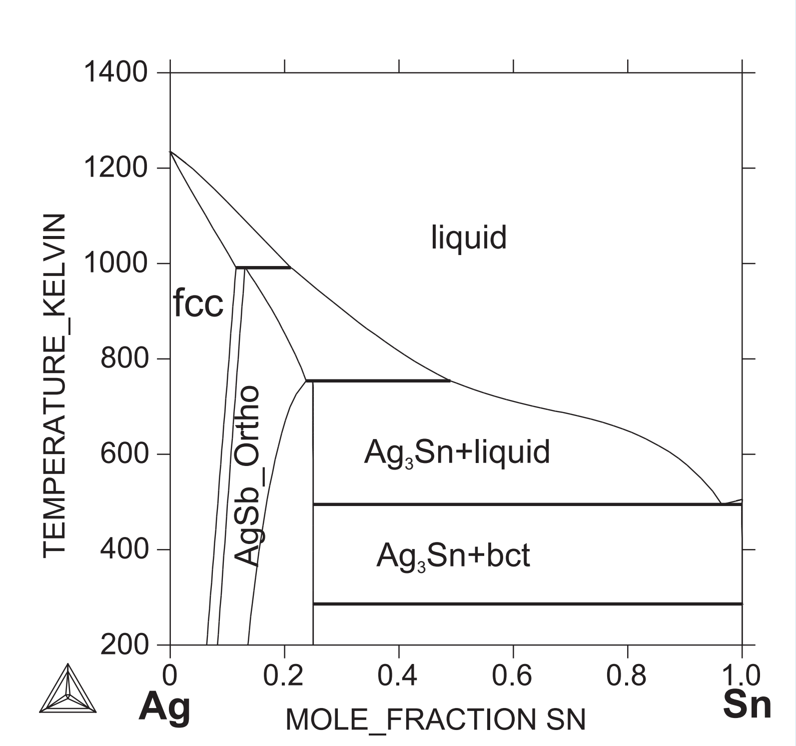

- Molar Gibbs Energies at 450 K



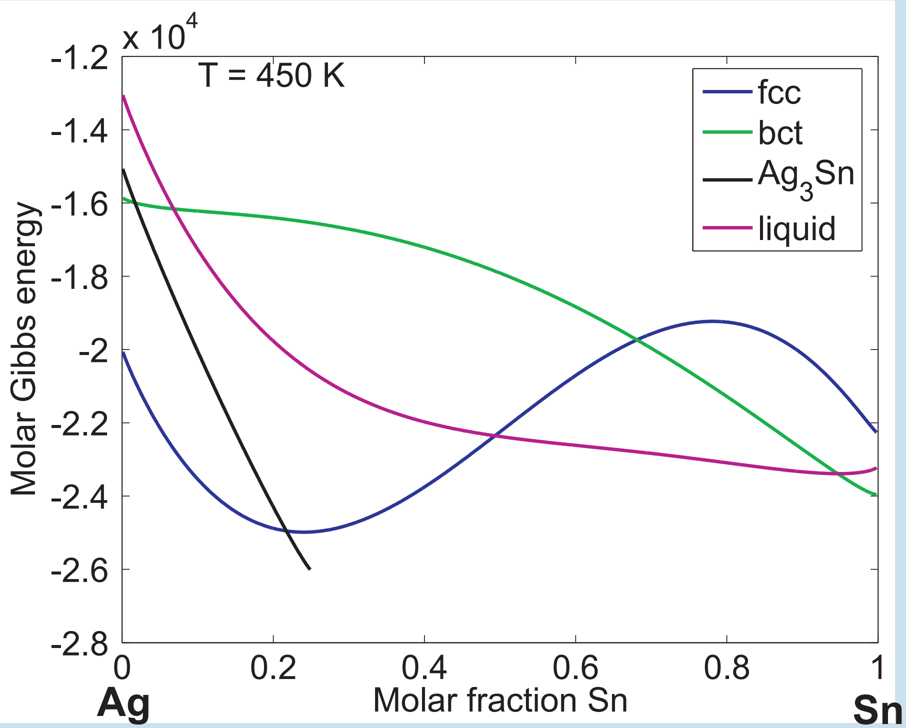

- Bulk contribution phase-field energy: $f_{bulk} = \sum_\rho \phi_\rho \frac{G_m^\rho(x_k^\rho)}{V_m}$
- Diffusion equation: $\mu_k^\rho - \mu_{Ag}^\rho = \frac{\partial G^\rho}{\partial x_k}, \frac{\partial^2 G^\rho}{\partial x_k x_l}, \quad k, l = Cu, Sn$

# COST-531 tdb: Ag-Sn

- Phase diagram




- Molar Gibbs energies at 450 K




- Sublattice representation $Ag_3Sn$: $(Ag)_{0.75}(Ag, Sn)_{0.25}$

# Model I: Stoichiometric phase

- Bulk contribution phase-field energy

$$f_{bulk} = \sum_{\rho} \phi_\rho \frac{G_m^\rho(x_k^\rho)}{V_m} + \phi_{stoich} \frac{G_m^{stoich}}{V_m}$$

  - Parallel tangent for solution phases

$$\frac{\partial f^\rho(x_k^\rho)}{\partial x_k^\rho} = \frac{\partial f^\sigma(x_k^\sigma)}{\partial x_k^\sigma},$$

$$\forall k, \rho \neq \sigma \quad \text{solution phases}$$

  - Mass balance

$$x_k - x_k^{stoich} = \sum_{\rho=sol} \phi_\rho (x_k^\rho - x_k^{stoich}), \quad \forall k$$

