



**MATERIALS SCIENCE
& ENGINEERING**
TEXAS A&M UNIVERSITY

Introduction to Microstructure Thermodynamics

MSEN 210 Thermodynamics of Materials
Texas A&M University

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Contact information

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- Research interests:
 - Thermodynamics and kinetics of materials
 - Microstructure Modeling
 - Electronic materials, Energy harvesting, Solder materials, Thermoelectrics
 - Microstructure Informatics, Deep Learning

Review I: Thermodynamics of multicomponent systems

- Last time, we covered:
 - $H = U + PV$
 - Thermodynamic equations still true whether single component or multi-component
 - Extensive equation
 - Single-component(*) $\rightarrow \frac{H}{n} = \frac{U}{n} + P \frac{V}{n}$ or $\bar{H} = \bar{U} + P\bar{V}$
 - Multi-component $\rightarrow \partial H / \partial n_i = \partial U / \partial n_i + P \partial V / \partial n_i$ or $\bar{H}_i = \bar{U}_i + P\bar{V}_i$
 - $\bar{H} = \bar{U} + P\bar{V}$
 - Intensive single-component equation
 - $\bar{H}_i = \bar{U}_i + P\bar{V}_i$
 - Intensive multi-component equation

Footnotes:

- The bar symbol indicates an intensive thermodynamic quantity.

* “n” is total mole fraction of component(s).

Review II: PyCALPHAD for computational thermodynamics

- Last time, we covered:
 - Calculation of binary and ternary phase diagrams,
 - Extracted free energy of different phases along diffusion lines,
 - Extracted free energy of different phases for fixed alloy composition and different temperatures,
 - Lever rule,
 - Equilibrium calculations,
 - Enthalpy of mixing,
 - Activity of different phases,
- Link to PyCalphad tutorials:
 - https://github.com/vahid2364/Phase-field_PyCalphad-Tutorial

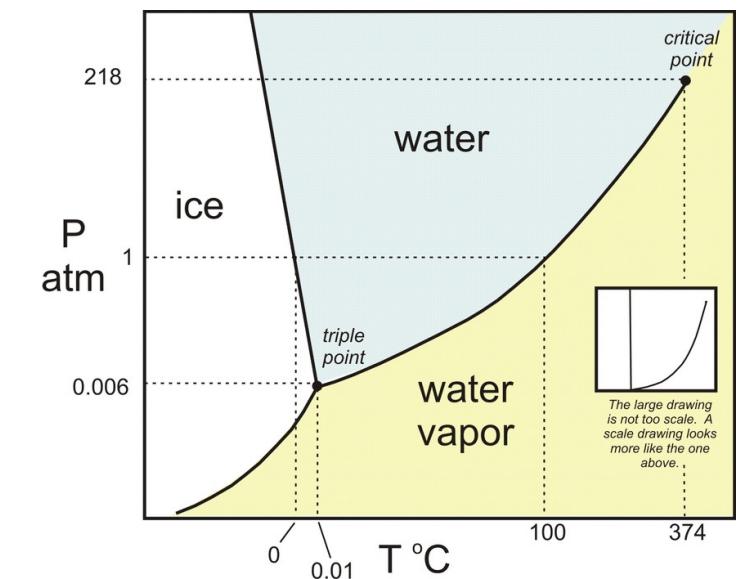
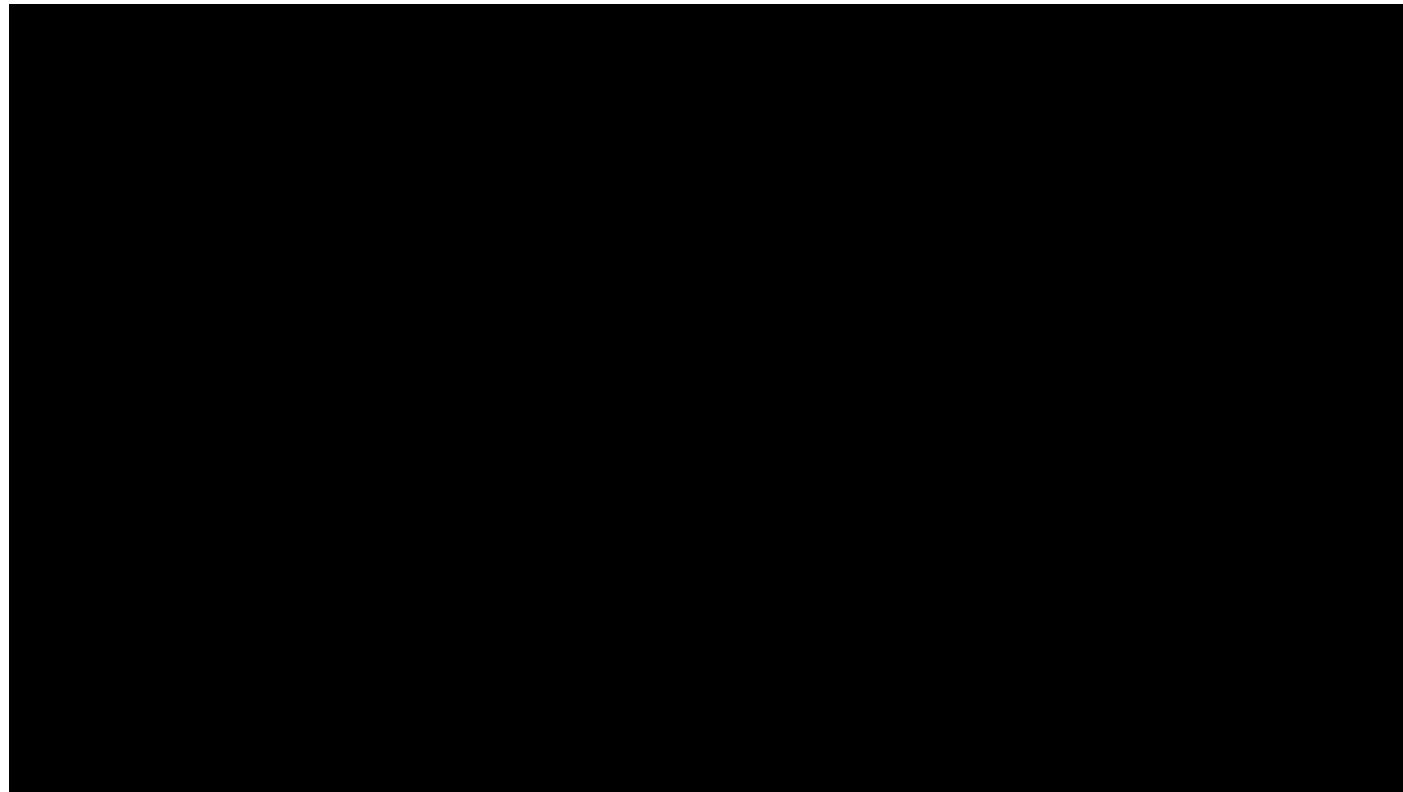
Topics to cover today

- Triple point and critical point in materials
 - How can water, ice, and steam exist at once?
- A few examples for complex microstructure modeling of alloys,
- The general notion of stability of microstructures,
 - Difference between stability, metastability, and instability,
- Driving forces for microstructural change - reduction of Gibbs free energy,
- Change in free energy during phase change in materials,
- Phase stability in microstructure of complex materials,
- Microstructure modeling of materials, (Jupyter notebook),
 - Phase separation
 - Ag-Cu binary alloy

Triple point in materials

Triple point experiment (existence of water, ice, and steam at once)

Click to play



- Thermodynamics determines which phases are stable at certain conditions.
- Kinetics determines the rate of transition of the unstable phases to stable phases at certain conditions.

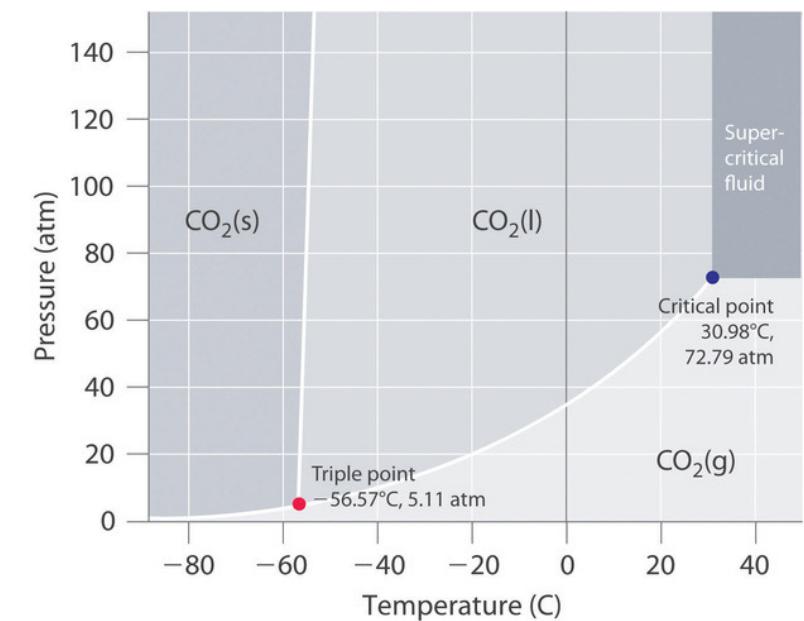
Critical point in materials

- Application: Solvents, Manufactured products, Working fluid, Power generation, Close cycle gas turbines, Aerogel production, Sterilization

Supercritical fluid



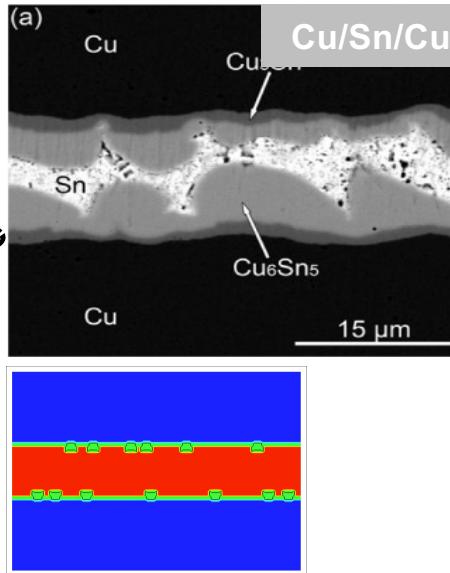
The critical point of CO₂ is easily accessible (critical temperature 31°C and critical pressure 74 bar) allowing the fluid to be used at mild conditions of temperatures (40-60°C) without leaving harmful organic residues.



