



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

Introduction to Microstructure Thermodynamics

MSEN 210 Thermodynamics of Materials
Texas A&M University

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

Review I: Thermodynamics of multicomponent systems

- $H = U + PV$
 - 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 $\rightarrow \frac{\partial H}{\partial n_i} = \frac{\partial U}{\partial n_i} + P \frac{\partial V}{\partial n_i}$ 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

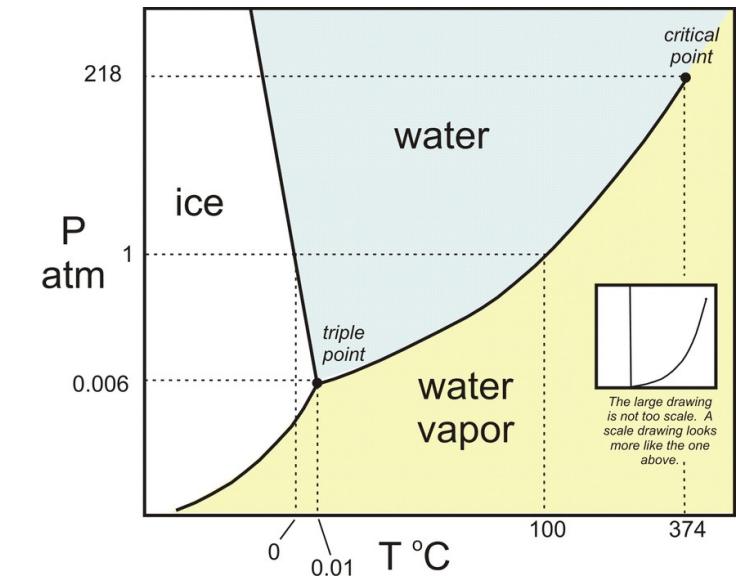
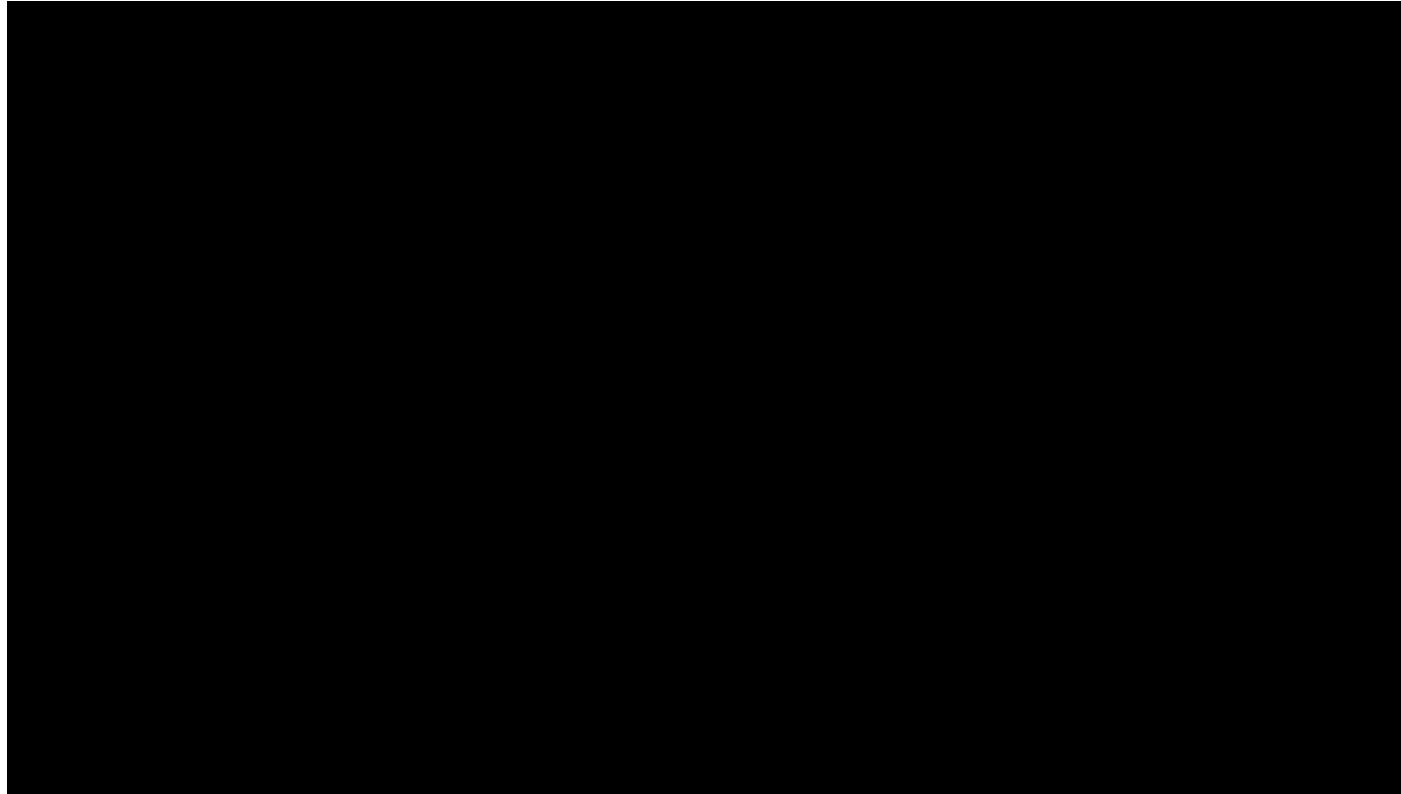
- Link to PyCALPHAD tutorials:
- Calculated binary and ternary phase diagrams
- Extracted free energy different phases along diffusion lines
- Extracted free energy different phases for an alloy with fixed composition for different temperatures
- Reviewed lever rule
- Performed equilibrium calculations
- Calculated enthalpy of mixing
- Calculated activity of different phases