- $D_{kl}^{stoich} = M_{kl}^{stoich} = 0$

# Model I: Stoichiometric phase

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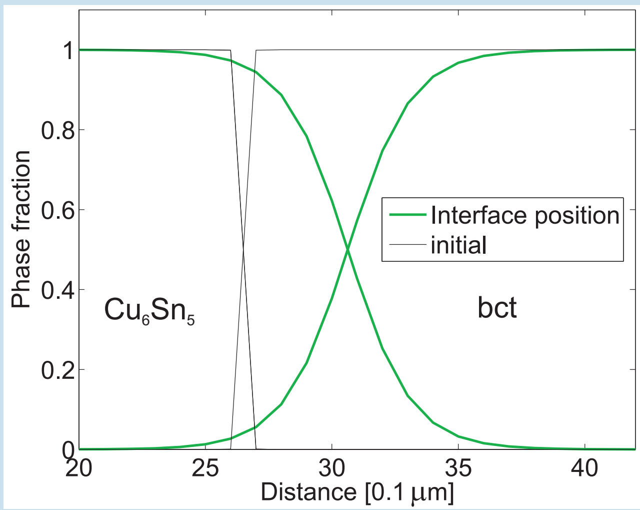
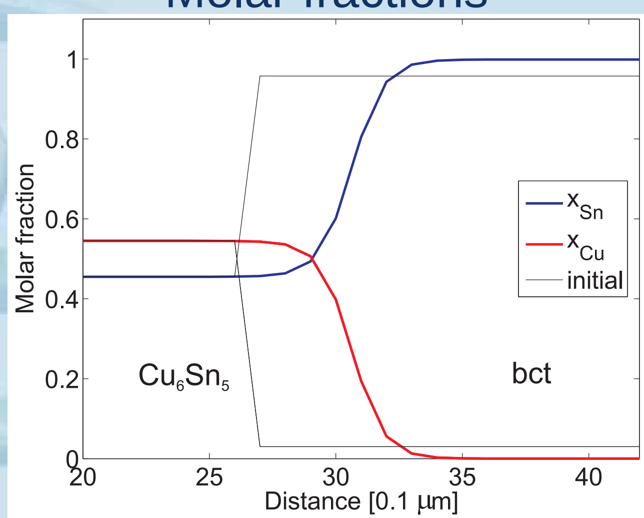
- Simulation precipitation IMC

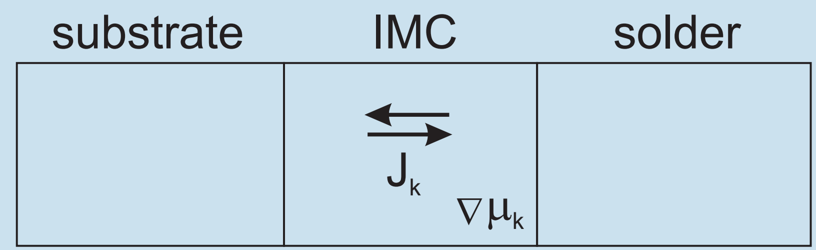
Phase fractions




Molar fractions



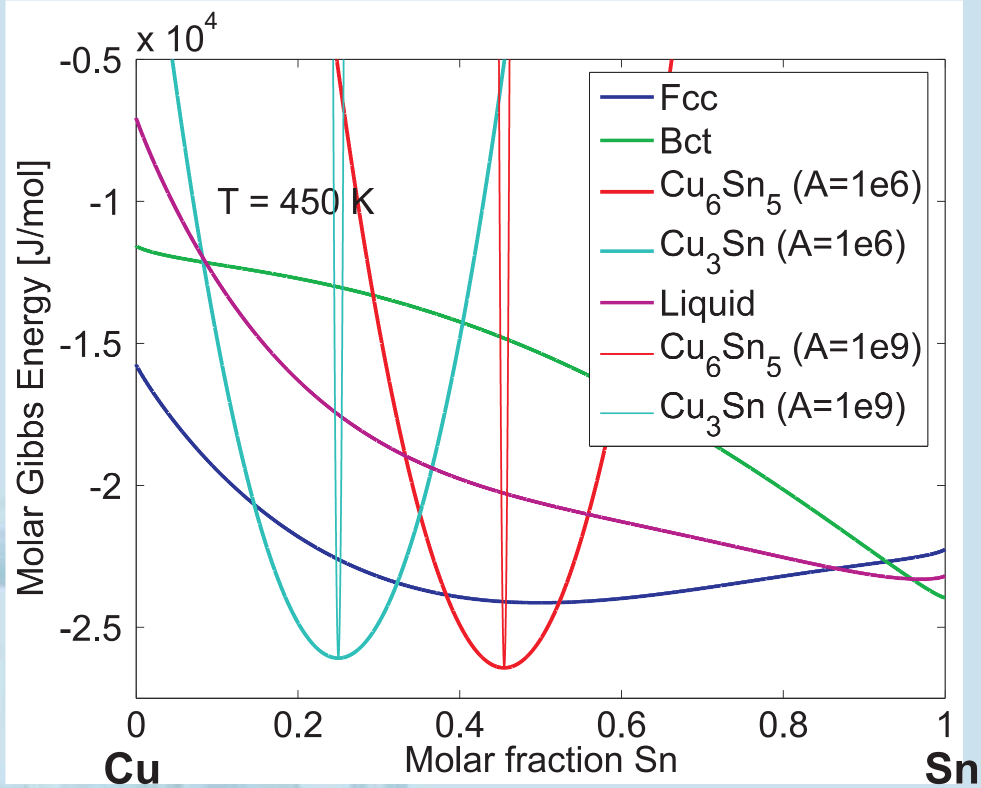

- Growth IMC layer
  - Needs diffusion through IMC




$\Rightarrow G^{\rho}(x_k)$ needed to model $\nabla \mu_k$ the driving force for diffusion