Materials Modeling and Microstructure Engineering

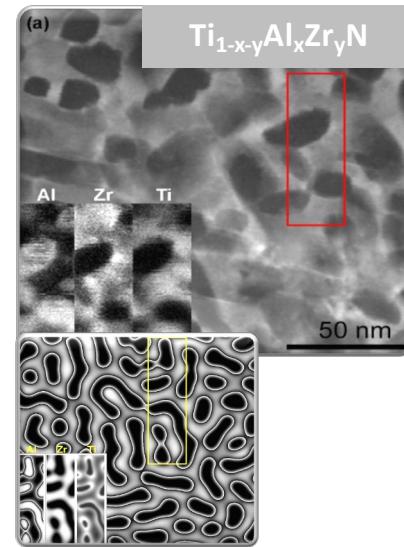
Process

Advanced interconnects
for 3D packaging



Structure

Designing high-
temperature
nanostructured
coating

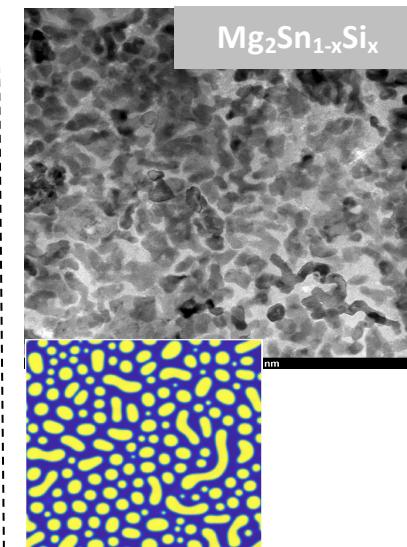


Property

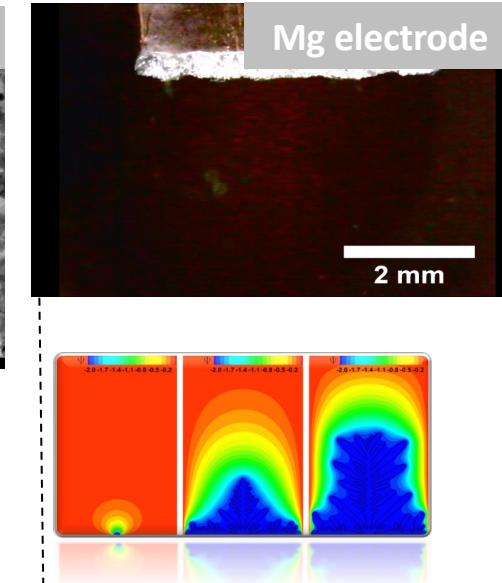
Failure Resistance

Tuning hardness and
toughness

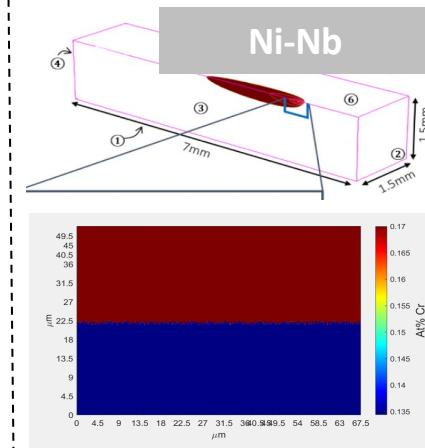
Squeezing efficient
thermoelectrics



Next-generation
battery electrodes

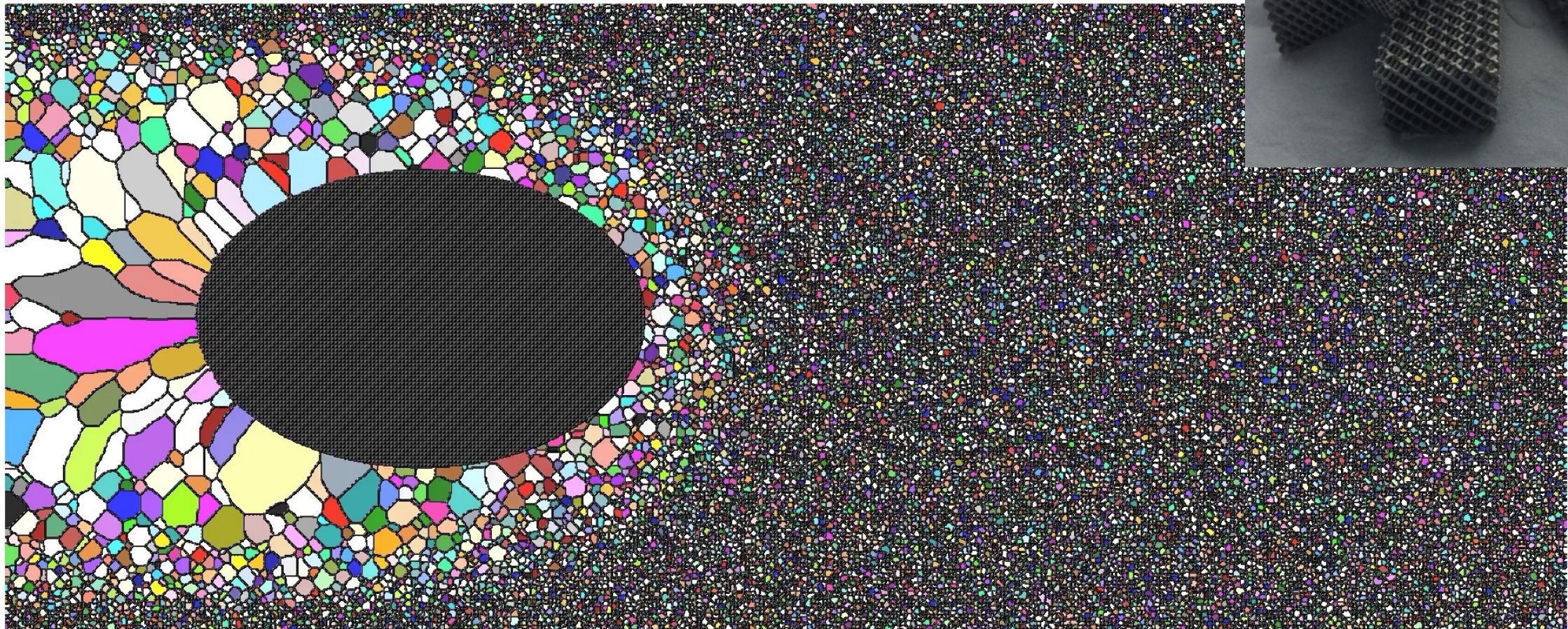