Topics to cover today

- Triple point and critical point in materials
 - How can water, ice, and steam exist at once?
- 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
 - Phase separation
 - Ag-Cu binary alloy

Triple point in materials

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

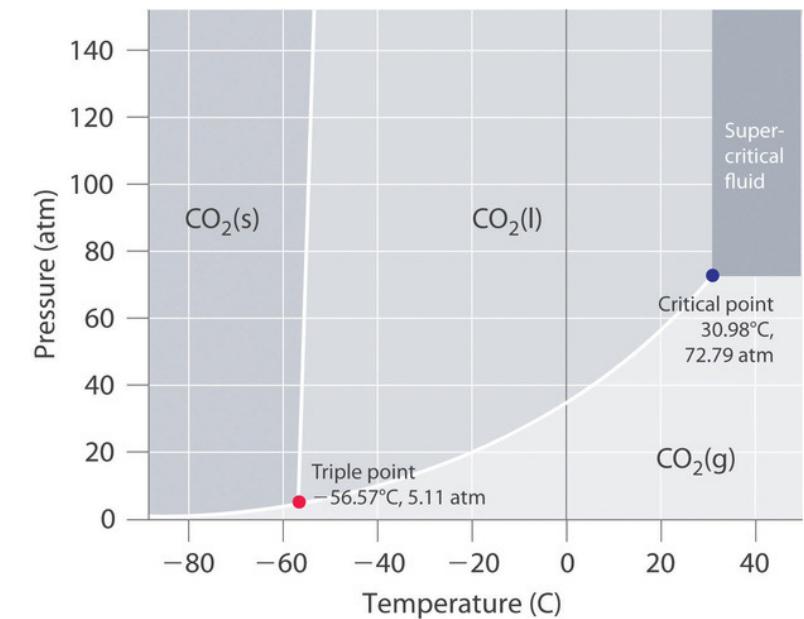


Critical point in materials

- Application:
- Solvents
- Supercritical fluid products



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.

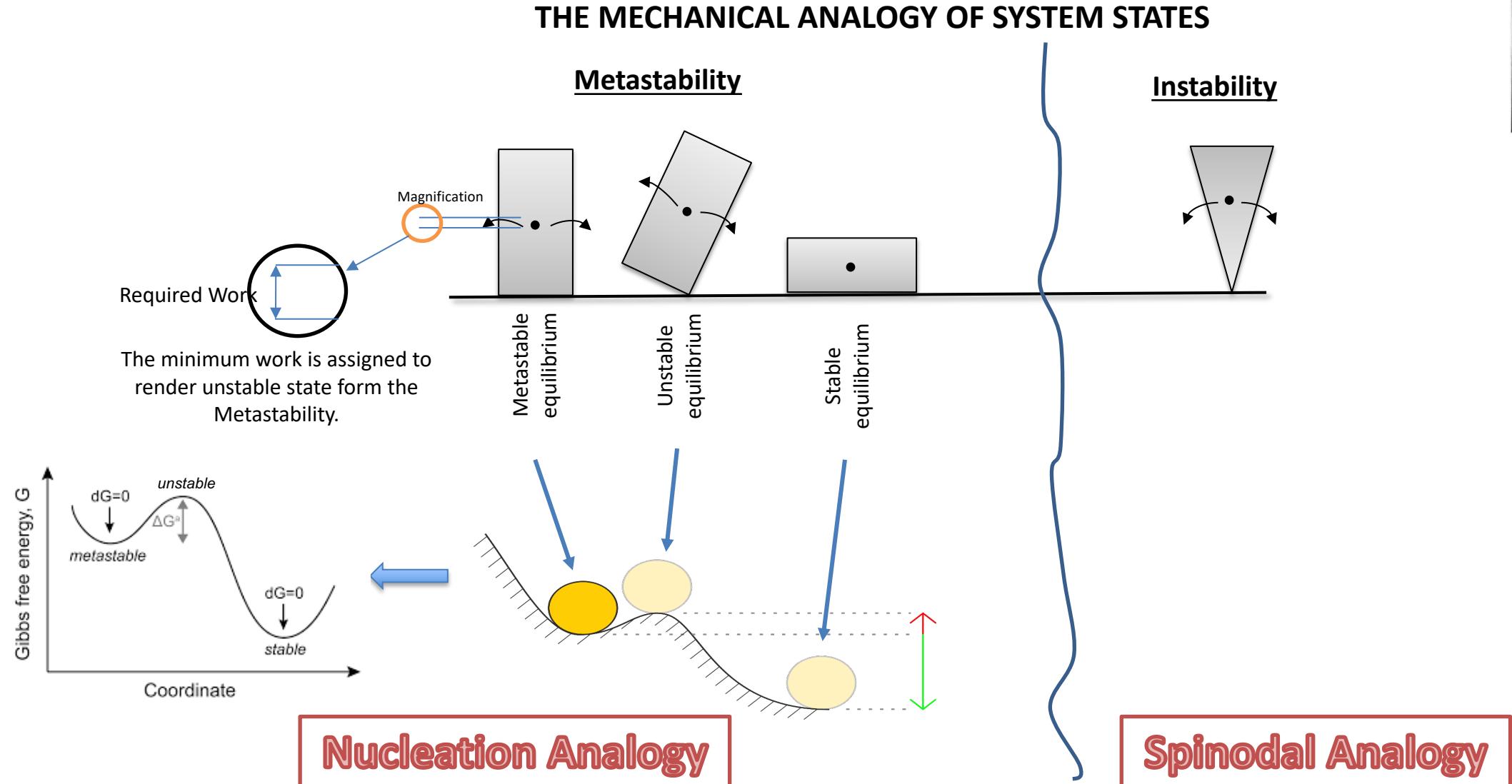


$$\frac{\partial c}{\partial t} = \nabla \cdot \left(M \nabla \left(\frac{\partial f}{\partial c} - 2\kappa \nabla^2 c \right) \right)$$