# Model II: Parabolic composition dependence

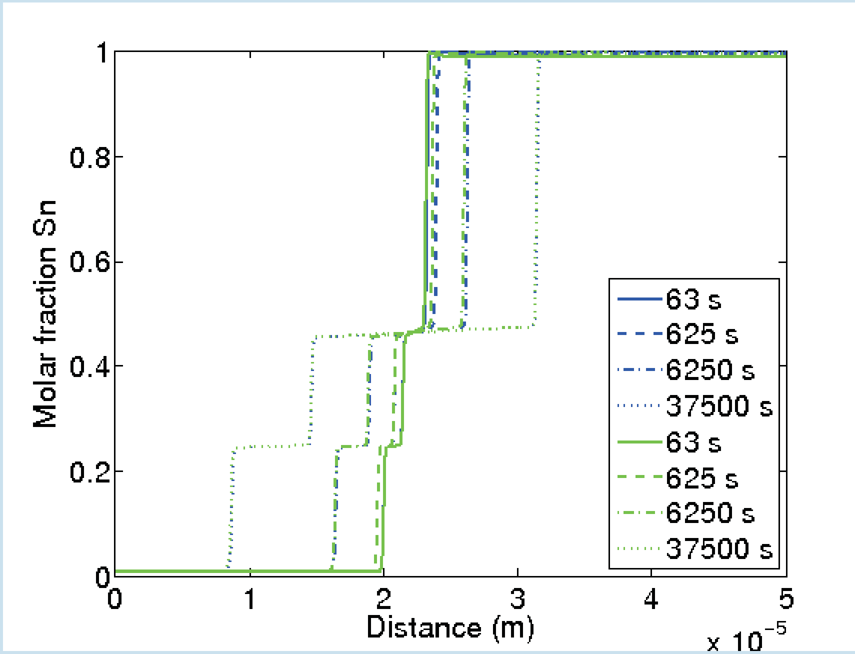
$$V_m f^{stoich} = \frac{A^{stoich}}{2}(x_{Sn} - x_{stoich,Sn})^2 + G_m^{stoich}(T = 450K) \quad (1)$$

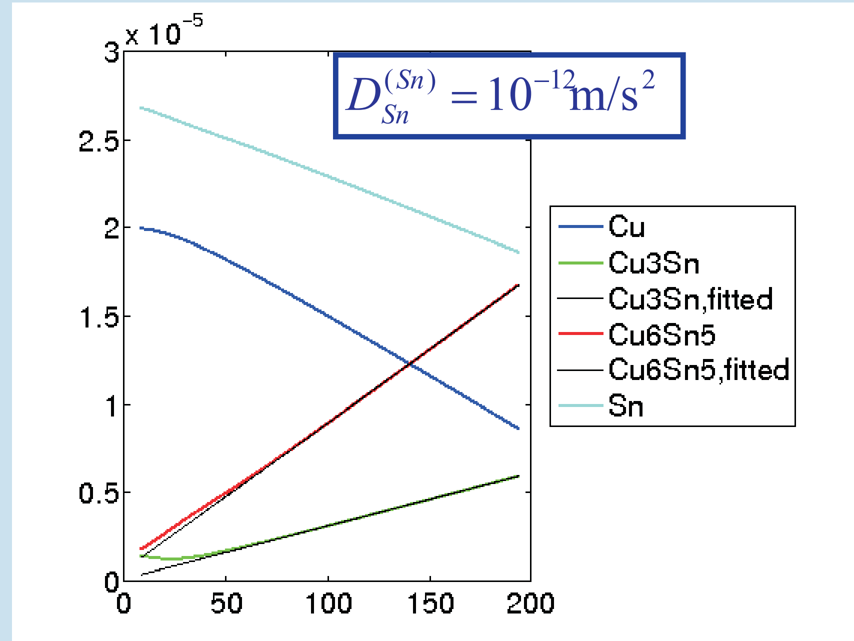



- Steepness $A^{stoich}$
- Induces small shift in equilibrium
- $M_{Sn}^{stoich} = \frac{D_{Sn}^{stoich}}{A^{stoich}}$ (Composition independent)

[S.Y. Hu, J. Murray, H. Weiland, Z.-K. Liu, L.-Q. Chen, Comp. Coupl. Phase Diagr. Thermoch., 31 (2007) p 303 ]

# Model II: Results




$$D_{Sn}^{(Cu)} = 10^{-25} m/s^2$$
$$D_{Sn}^{Cu_3Sn} = 10^{-13} m/s^2$$
$$D_{Sn}^{Cu_6Sn_5} = 10^{-13} m/s^2$$
$$D_{Sn}^{(Sn)} = 10^{-12} m/s^2$$

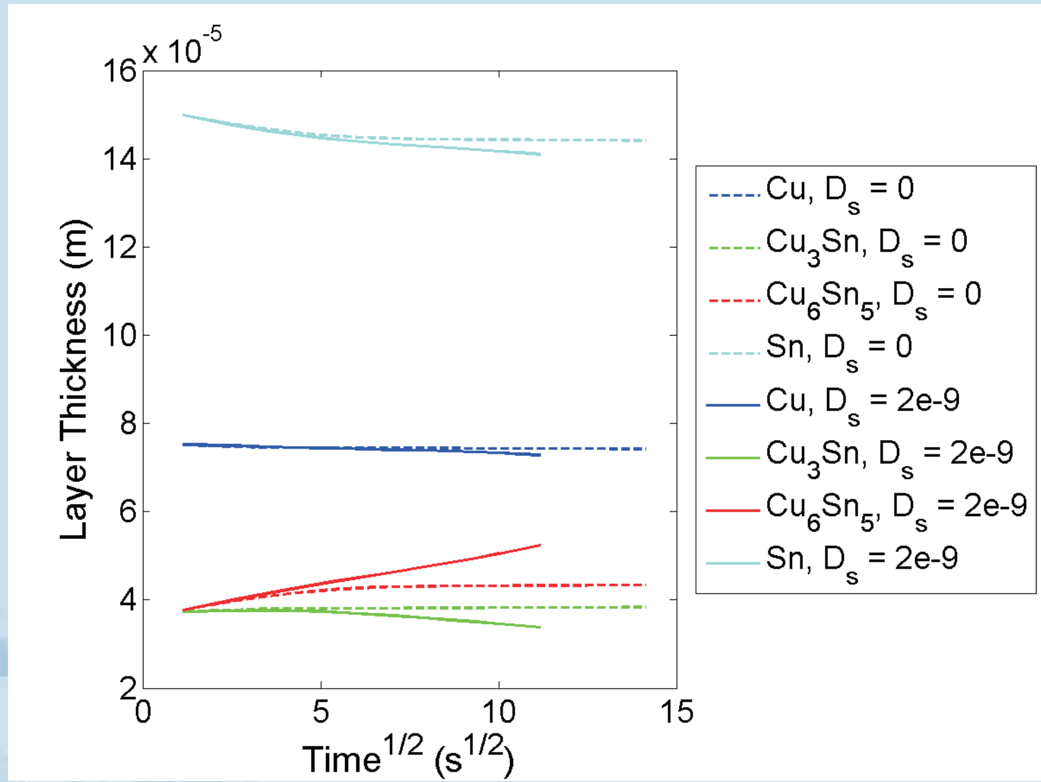
$$D_{Sn}^{(Cu)} = 10^{-25} m/s^2$$
$$D_{Sn}^{Cu_3Sn} = 10^{-13} m/s^2$$
$$D_{Sn}^{Cu_6Sn_5} = 10^{-13} m/s^2$$
$$D_{Sn}^{(Sn)} = 10^{-14} m/s^2$$