Multiphysics
phenomena in
additive
manufacturing

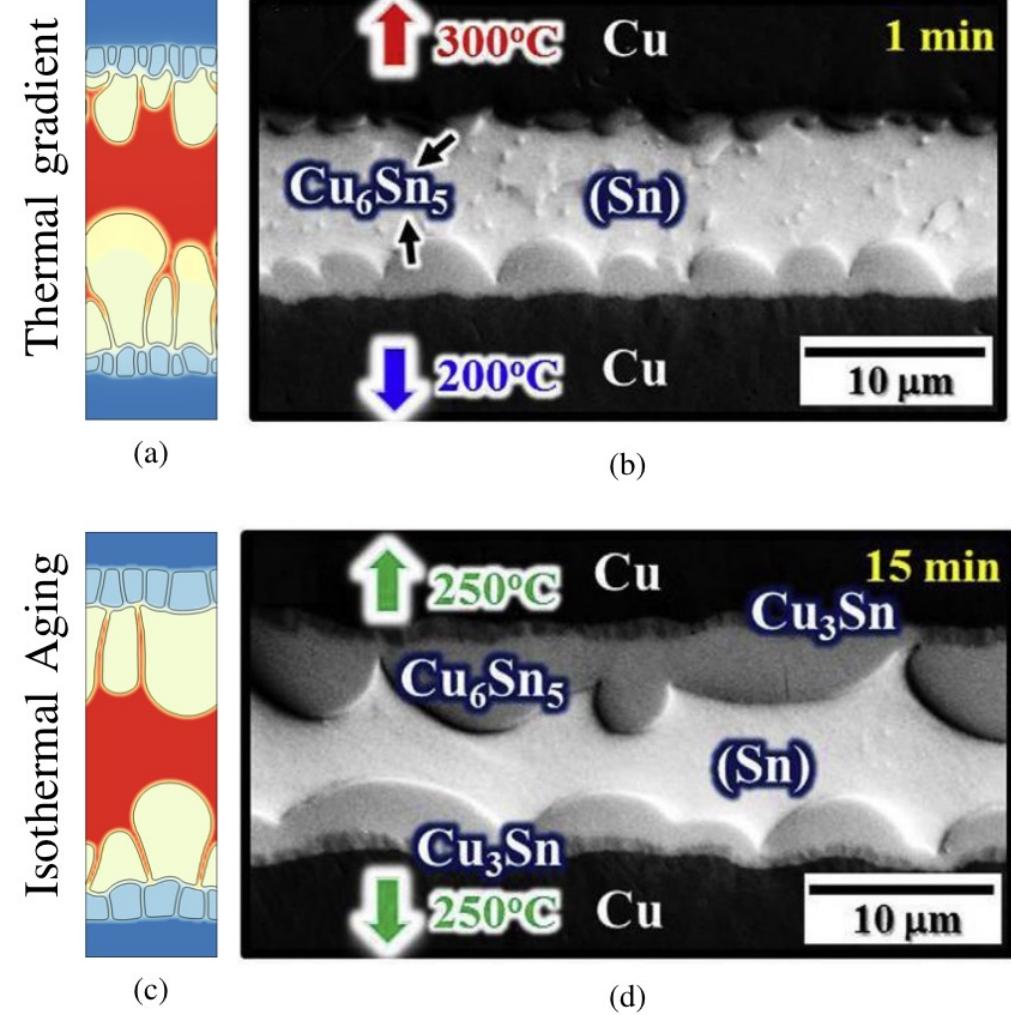
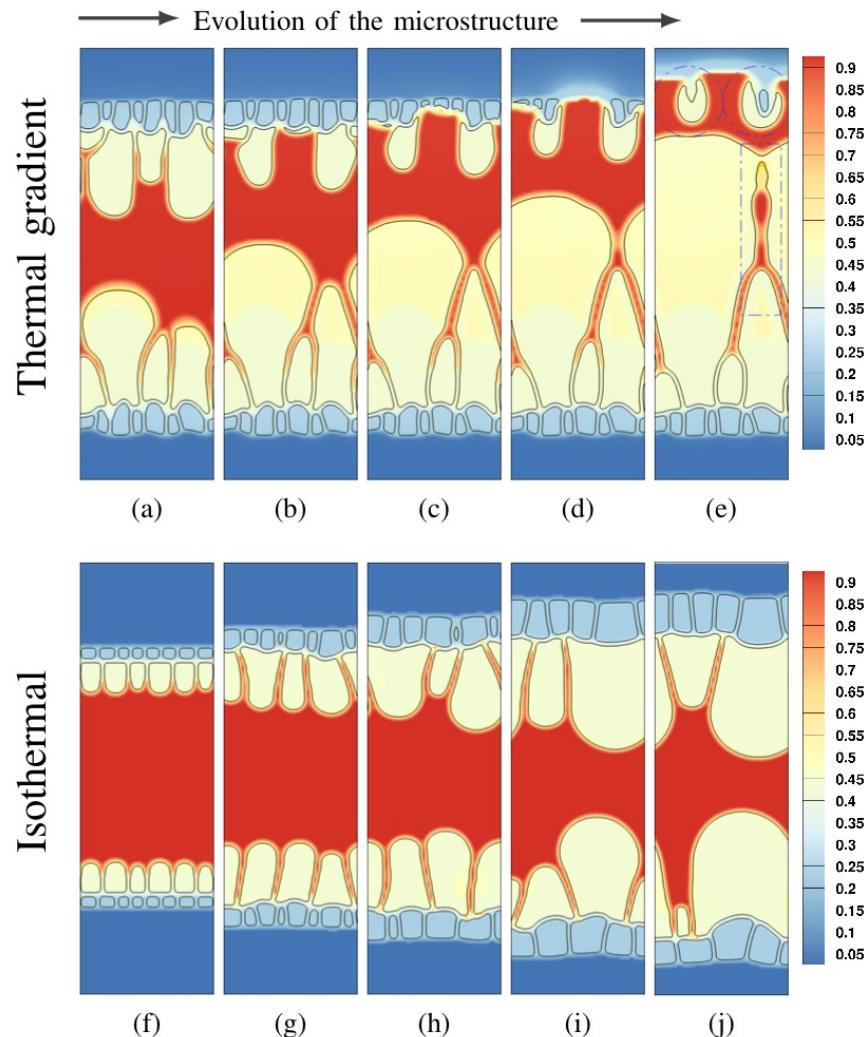


Significance of phase transitions in Additive Manufacturing Processes

The development of grain structure during additive manufacturing of metals

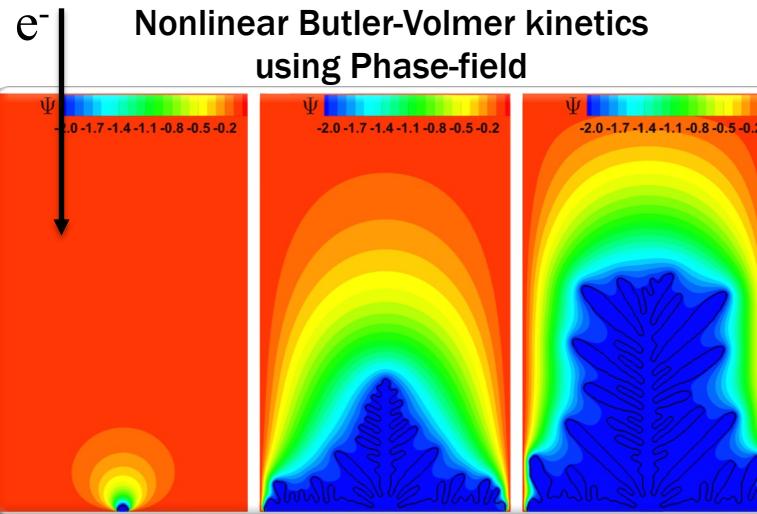


Significance of phase transitions in Microchip Packaging Materials



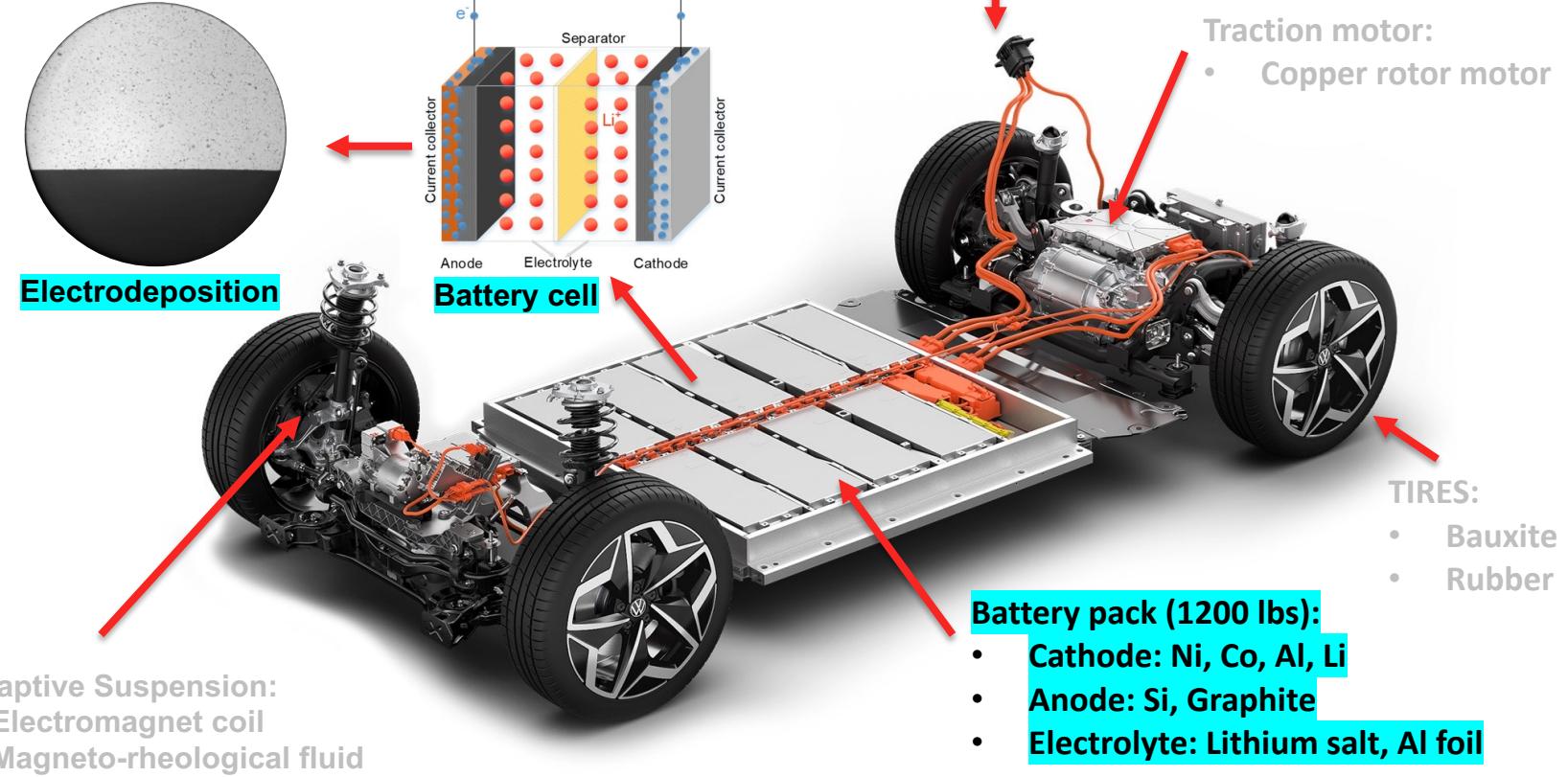
Significance of phase transitions in Automotive Battery cells