Difference between stability, metastability, and instability



John W. Cahn

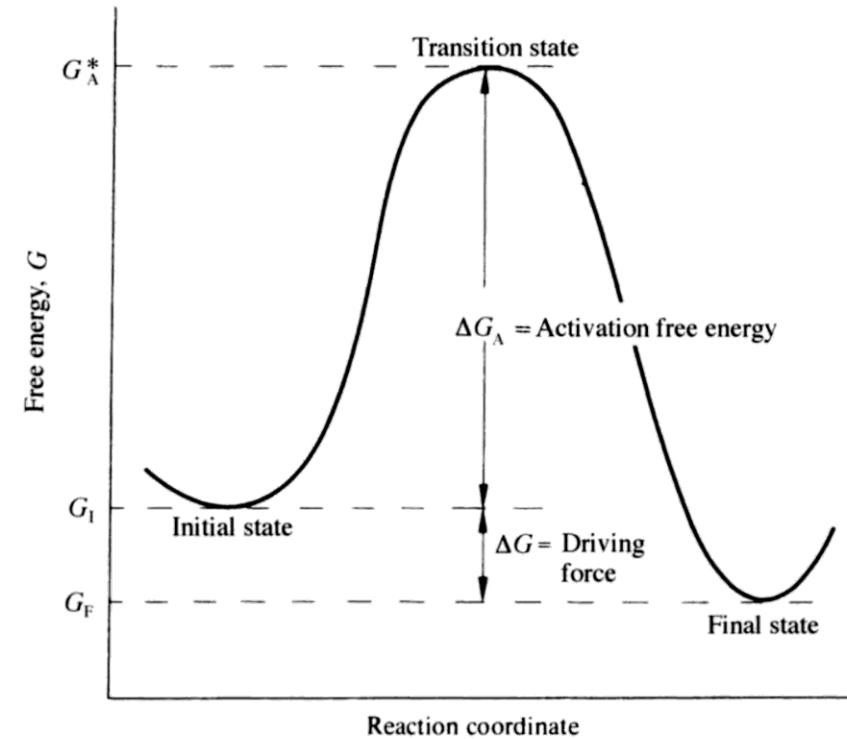


Driving forces for microstructural change - reduction of Gibbs free energy

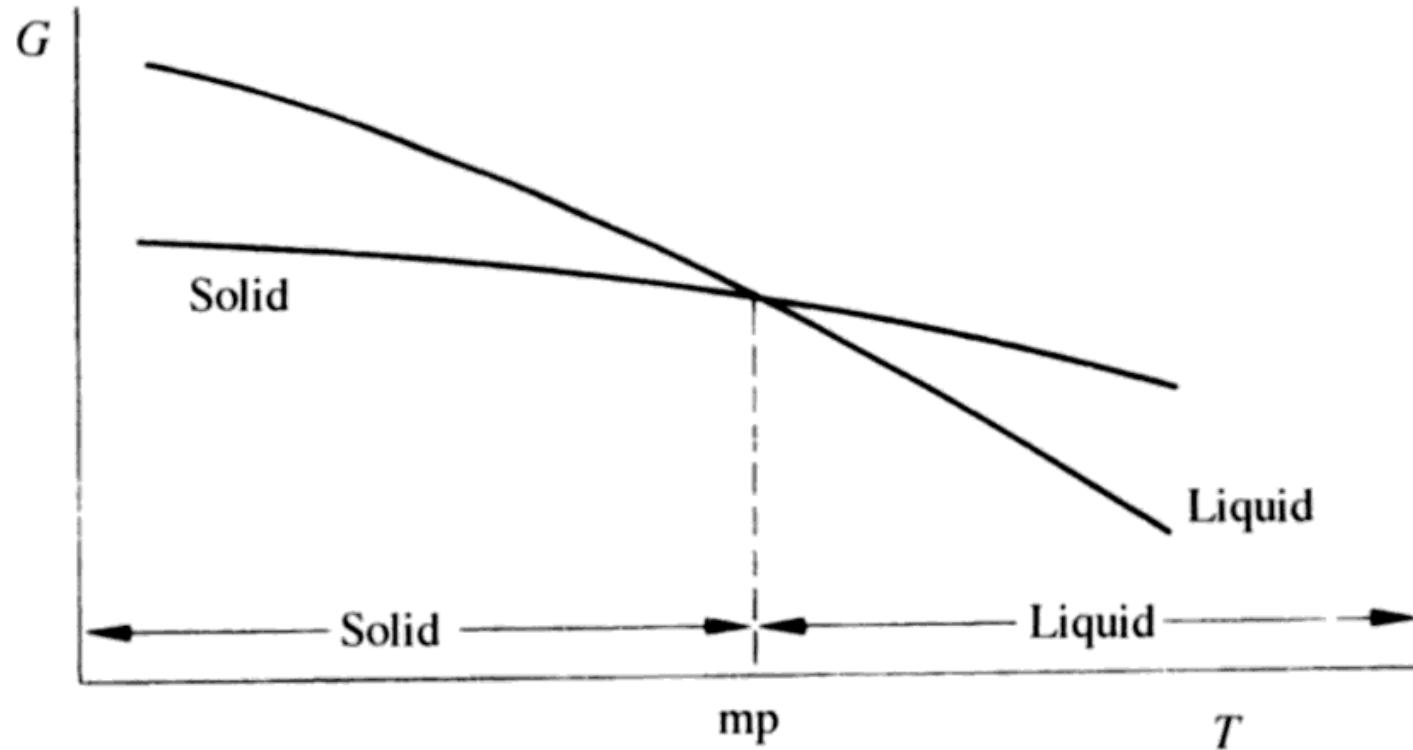
- The parameter driving all solid state structural phase transformations at constant temperature and pressure is the reduction of Gibbs free energy,