$$\Rightarrow \quad k_{Cu3Sn} = 0.0301 \cdot 10^{-6}$$
$$k_{Cu6Sn5} = 0.0833 \cdot 10^{-6}$$

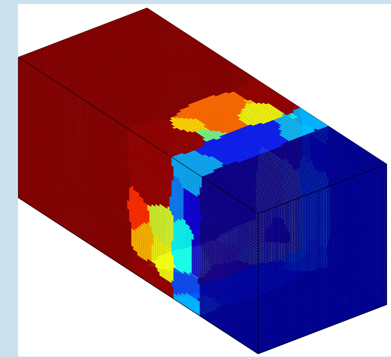
$$\Rightarrow \quad k_{Cu3Sn} = 0.0306 \cdot 10^{-6}$$
$$k_{Cu6Sn5} = 0.0849 \cdot 10^{-6}$$

# Model II: Results

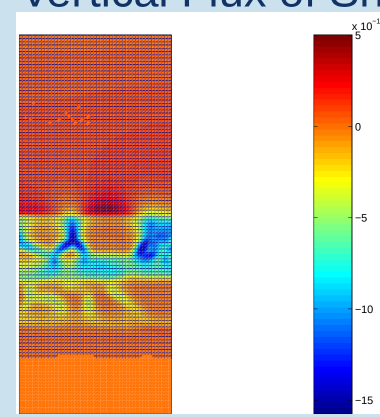
- With grain boundary diffusion




Grain structure



Vertical Flux of Sn

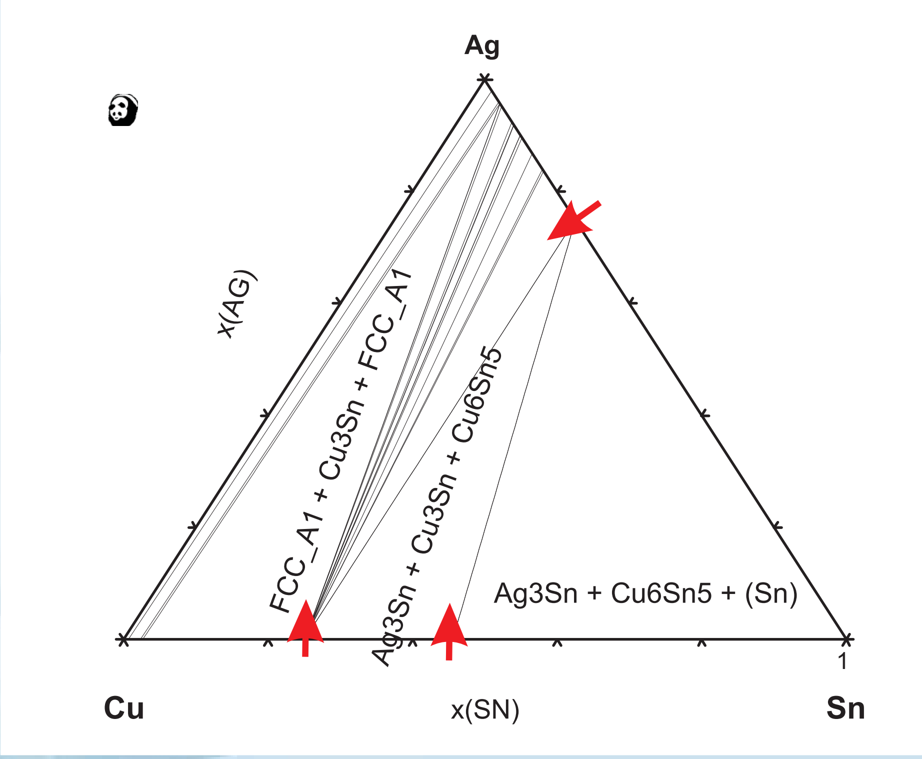



- $D_{Sn}^{fcc} = 2 \cdot 10^{-25}$ m$^2$/s; $D_{Sn}^{Cu3Sn} = 2 \cdot 10^{-15}$ m$^2$/s; $D_{Sn}^{Cu6Sn5} = 2 \cdot 10^{-15}$ m$^2$/s; $D_{Sn}^{bct} = 2 \cdot 10^{-12}$ m$^2$/s;