Electric field



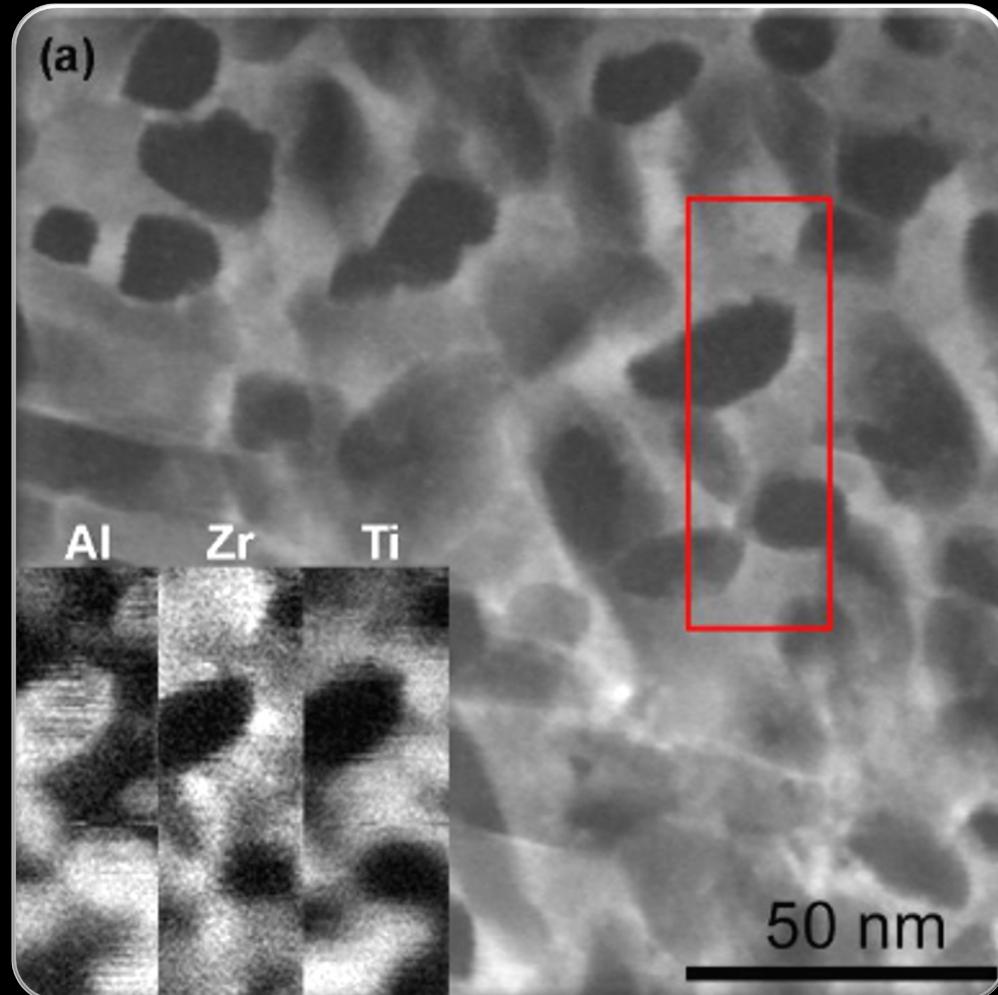
Evolution of dendritic pattern from an initial seed located in the bottom center of the domain

Formation of magnesium dendrites during electrodeposition



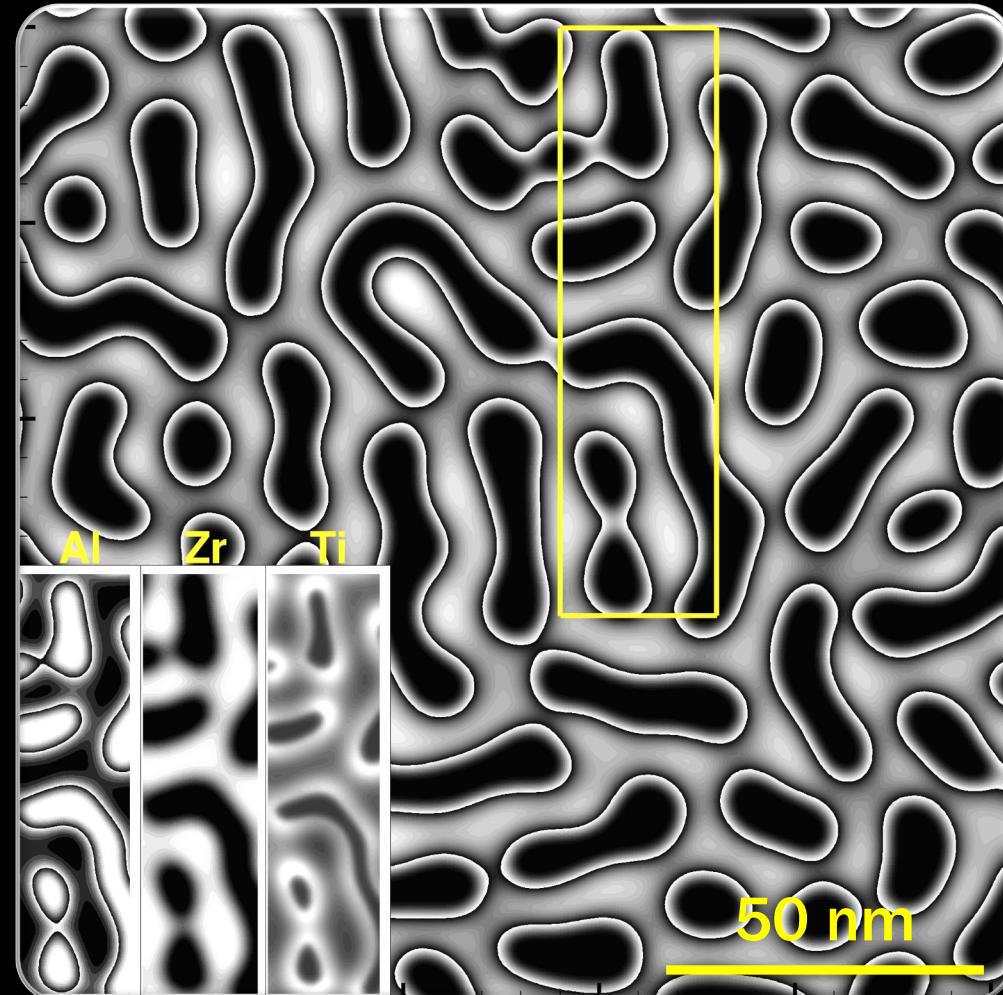
Elemental STEM Versus Phase-field Model ($\text{Ti}_{0.30}\text{Al}_{0.46}\text{Zr}_{0.24}\text{N}$)

STEM overview micrograph



Ref: Lind, H., et al. *AIP Advances* 4.12 (2014): 127147.

Phase-field overview micrograph



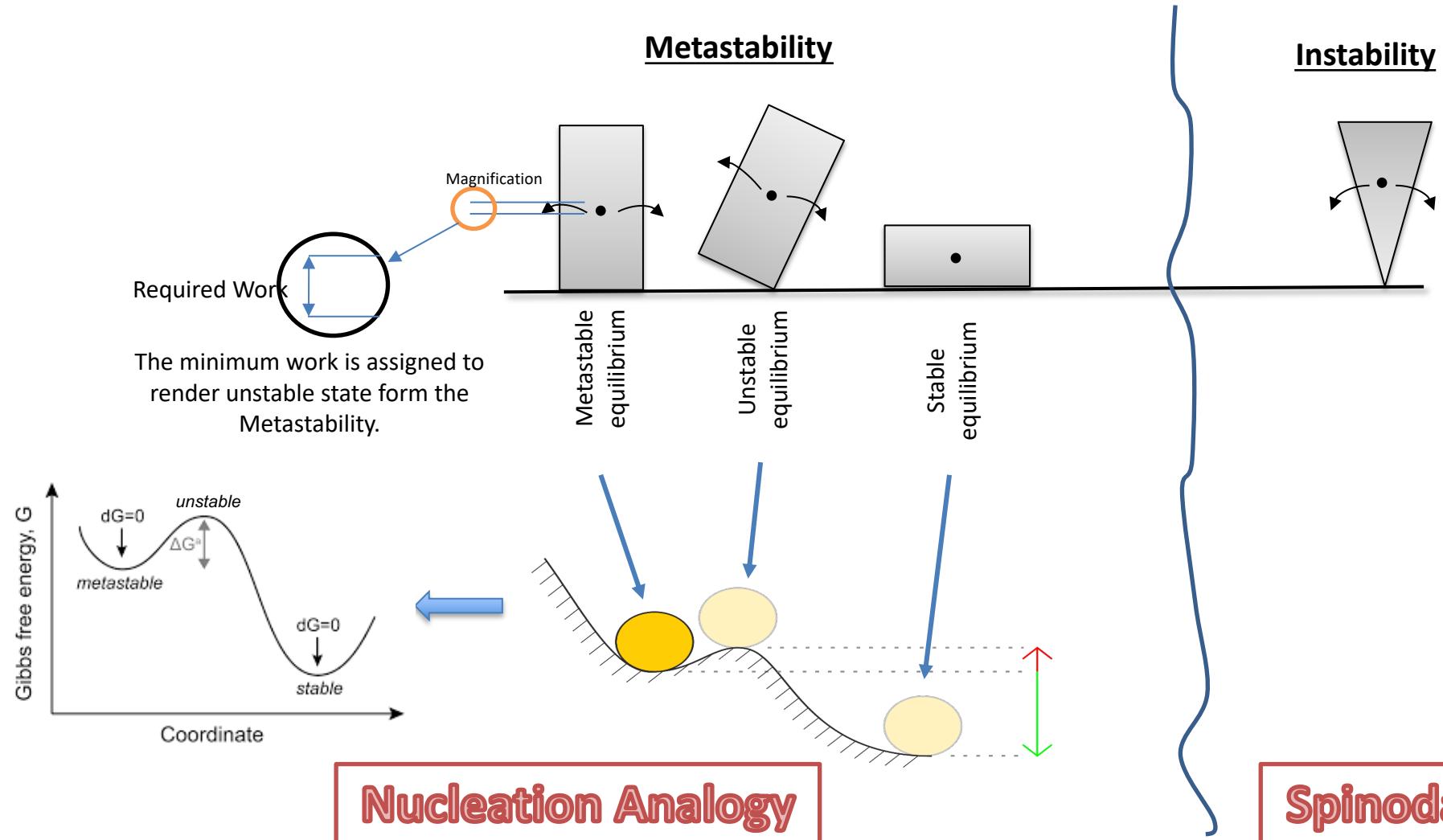
Ref: Attari, V., et al., *Acta Materialia* (2019).

