MATE 664 Lecture 16

Continuous Phase Transformation: Spinodal Decomposition

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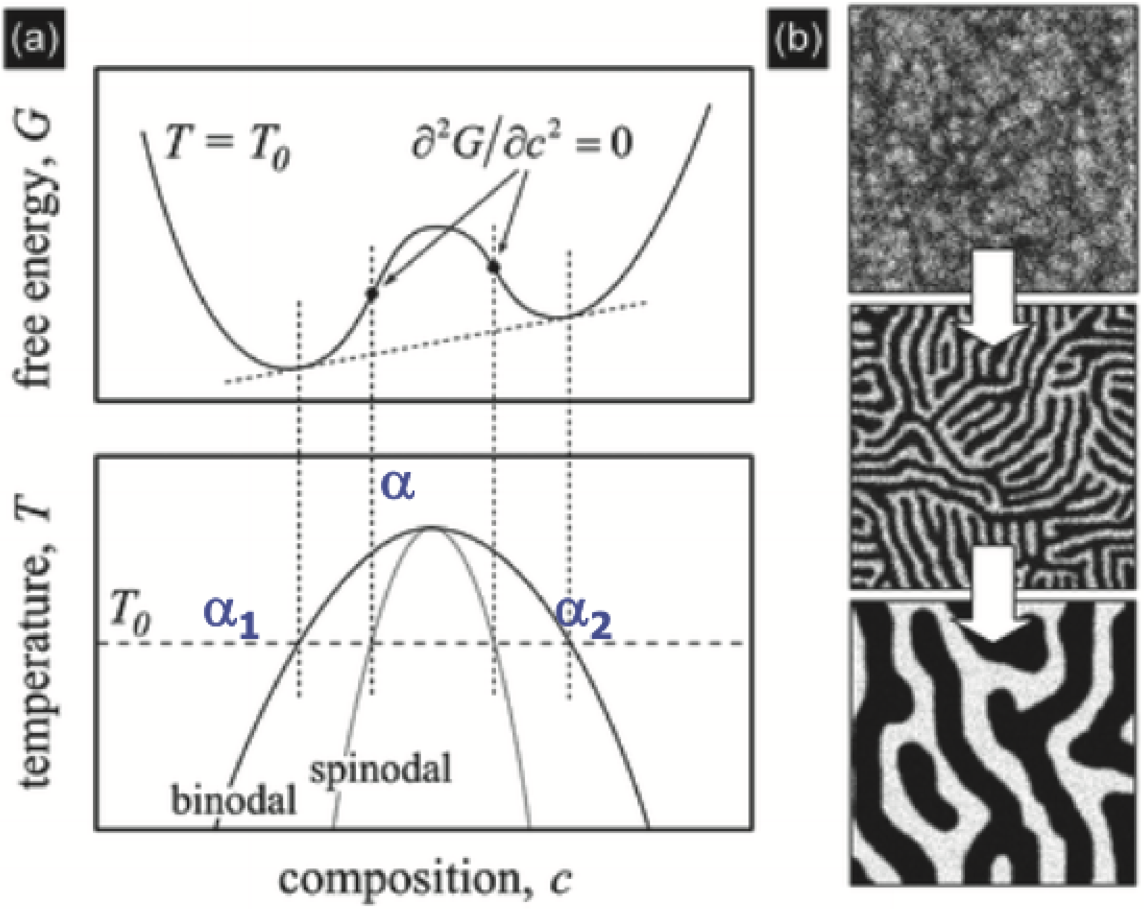
Learning outcomes

After this lecture, you will be able to:

- **Recall** the difference between continuous and discontinuous phase transformations
- **Describe** spinodal decomposition as a continuous phase transformation process
- **Identify** the chemical-potential driving force in spinodal decomposition
- **Analyze** the Cahn-Hilliard equation and its gradient driving force

Recall: general picture of phase transformation

Stability regions in $T - X_B$ and $G - X_B$ plots - spinodal: "spine-like" shape in the free energy diagram



Stability of phase transformation: second derivative of free energy

Taylor expansion of the Gibbs free energy

$$\begin{aligned} G(x_B^0 + \delta x_B) &= G(x_B^0) + \left.\frac{\partial G}{\partial x_B}\right|_{x_B^0} \delta x_B + \frac{1}{2} \left.\frac{\partial^2 G}{\partial x_B^2}\right|_{x_B^0} (\delta x_B)^2 \\ &= G(x_B^0) + \frac{1}{2} \left.\frac{\partial^2 G}{\partial x_B^2}\right|_{x_B^0} (\delta x_B)^2 \end{aligned} \tag{1}$$

Key questions to be answered for continuous transformation

- **Where**: which region in a phase diagram does continuous phase transformation occur?