- $D_{interf} = 2 \cdot 10^{-9}$ m$^2$/s, $\delta_{gb} = 1$nm

# Model II: Parabolic composition dependence

$$V_m f^{stoich} = \frac{A^{stoich}}{2}(x_{Sn} - x_{stoich,Sn})^2 + \frac{A^{stoich}}{2}(x_{Ag} - x_{shift})^2 + G_m^{stoich}(T = 450K)$$




- Steepness $A^{stoich}$
- Small shift in equilibrium
- $M_{kl}^{stoich} = \frac{D_{kl}^{stoich}}{A^{stoich}}$
- $x_{shift}$, e.g. $= 0.001$

# Model III: Order-disorder CALPHAD description

- Sublattice representation Cu$_3$Sn: $(Ag, Cu, Sn)_{0.75}(Ag, Cu, Sn)_{0.25}$
- Molar Gibbs Energy

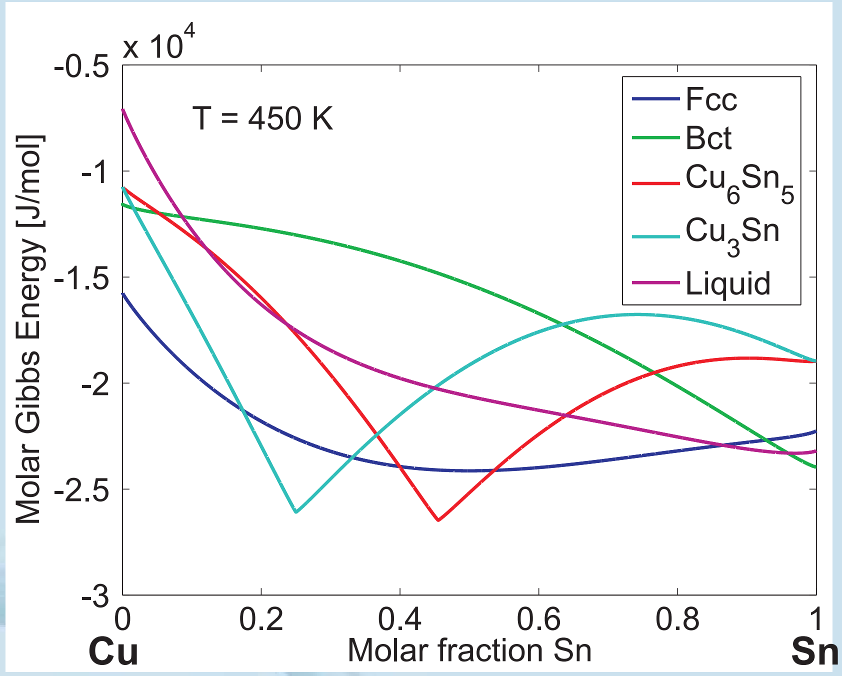
$$
\begin{aligned}
G_m^{Cu3Sn} = \; & x_{Ag} G^0_{Ag} + x_{Cu} G^0_{Cu} + x_{Sn} G^0_{Sn} \\
& + x_{Ag} x_{Cu} L_{Ag,Cu} + x_{Ag} x_{Sn} L_{Ag,Sn} \\
& + x_{Cu} x_{Sn} L_{Cu,sn} \\
& + (y^1_{Cu} y^2_{Sn} - x_{Cu} x_{Sn}) G^{ord}_{Cu3Sn} \\
& + RT \Big[ 0.75 (y^1_{Ag} \ln(y^1_{Ag}) + y^1_{Cu} \ln(y^1_{Cu}) \\
& \quad + y^1_{Sn} \ln(y^1_{Sn})) \\
& + 0.25 (y^2_{Ag} \ln(y^2_{Ag}) + y^2_{Cu} \ln(y^2_{Cu}) \\
& \quad + y^2_{Sn} \ln(y^2_{Sn})) \Big]
\end{aligned}
$$

- $G^0_{Ag} = GHSER + 5000$ and $L_{Ag,Cu}$,$L_{Ag,Sn}$,$L_{Cu,Sn}$ and $G^{ord}_{Cu3Sn}$ optimized

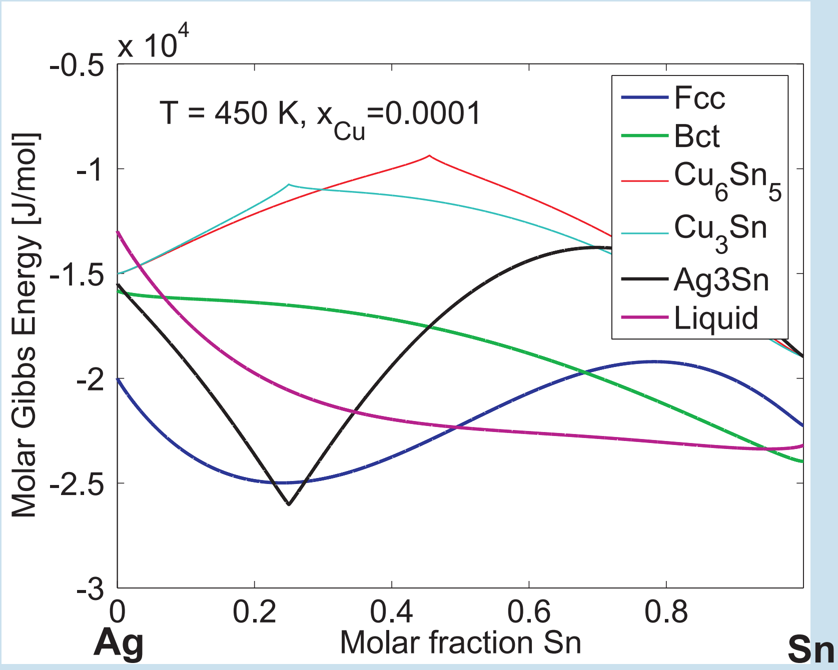
[N. Dupin, I Ansara, B. Sundman, Comp. Coupl. Phase Diagr. Thermoch., 25 (2001) p279]