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

- 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

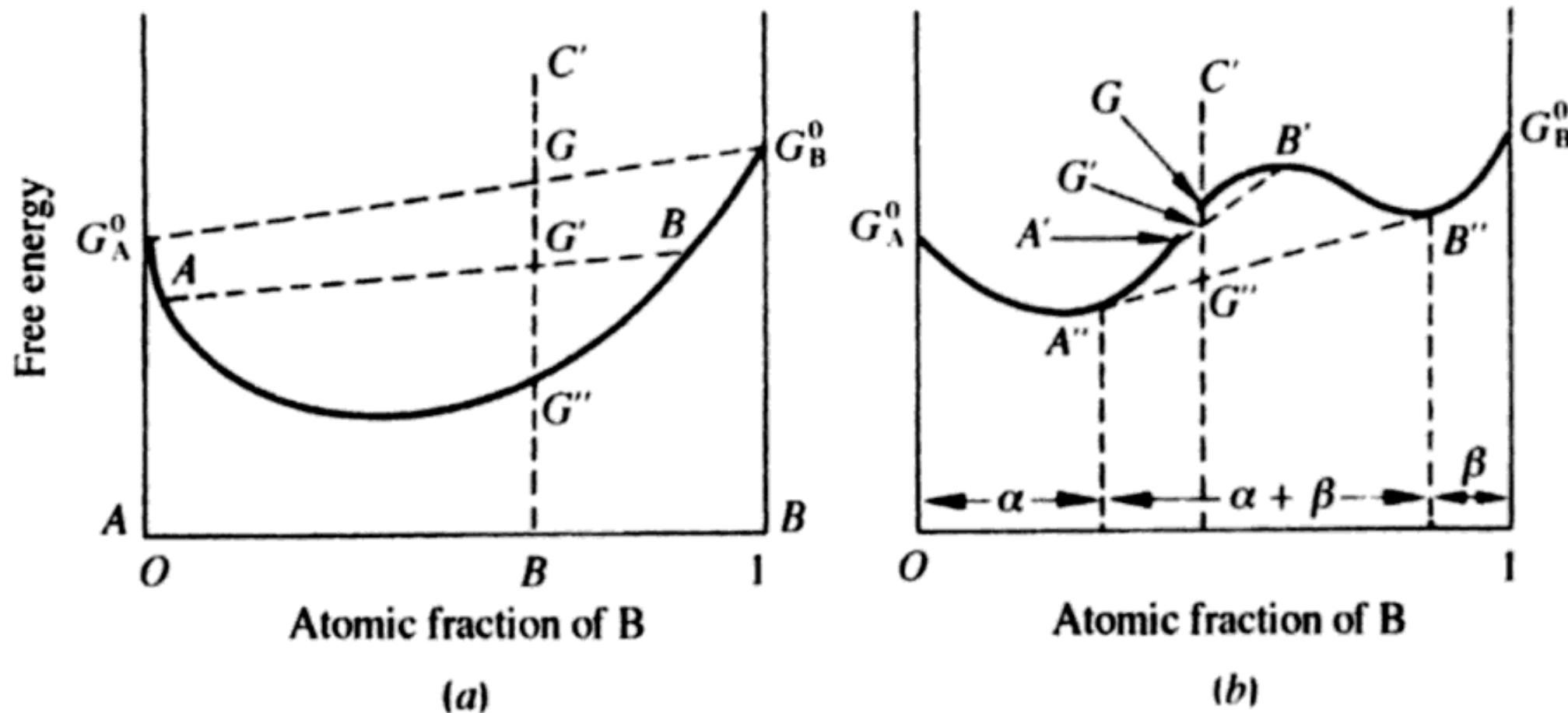


Solidification of pure metal

Variation of free energy by temperature

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

Example II: Precipitation of a 2nd phase from a supersaturated solid solution



Homogenous equilibrium vs. heterogenous equilibrium

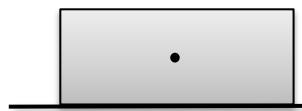
Difference between stability, metastability, and instability

- 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:

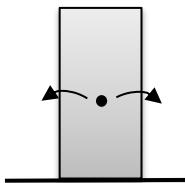
- Stable region ($\partial^2 G / \partial C^2|_{P,T} > 0$)