- **How**: how does the continuous transformation differ from discontinuous one (e.g. nucleation)?
- **Why**: why do we see the continuous behaviour?

Comparison: nucleation vs spinodal decomposition

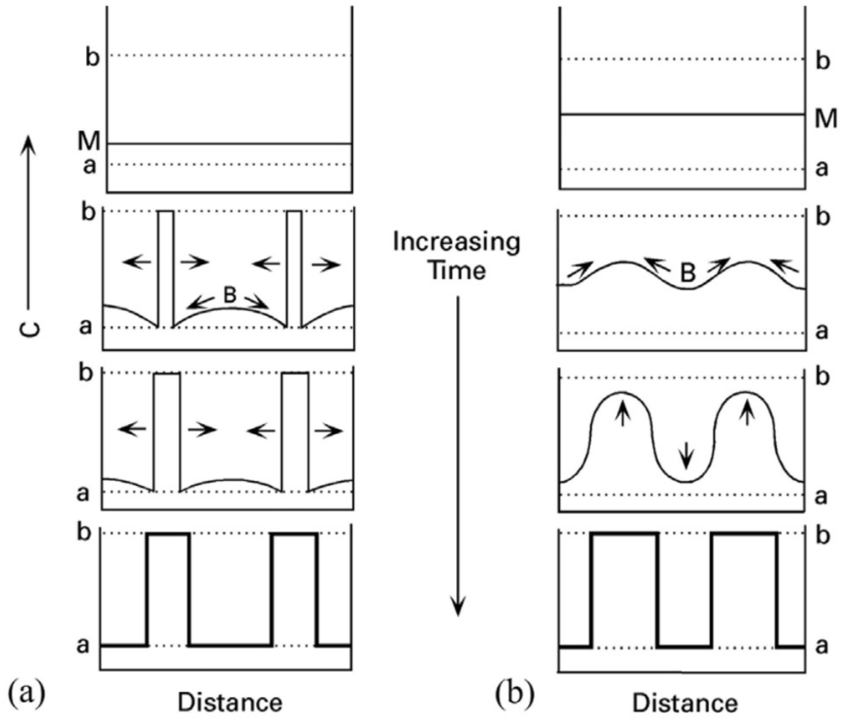


Figure 13.6 (a) Droplet nucleation and (b) spinodal decomposition over time. *(Reproduced from Varshneya and Mauro [1]).*

Continuous transformation: irreversible thermodynamics view (1)

From Lecture 08 we know the fluxes between an A-B binary mixture follows:

- C-frame: J_A^C & J_B^C
- V-frame: J_A^V & J_B^V
- Conservation equations

Continuous transformation: irreversible thermodynamics view (2)

Expanding the flux conservation and Gibbs-Duhem equation we get the J_B^V as

$$\begin{aligned} J_B^V &= -\Omega^2 (c_A^2 L_B + c_B^2 L_A)(\nabla \mu_B - \nabla \mu_A) && (2) \\ &= -\Omega^2 (c_A^2 L_B + c_B^2 L_A)\nabla(\mu_B - \mu_A) && (3) \\ &= -M\nabla(\mu_B - \mu_A) && (4) \end{aligned}$$

So far this is just a formal diffusion equation using chemical potential driving force

Meaning of J_B^V equation

- Mobility $M > 0$ satisfies the $\dot{\sigma} \geq 0$ postulate
- What is $\mu_B - \mu_A$? Slope $\partial G / \partial X_B$ on the free energy diagram!
- What is $\nabla(\mu_B - \mu_A)$? Spatial variation of the $\partial G / \partial X_B$ driving force

$$\begin{aligned} J_B^V &= -M\nabla(\mu_B - \mu_A) && (5) \\ &= -\frac{M\Omega}{N_0}\frac{\partial^2 G}{\partial X_B^2}\nabla c_B && (6) \\ &= -\tilde{D}\nabla c_B && (7) \end{aligned}$$

Negative interdiffusivity?