# Model III: Order-disorder CALPHAD description

- Cu-Sn, T=450K




- Ag-Sn-0.01%Cu, T= 450 K




- Miscibility gap is inherent

# Model IV: Extended sublattice CALPHAD description

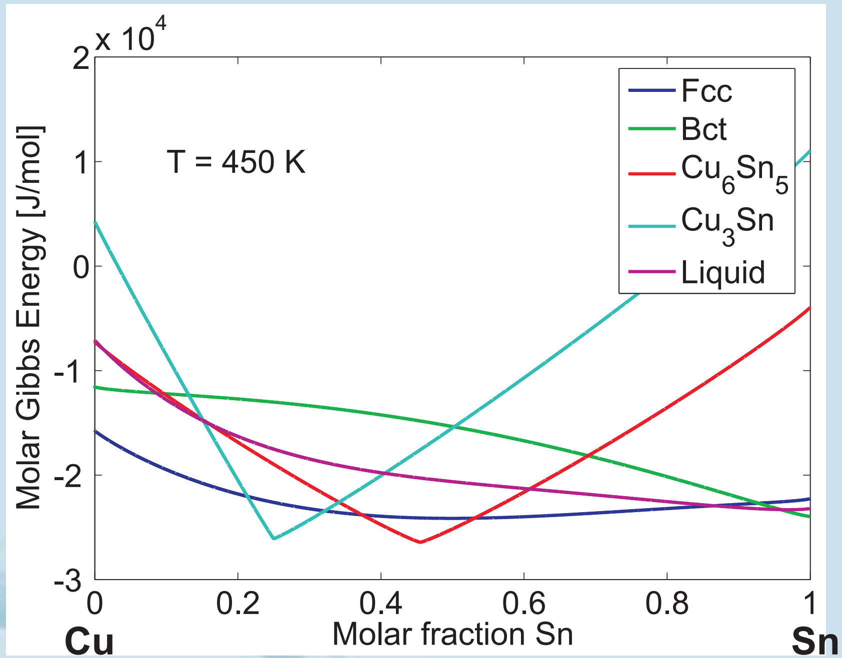
- Sublattice representation $Cu_3Sn$: $(Ag, Cu, Sn)_{0.75}(Ag, Cu, Sn)_{0.25}$
- Molar Gibbs Energy

$$
\begin{aligned}
G_m^{Cu3Sn} \quad = \quad & y_{Ag}^1 y_{Ag}^2 G_{Ag}^0 + y_{Cu}^1 y_{Cu}^2 G_{Cu}^0 + y_{Sn}^1 y_{Sn}^2 G_{Sn}^0 \\
& + y_{Cu}^1 y_{Sn}^2 G_{Cu3Sn}^0 + y_{Sn}^1 y_{Cu}^2 G_{Sn3Cu}^0 \\
& + RT \Big[ 0.75 ( y_{Ag}^1 \ln(y_{Ag}^1) + y_{Cu}^1 \ln(y_{Cu}^1) \\
& \qquad + y_{Sn}^1 \ln(y_{Sn}^1)) \\
& \quad + 0.25 ( y_{Ag}^2 \ln(y_{Ag}^2) + y_{Cu}^2 \ln(y_{Cu}^2) \\
& \qquad + y_{Sn}^2 \ln(y_{Sn}^2)) \Big]
\end{aligned}
$$

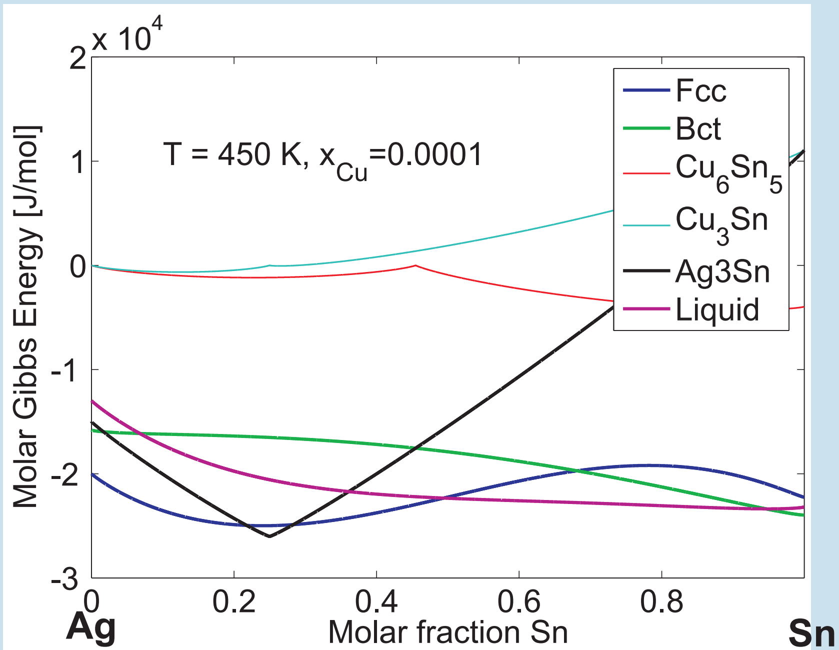
using $\quad G_{Sn3Cu}^0 = G_{Cu}^0 + G_{Sn}^0 - G_{Cu3Sn}^0$