Difference between stability, metastability, and instability



John W. Cahn

THE MECHANICAL ANALOGY OF SYSTEM STATES

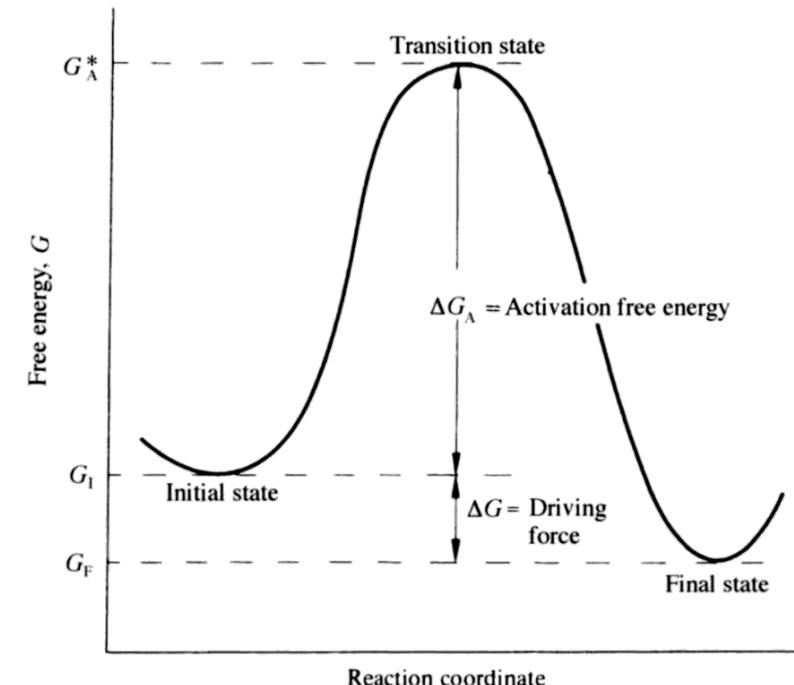


Driving forces for microstructural change - reduction of Gibbs free energy

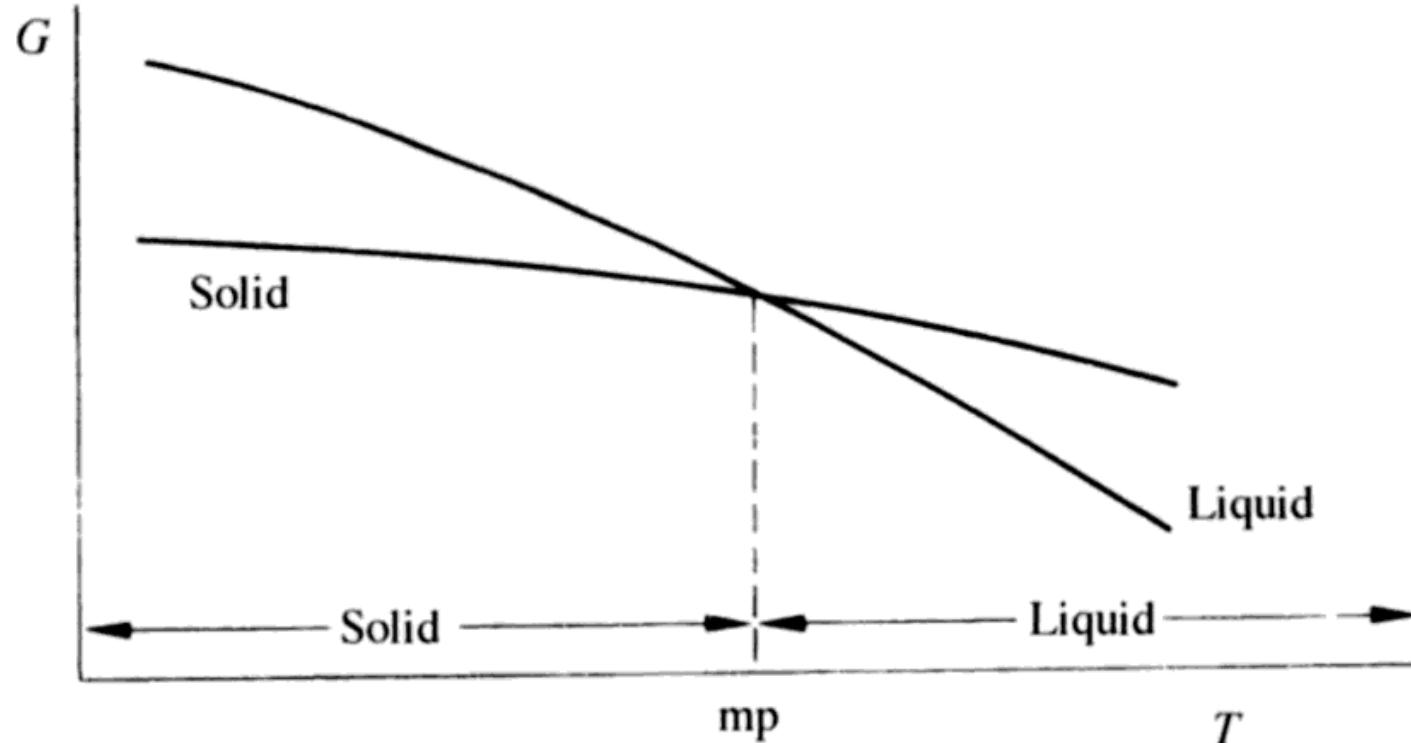
- The parameter driving all solid-state structural phase transformations at constant temperature and pressure is the reduction of Gibbs free energy,

$$G = H - TS = U + PV - TS$$

- G_l : mean free energy of atom in the initial configuration,
- G_F : mean free energy of atom after transformation,
- $\Delta G = G_F - G_l$: driving force for phase transformation,
- ΔG_A : activation free energy of the reaction.