From previous analysis we see that the apparent interdiffusivity $\tilde{D}$ follows:

$$\tilde{D} = \frac{M\Omega}{N_0}\frac{\partial^2 G}{\partial X_B^2}$$

- $\tilde{D} < 0$ uphill diffusion
- In continuous transformation, we see the local concentration difference amplifies!
- In contrast, normal diffusion $\tilde{D} > 0$ tries to smoothen the concentration curvature.

Diffusion (homogenization) vs phase separation

Very rough estimation of the composition change using Fick's second law

$$\frac{\partial c_B}{\partial t} = \tilde{D}\nabla^2 c_B$$

Summary for “where” and “why” questions

- Continuous phase transformation occurs **where** the second derivative of free energy is **negative**
- The continuous phase separation is dominated by **barrierless** diffusion
- The process is triggered by infinitesimal spatial fluctuation
- Amplification of concentration fluctuation is enhanced by **negative interdiffusivity** $\tilde{D} = \frac{M\Omega}{N_0}\frac{\partial^2 G}{\partial X_B^2} < 0$

The “how” question: evolution of patterns in spinodal decomposition

Let’s still use the 1D Fick’s second law, assuming $\tilde{D}$ is constant everywhere

$$\frac{\partial c_B}{\partial t} = \tilde{D}\frac{\partial^2 c_B}{\partial x^2}$$

From Lecture 07 we know that the diffusion equation can be decomposed into spatial and temporal parts. Use a wave form $c_B(x,t) = \overline{c_B} + \exp(i\beta x)A(t)$, we can solve the $c_B(x,t)$ profile.

Amplification in continuous transformation

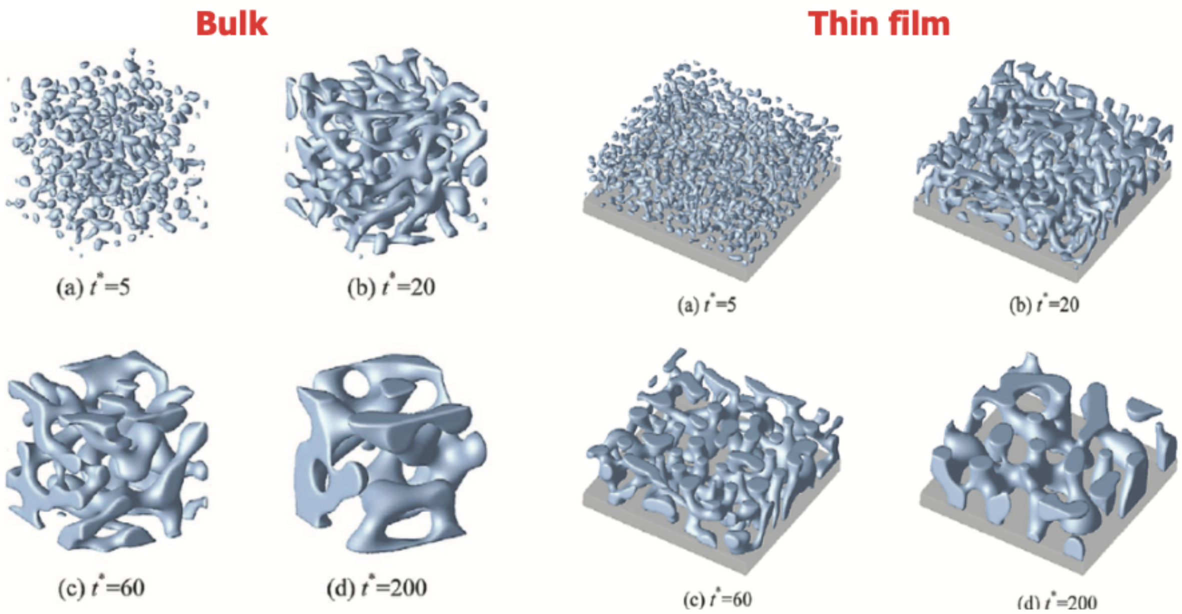
The general solution to the waveform c_B is:

$$\begin{aligned} c_B - \overline{c_B} &= A(\beta, 0)\exp(-\beta^2\tilde{D})exp(i\beta x) && (8)\\ &= A(\beta, 0)\exp(-R(\beta))exp(i\beta x) && (9) \end{aligned}$$