# Model IV: Extended sublattice CALPHAD description

- Cu-Sn, T=450K

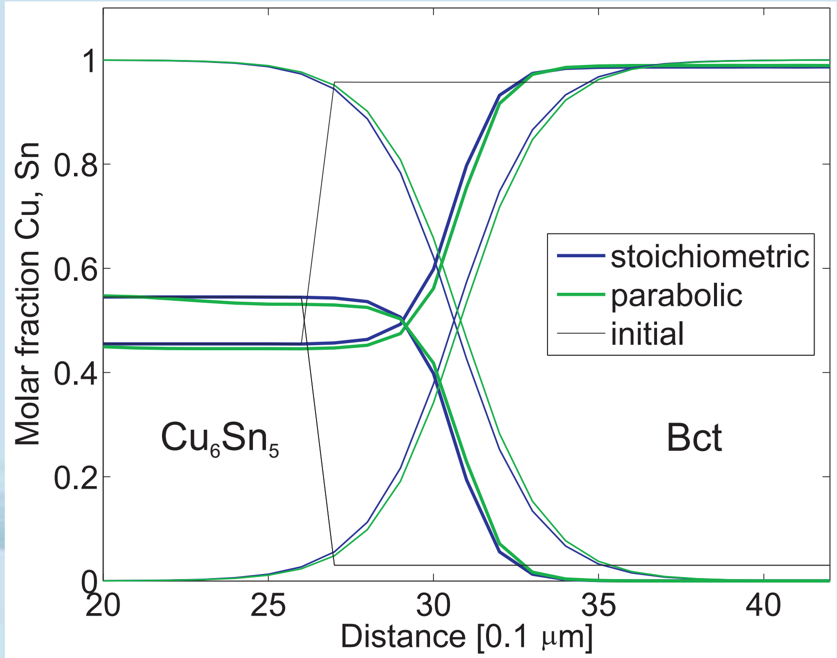


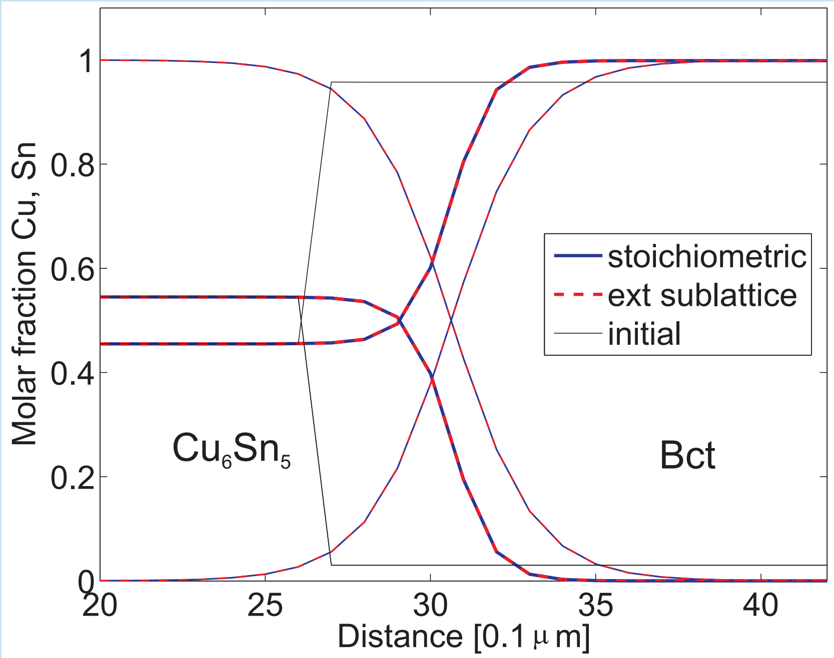

- Ag-Sn-0.01%Cu, T= 450 K



# Comparison: Growth $Cu_6Sn_5$ from supersaturated Bct

- Comparison stoichiometric (I) – parabolic (II)
- Comparison stoichiometric (I) – sublattice (II)

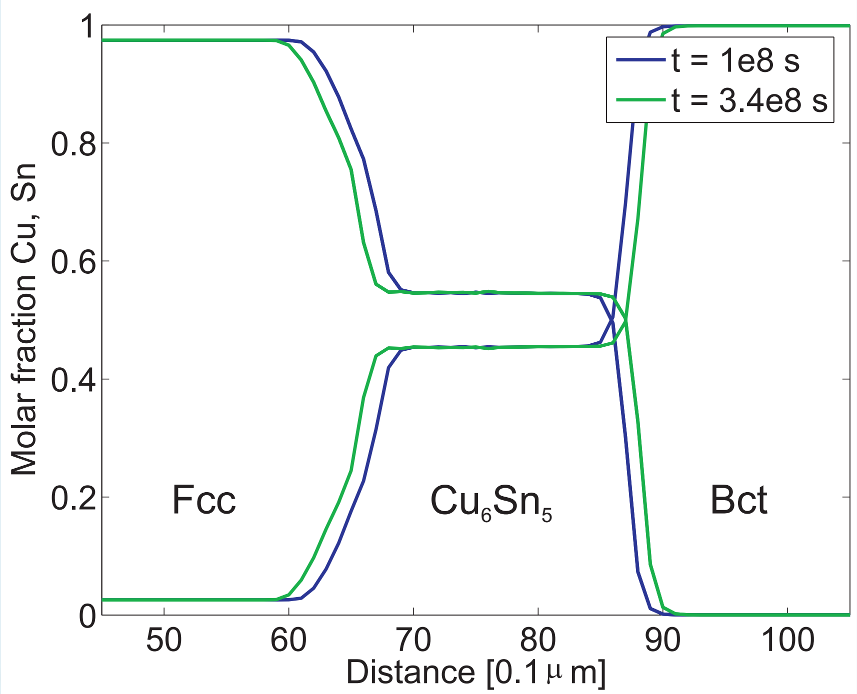



- $M^{Cu6Sn5} = 0$
- $M^{bct}_{kk} = \beta^{bct} x^{bct}_k (1 - x^{bct}_k)$, $M^{bct}_{kl,k \neq l} = -\beta^{bct} x^{bct}_k x^{bct}_l$