Example I: change in free energy during phase change in materials

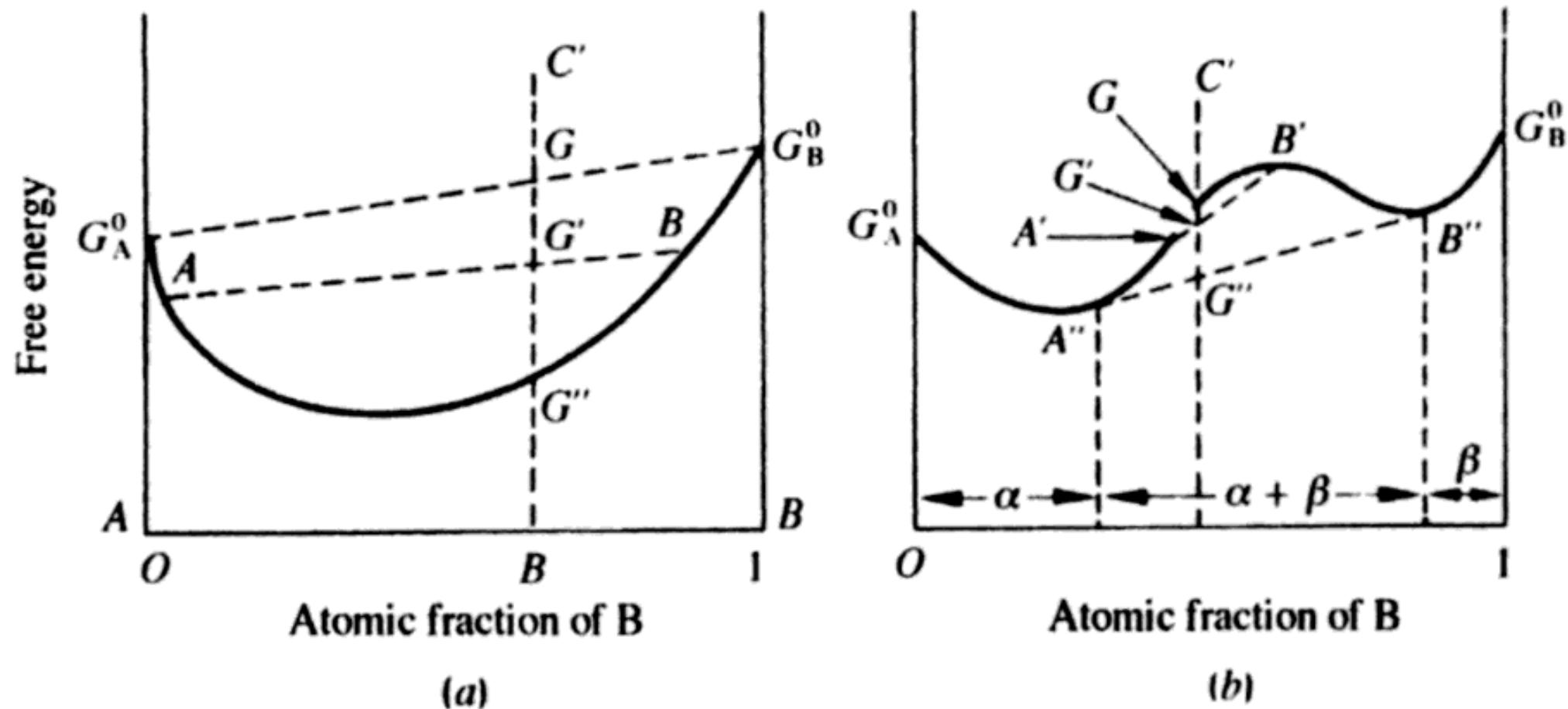


Solidification of
pure metal

Variation of free
energy by
temperature

$$\left. \frac{-dG}{dT} \right|_P = S$$

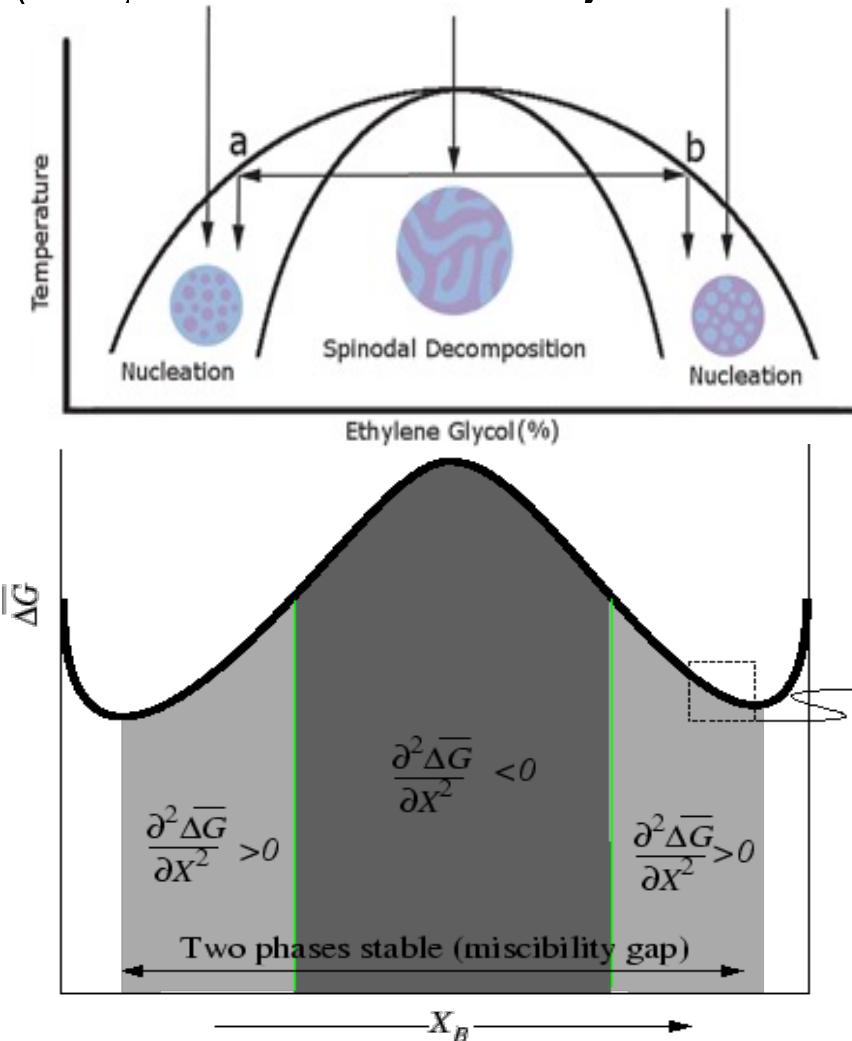
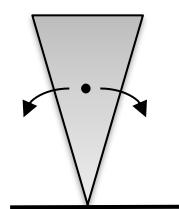
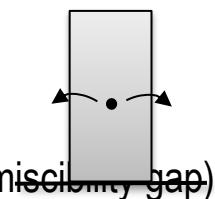
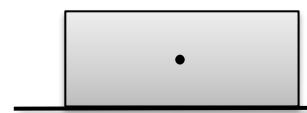
Example II: Homogenous equilibrium vs. heterogenous equilibrium



Homogenous equilibrium vs. heterogenous equilibrium

Difference between stability, metastability, and instability

- The distinction between transition states in materials was first made by Gibbs (1878), the founder of the subject
- Free energy in form of double-well potential, characterizing:
 - Stable region ($\partial^2 G / \partial C^2|_{P,T} > 0$)
 - Minimum in the free energy curve
 - Positive curvature
 - Metastable region ($\partial^2 G / \partial C^2|_{P,T} = 0$)
 - Resistant to small fluctuations
 - A barrier to the formation of phases (still within the miscibility gap)
 - Unstable region ($\partial^2 G / \partial C^2|_{P,T} < 0$)
 - Maximum in the free energy curve
 - Called spinodal.



Microstructure thermodynamics and kinetics

Formulation of the Non-equilibrium Coarse-grained Energy

$$F^{tot}(c, \eta) = \int_V [f^{bulk} + f^{interfacial} + f^{coupled}] dV$$

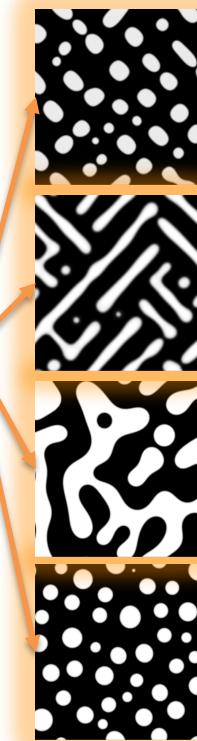
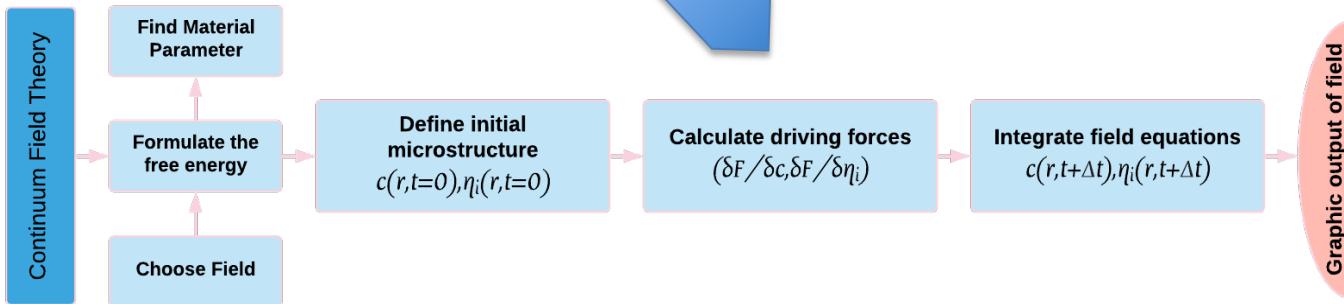
CALPHAD