- Minimum in the free energy curve
 - Positive curvature



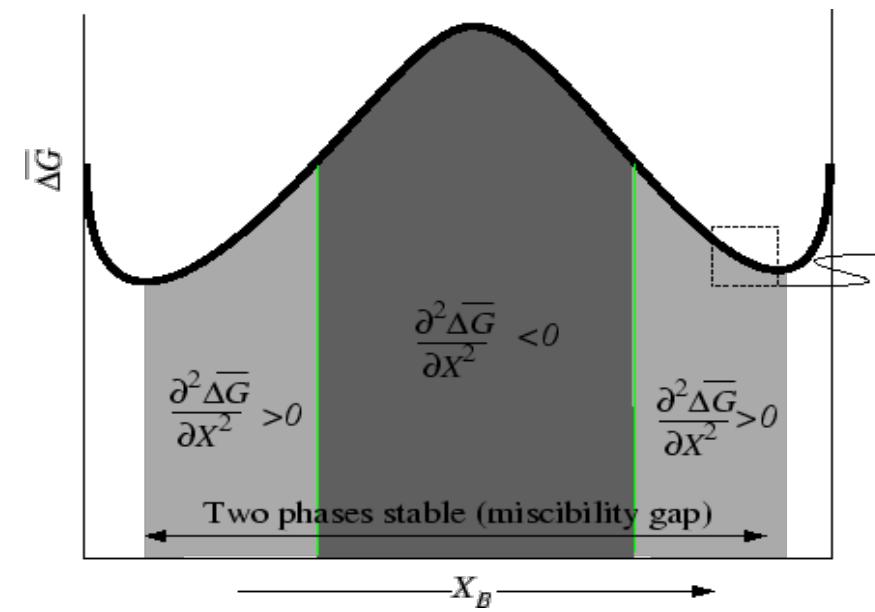
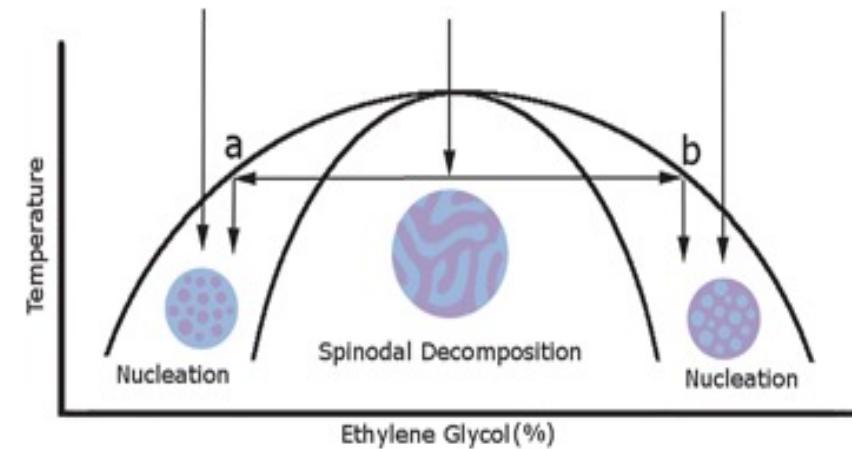
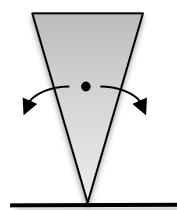
- Metastable region ($\partial^2 G / \partial C^2|_{P,T} = 0$)

- Resistant to small fluctuations
 - A barrier to the formation of phases (still within the miscibility gap)

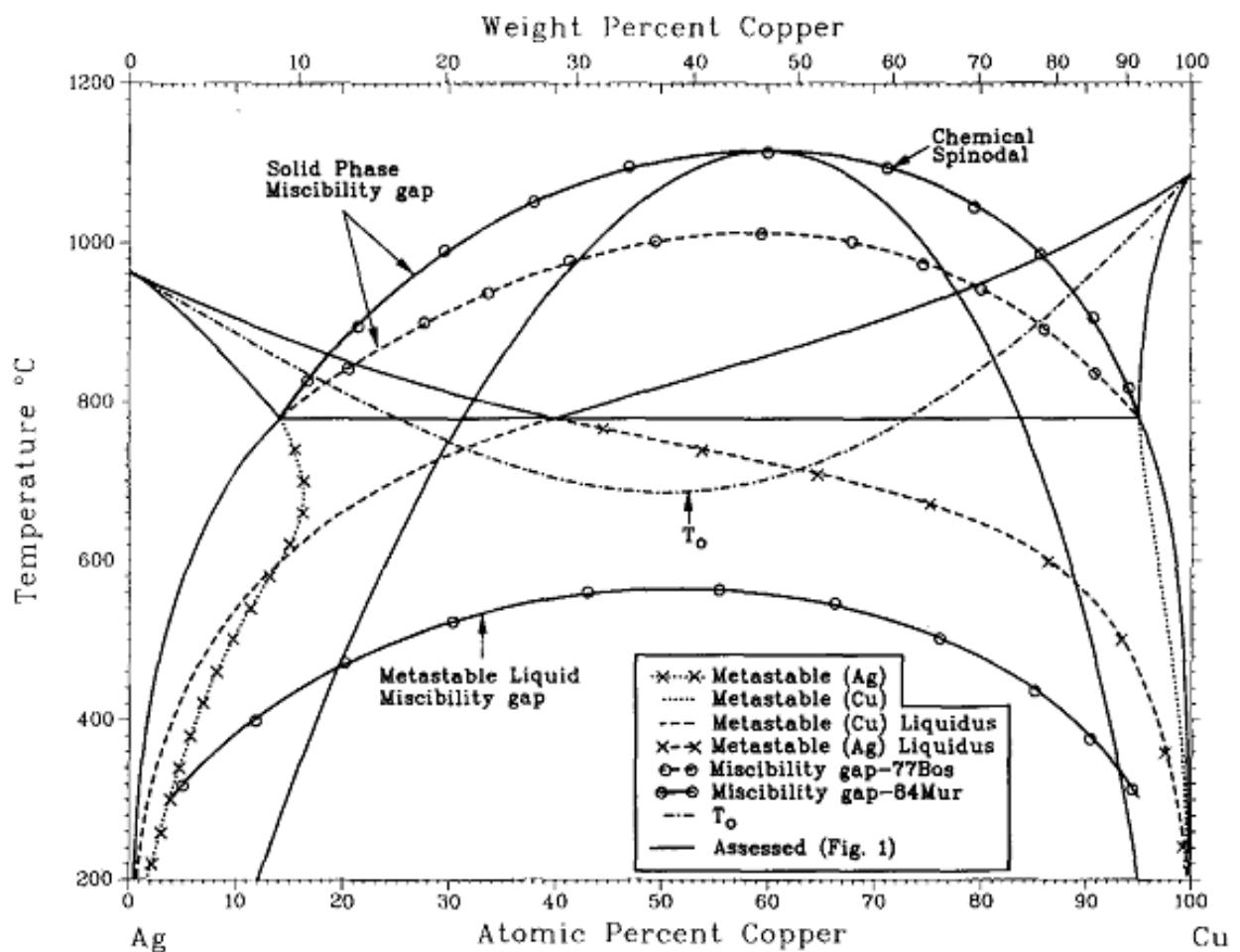
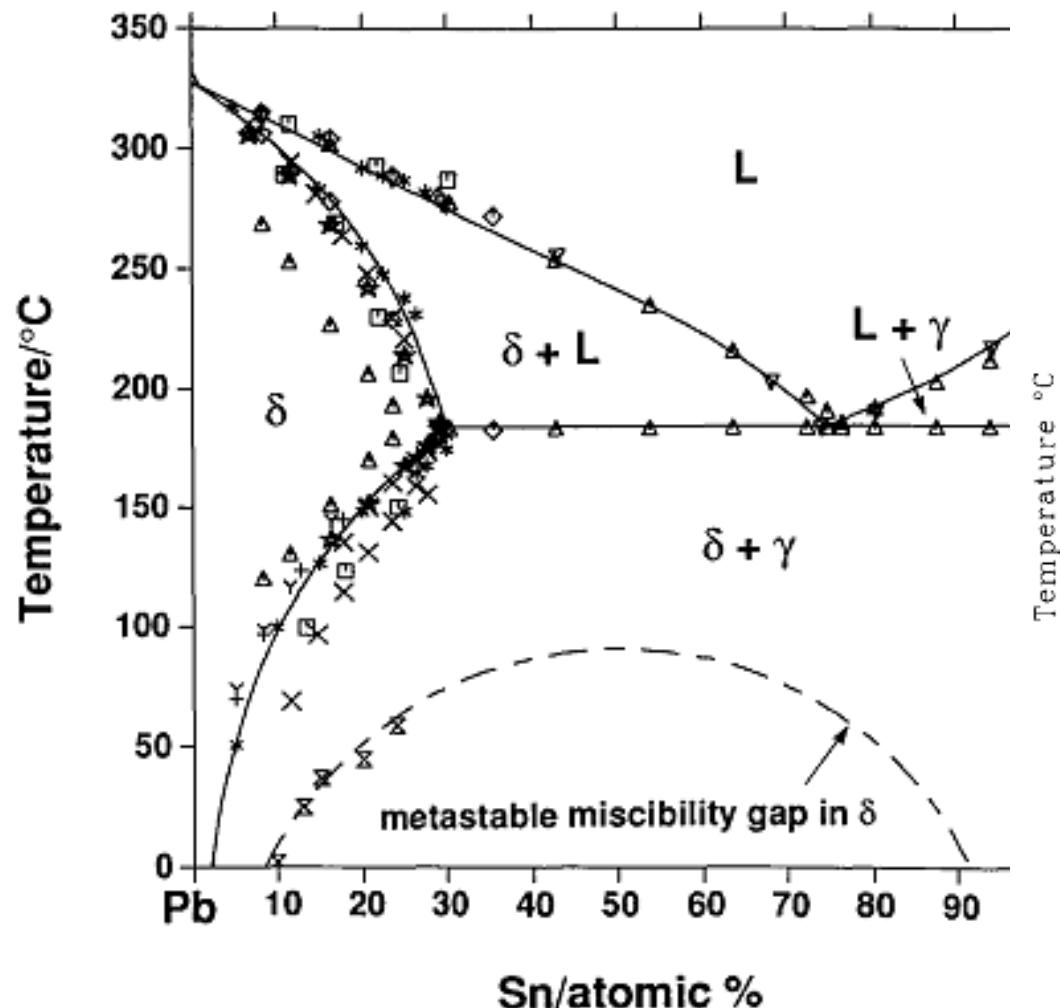