# Model IV: Growth $Cu_6Sn_5$ between Fcc and Bct





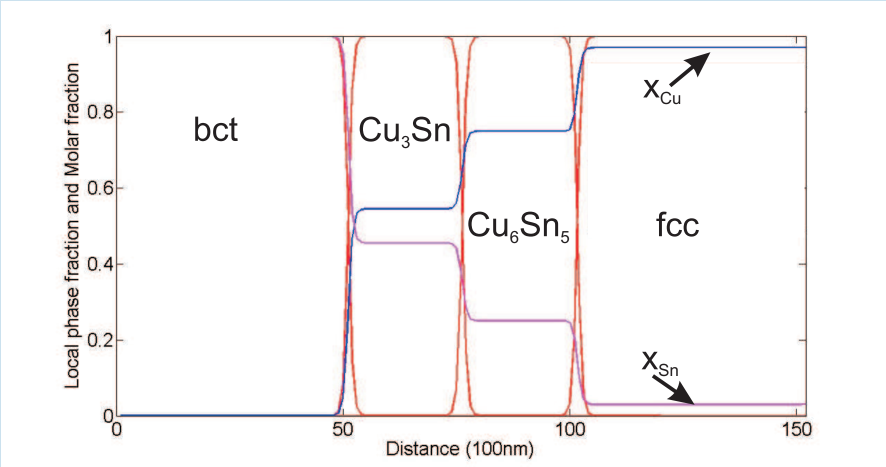

- Diffusion equation

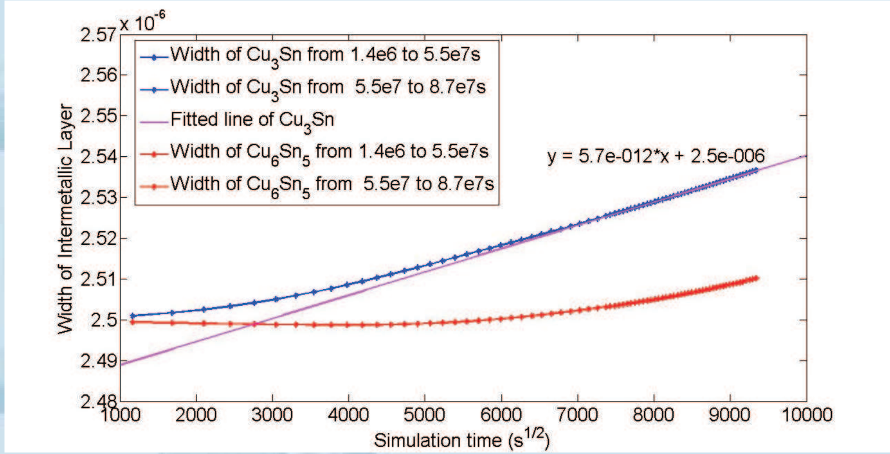
$$\frac{\partial x_k}{\partial t} = \nabla \cdot \left[ \sum_l \left[ \left( \sum_\rho \phi_\rho M_{kl}^\rho \right) \nabla \left( \frac{\partial f^\rho}{\partial x_l^\rho} \right) \right] \right]$$

- $M_{kk}^{bct/fcc} = \beta^{bct/fcc} x_k (1 - x_k)$; $M_{kl,k \neq l}^{bct/fcc} = -\beta^{bct/fcc} x_k x_l$
- $M^{Cu6Sn5} = \beta^{Cu6Sn5}(0.545 y_k^1 (1 - y_k^1) + 0.455 y_k^2 (1 - y_k^2))$, $M_{kl,k \neq l}^{Cu6Sn5} = -\beta^{Cu3Sn}(0.545 y_k^1 y_l^1 + 0.455 y_k^2 y_l^2)$
- $\beta^\rho$ estimated based on interdiffusion coefficients of [A. Paul, C. Ghosh and W.J. Boettinger, Metall. Mater. Trans. A, 42A (2011) p952].

# Model IV: Growth rate $Cu_3Sn$ and $Cu_6Sn_5$

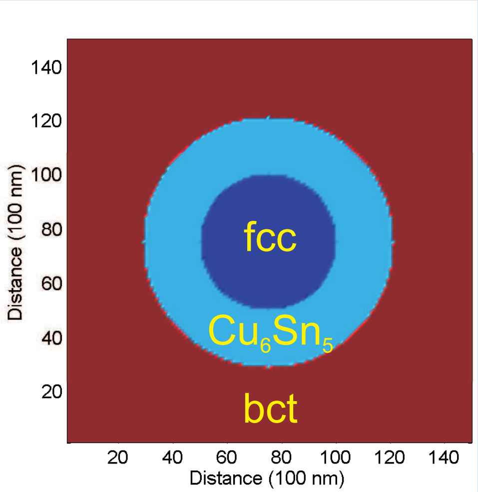
- 1D system

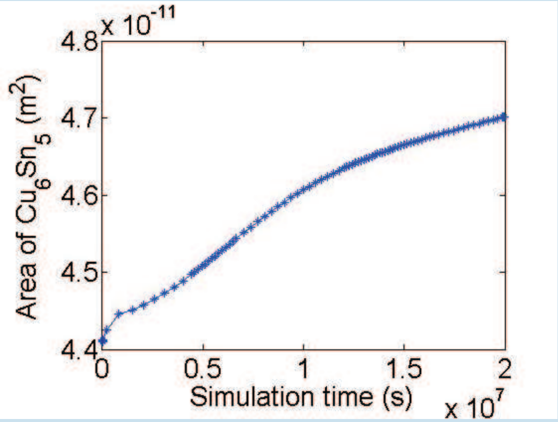



$Cu_3Sn$ grows faster than $Cu_6Sn_5$ !

- 2D system



# Conclusions

- Form of the Gibbs energies influences microstructure simulations of interdiffusion phenomena at interfaces (diffusion couples)
  - Determines which IMC grows fastest/first
- For a general coupling of phase-field with CALPHAD, an extended sublattice model is most suitable
  - Or order-disorder model if based on physics
- Presented approaches also valuable for sharp interface diffusion techniques, e.g. DICTRA
- Databases with extended sublattice representations can be improved iteratively