Gradients in fields

$$f^{coupled} = - \int_V x Y dV$$

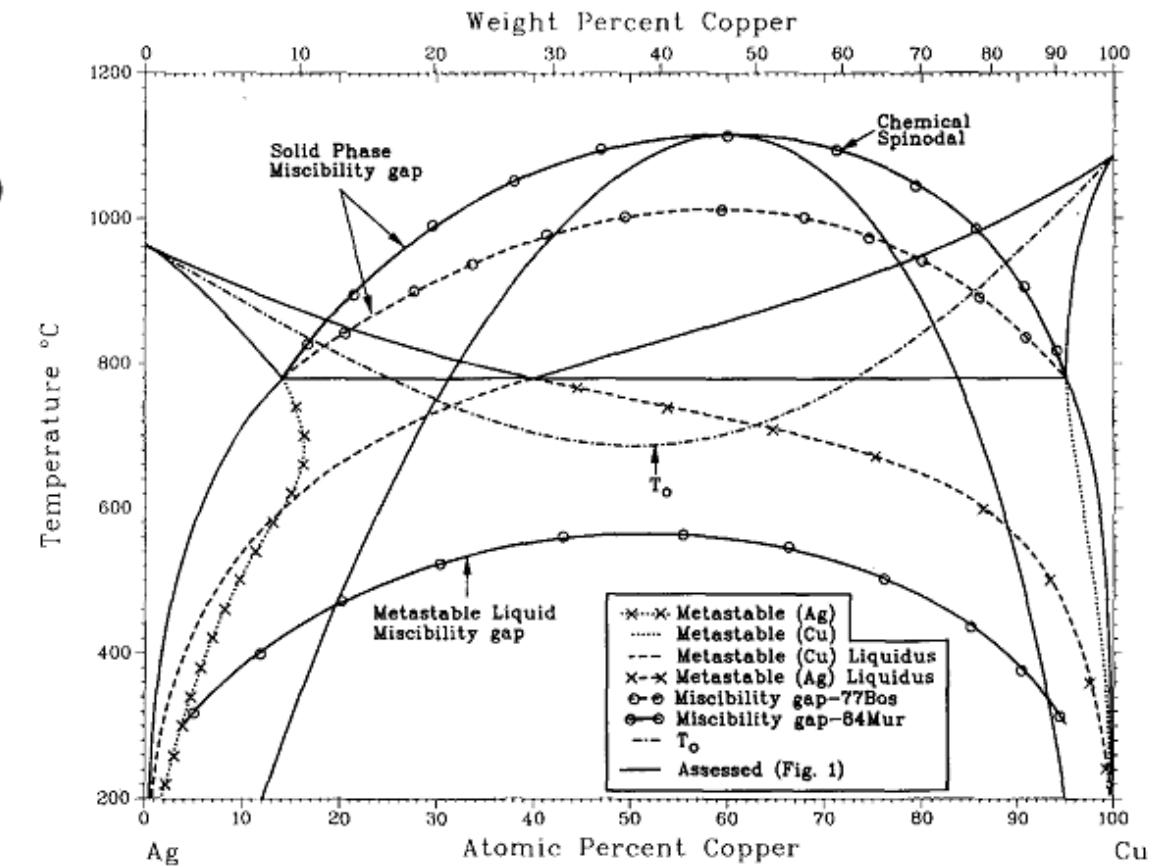
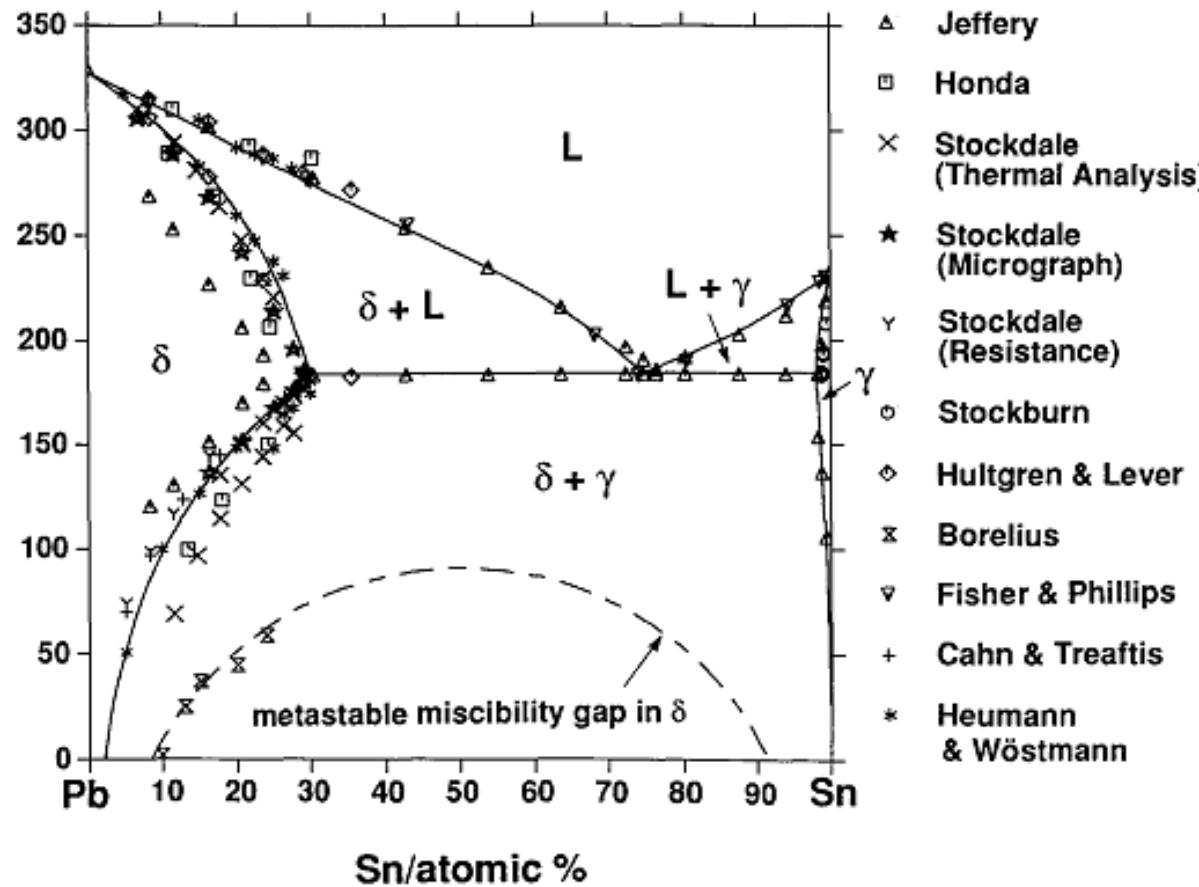
x : local field (local strain, local polarization, local magnetic moment)

Y : Applied stress, electric, magnetic field



Investigation of spinodal decomposition in binary alloys

Temperature /°C



Microstructure modeling - Cahn-Hilliard equation

Point 1: Free energy

$$F = \int_V [\text{Bulk energy density} + \text{Interface energy density} + \text{Elastic energy} + \dots] dV$$

In the general case

$$F\left(c, \emptyset, \frac{\partial c}{\partial x}, \frac{\partial \phi}{\partial x}, \dots\right)$$

Point 2: Diffusion potential

$$\mu_A - \mu_B = \frac{\delta F}{\delta c} = \frac{\partial f}{\partial c} - 2\kappa\nabla^2 c$$

Chemical or diffusional potential!?

$$\begin{aligned}f_A - cf'_A &= \mu_A \\f_B - cf'_B &= \mu_B\end{aligned}$$

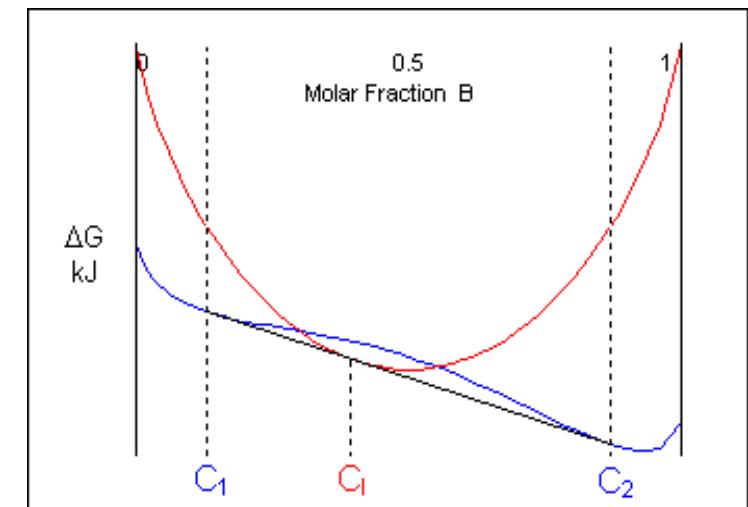
$$@ C_1: f_A - cf'_A = f_B - cf'_B \rightarrow f'_A = f'_B$$

$$\mu_A - \mu_B$$

Diffusion potential

$$\frac{\partial c}{\partial t} = M \left(\frac{\partial^2 f}{\partial c^2} \nabla^2 c - 2\kappa\nabla^4 c \right)$$