- Unstable region ($\partial^2 G / \partial C^2|_{P,T} < 0$)

- Maximum in the free energy curve
 - Called spinodal.



Investigation of spinodal in binary alloys



Microstructure Modeling

Point 1: Free energy

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

In the general case

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

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!?

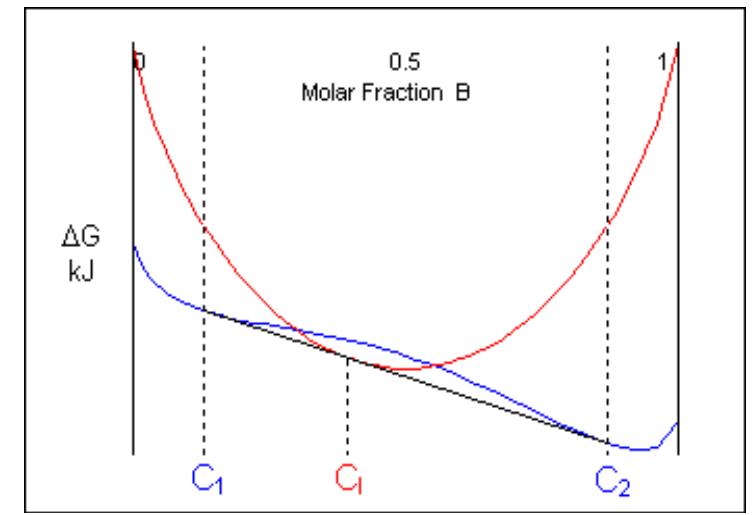
$$\begin{aligned}f_A - cf'_A &= \mu_A \\f_B - cf'_B &= \mu_B\end{aligned}$$

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

$$\mu_A - \mu_B$$

Diffusion potential

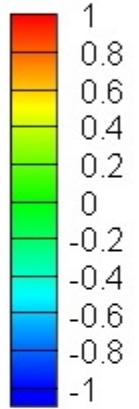
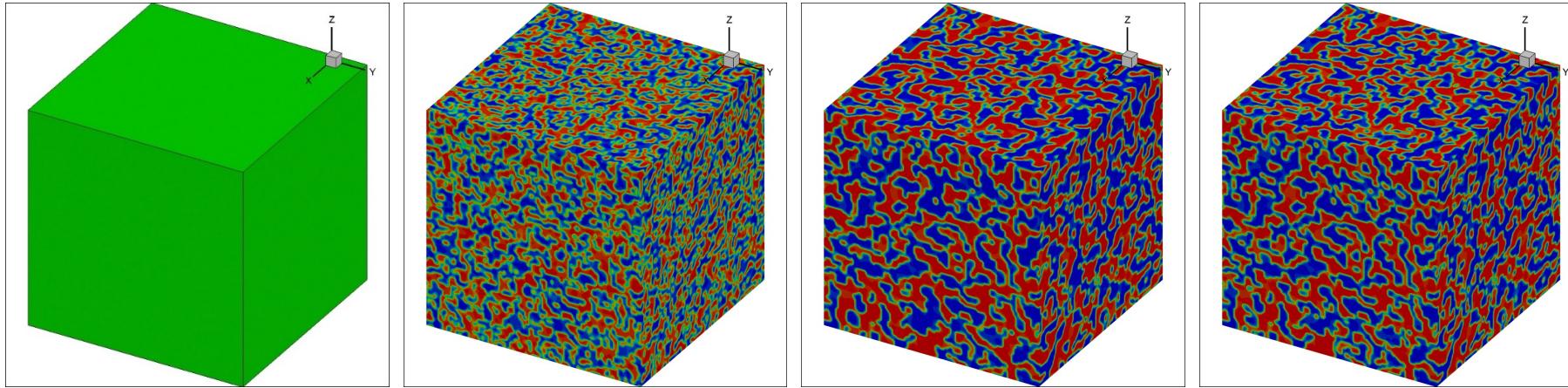
$$\frac{\partial c}{\partial t} = M \left(\frac{\partial^2 f}{\partial c^2} \nabla^2 c - 2\kappa\nabla^4 c \right) \quad \text{CAHN-HILLIARD EQUATION}$$