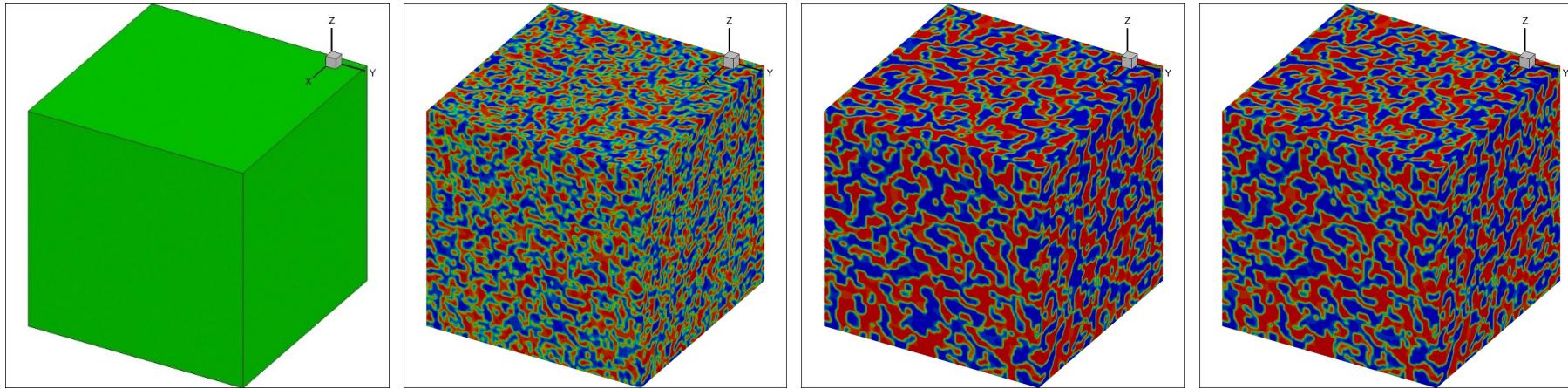
CAHN-HILLIARD EQUATION



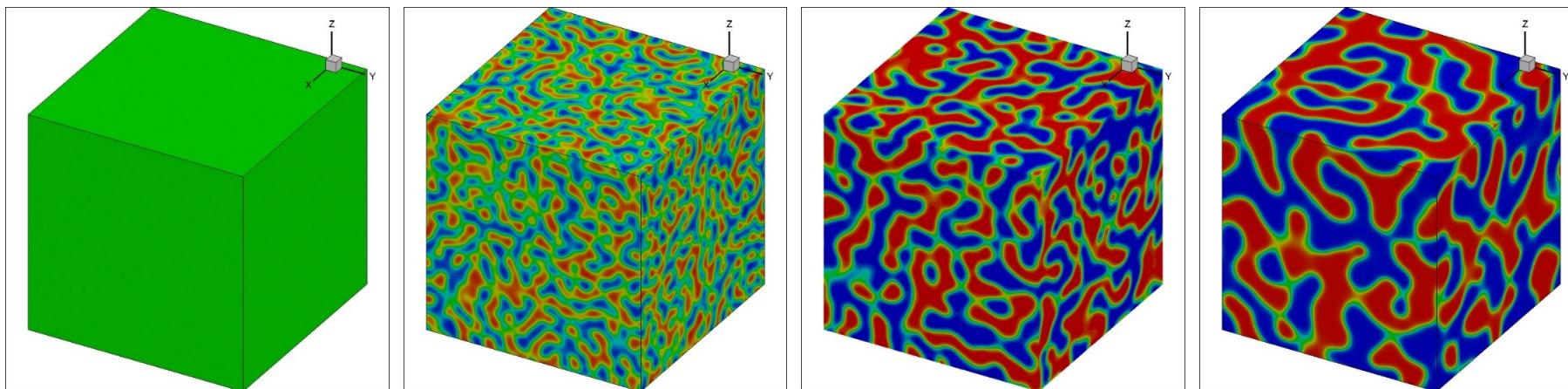
Common tangent construction

Modeling Spontaneous Phase Separation in Materials

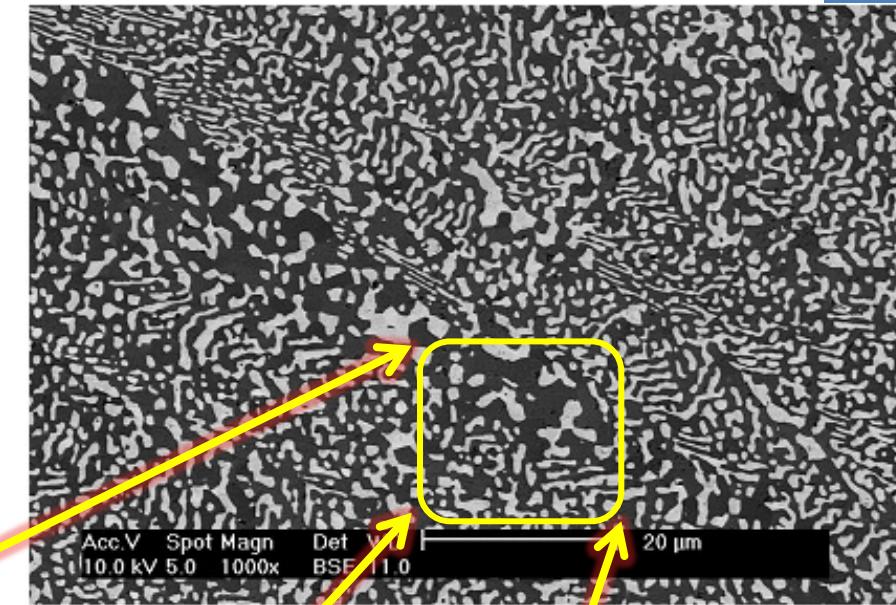
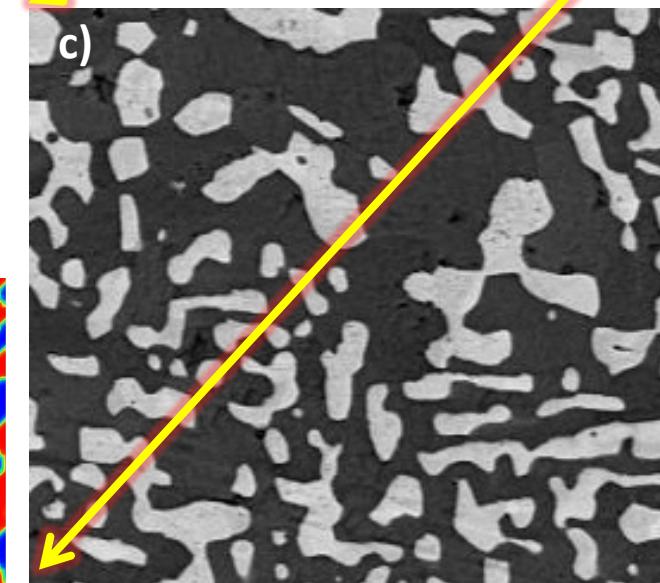
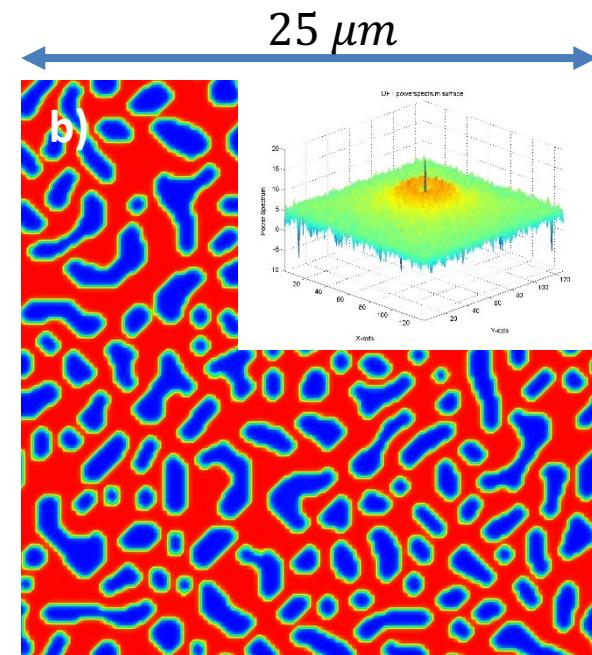
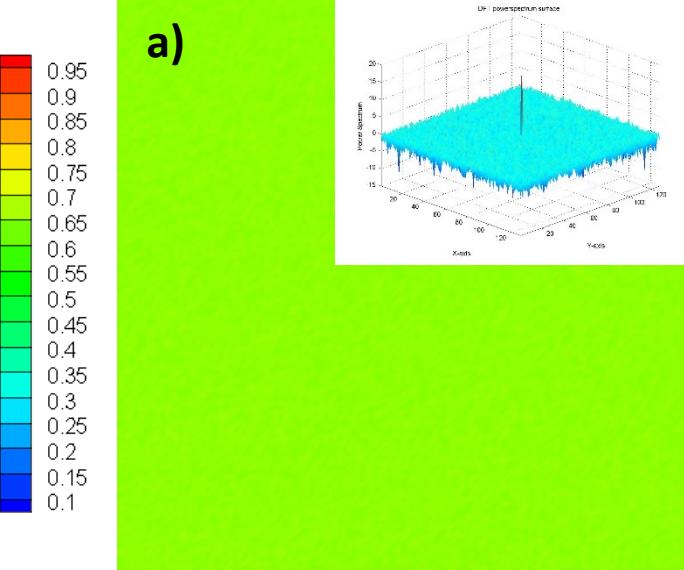
$\kappa = 0.005$



$\kappa = 0.03$

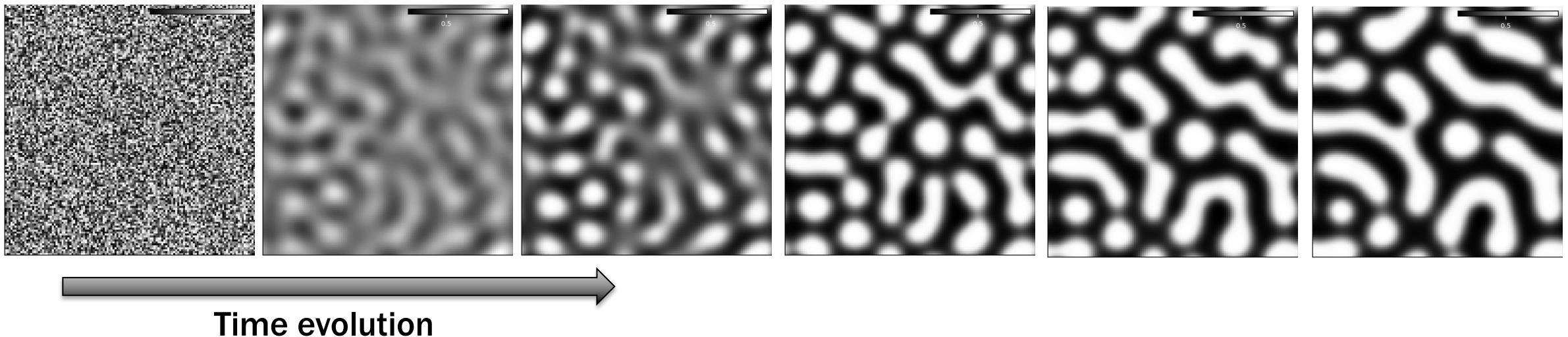


How Cahn-Hilliard model leads the way...



Calculated microstructures over time

Jupyter Notebook time...



Link to notebook and slides:

https://github.com/vahid2364/Phase-field_PyCalphad-Tutorial

Good reads and references

- Martin JW, Doherty RD, Cantor B. Stability of microstructure in metallic systems. Cambridge University Press; 1997 Mar 6.
- Attari V, Ghosh S, Duong T, Arroyave R. On the interfacial phase growth and vacancy evolution during accelerated electromigration in Cu/Sn/Cu microjoints. *Acta Materialia*. 2018 Nov 1;160:185-98.
- Moelans N, Blanpain B, Wollants P. An introduction to phase-field modeling of microstructure evolution. *Calphad*. 2008 Jun 1;32(2):268-94.
- Karayagiz K, Johnson L, Seede R, Attari V, Zhang B, Huang X, Ghosh S, Duong T, Karaman I, Elwany A, Arróyave R. Finite interface dissipation phase field modeling of Ni–Nb under additive manufacturing conditions. *Acta Materialia*. 2020 Feb 15;185:320-39.
- Attari V, Cruzado A, Arroyave R. Exploration of the microstructure space in TiAlZrN ultra-hard nanostructured coatings. *Acta Materialia*. 2019 Aug 1;174:459-76.
- Yi SI, Attari V, Jeong M, Jian J, Xue S, Wang H, Arroyave R, Yu C. Strain-induced suppression of the miscibility gap in nanostructured Mg₂Si–Mg₂Sn solid solutions. *Journal of Materials Chemistry A*. 2018;6(36):17559-70.

Thanks!

Questions?