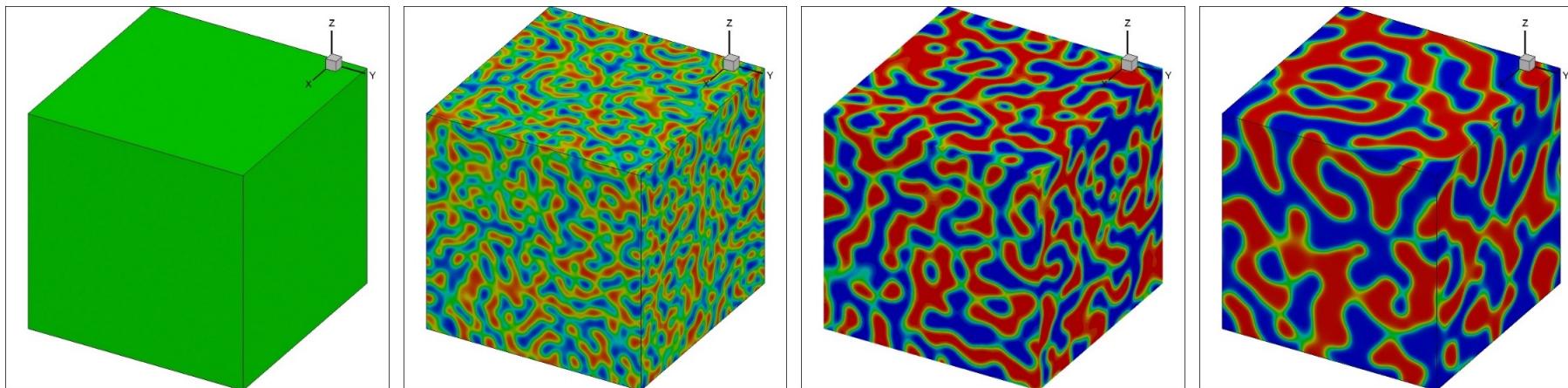
Common tangent construction

Modeling Spontaneous Phase Separation in Materials

$\kappa = 0.005$

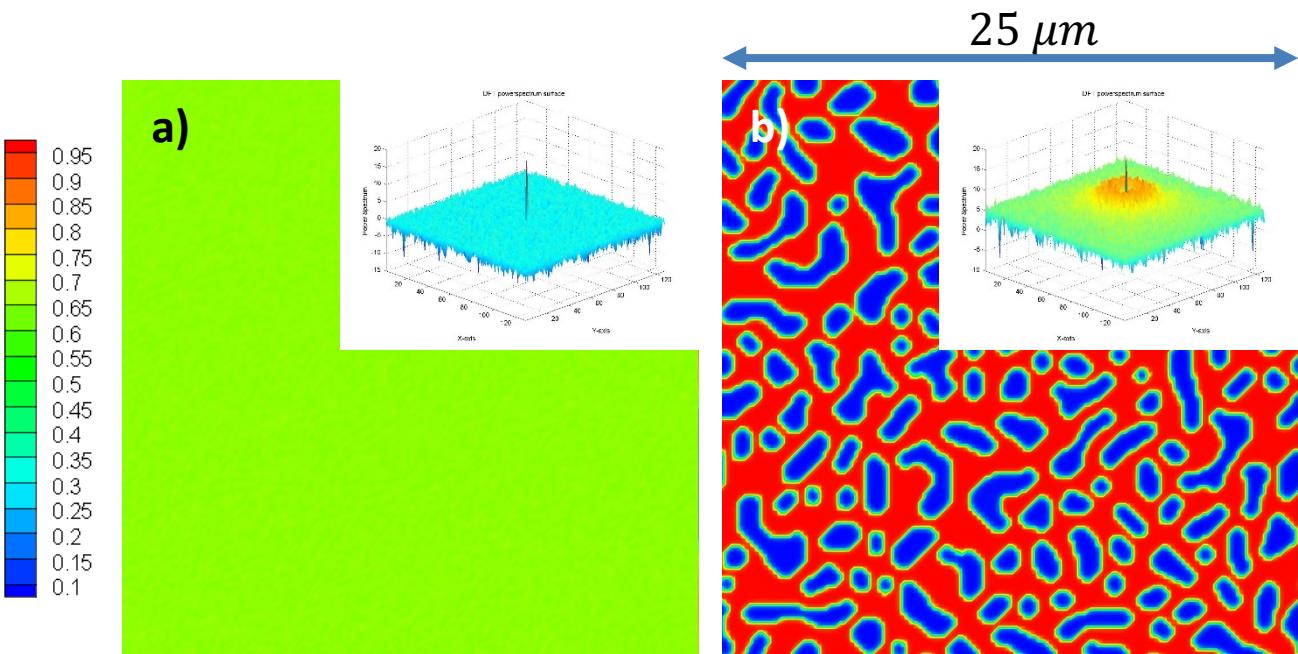
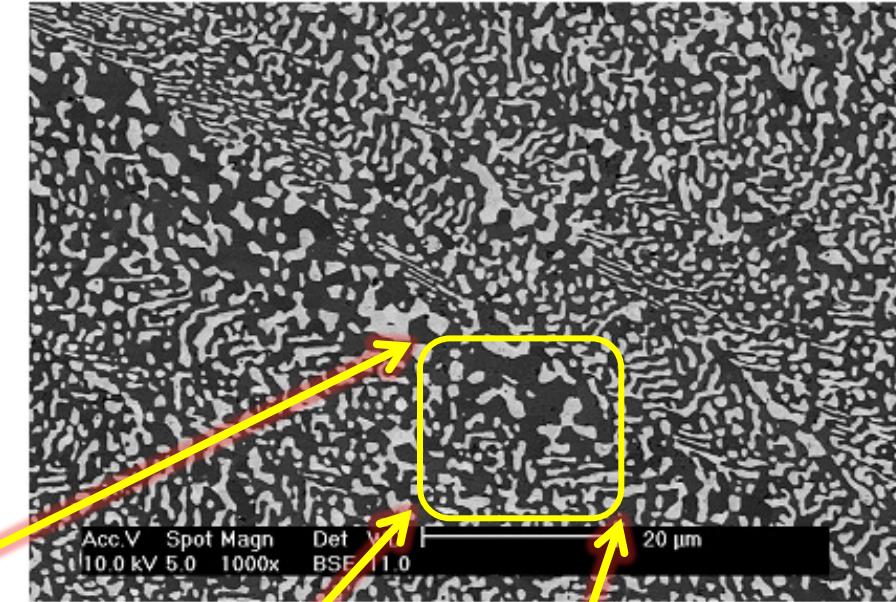


$\kappa = 0.03$



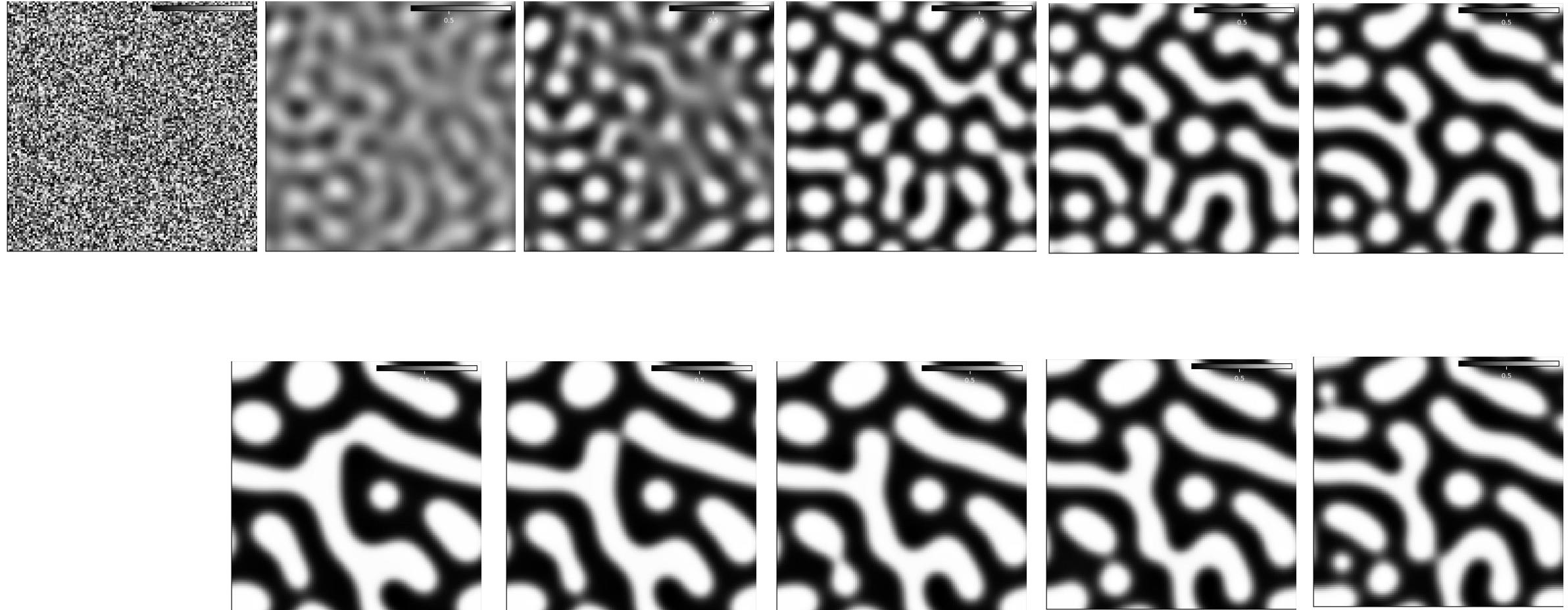
How Cahn-Hilliard model leads the way!

Mobility ($m^5/(Js)$)	Internal length scale (m)	Interface tension coefficient (J)	C_0	Grid size (m)
6.32×10^{-25}	12×10^{-9}	20×10^9	$0.63 \pm 1\%$	2×10^{-7}



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Calculated microstructures over time



Thanks