- Wavelength $\lambda = 2\pi/\beta$
- $R(\beta) = -\beta^2\frac{M\Omega}{N_0}\frac{\partial^2 G}{\partial X_B^2}$: amplification factor
- $\beta \to \infty$ should give maximal amplification ?! We always end up with noise ?!
- Not the case in real scenario **stablization** by interfaces!

Example: spinodal decomposition in computer simulations

- See Seol, et al. *Acta Materialia* 51, 5173–5185 (2003)
- Final pattern always has a principal wavelength, why?



Interfacial energy as stabilization term

- The term $R(\beta) = -\beta^2 \frac{M\Omega}{N_0} \frac{\partial^2 G}{\partial X_B^2}$ uses *homogeneous* free energy of a mixture
- In reality creating a new phase always increase the free energy by surface energy (similar to nucleation in Lecture 14)
- In spinodal decomposition, surface energy acts as "stablization" for pattern formation!

Energy at gradient interfaces

- Unlike in nucleation where sharp interface can be defined (thus γ), spinodal decomposition usually accompanies **diffuse interface**
- c_B has a finite gradient, not sharp step function

Additional term for interface gradient to Helmholtz free energy density

$$f_\gamma = \kappa \left(\frac{\partial c_B}{\partial x} \right)^2$$

- $\kappa > 0$ is the gradient energy coefficient that penalizes the creation of sharp interface
- At interface $\left(\frac{\partial c_B}{\partial x} \right)^2$ becomes large!

Cahn-Hilliard equation for spinodal decomposition

- It is just Fick's second law with a more precise $\tilde{D}$ counting the interfacial term
- Total Helmholtz free energy comes from both homogeneous free energy density f^{homo} and $\kappa(\partial c_B/\partial x)^2$

Define a general "diffusion potential" for inhomogeneous system:

$$\begin{aligned}\Phi(x) &= \frac{\partial F}{V\partial cB} &(10)\\ &= \frac{\partial f^{\text{homo}}}{\partial c_B} - 2\kappa\nabla^2 c_B &(11)\end{aligned}$$

Cahn-Hilliard equation (2)

Instead of chemical potential $\mu_B - \mu_A$, we use Φ as the overall potential

- Fick's 1st law

$$\begin{aligned}J_B &= -L\nabla\Phi &(12)\\ &= -\frac{\tilde{D}}{(\partial^2 f^{\text{homo}}/\partial X_B^2)}\nabla\{\frac{\partial f^{\text{homo}}}{\partial c_B} - 2\kappa\nabla^2 c_B\} &(13)\end{aligned}$$

- Fick's 2nd law

$$\begin{aligned}\frac{\partial c_B}{\partial t} &= -\nabla\cdot J_B &(14)\\ &= \nabla\cdot\{\frac{\tilde{D}}{(\partial^2 f^{\text{homo}}/\partial X_B^2)}\nabla\{\frac{\partial f^{\text{homo}}}{\partial c_B} - 2\kappa\nabla^2 c_B\}\} &(15)\end{aligned}$$

Cahn-Hilliard equation (3)

Final format of Cahn-Hilliard equation

$$\frac{\partial c_B}{\partial t} = M_0\left[\frac{\partial^2 f^{\text{homo}}}{\partial c_B^2}\nabla^2 c_B - 2\kappa\nabla^4 c_B\right] \tag{16}$$

Perturbation analysis for Cahn-Hilliard equation

Toy model for the Helmholtz free energy

$$f^{\text{homo}} = 16\frac{f^m}{(c^\beta - c^\alpha)^4}\left[(c_B - c^\alpha)(c_B - c^\beta)\right]^2$$

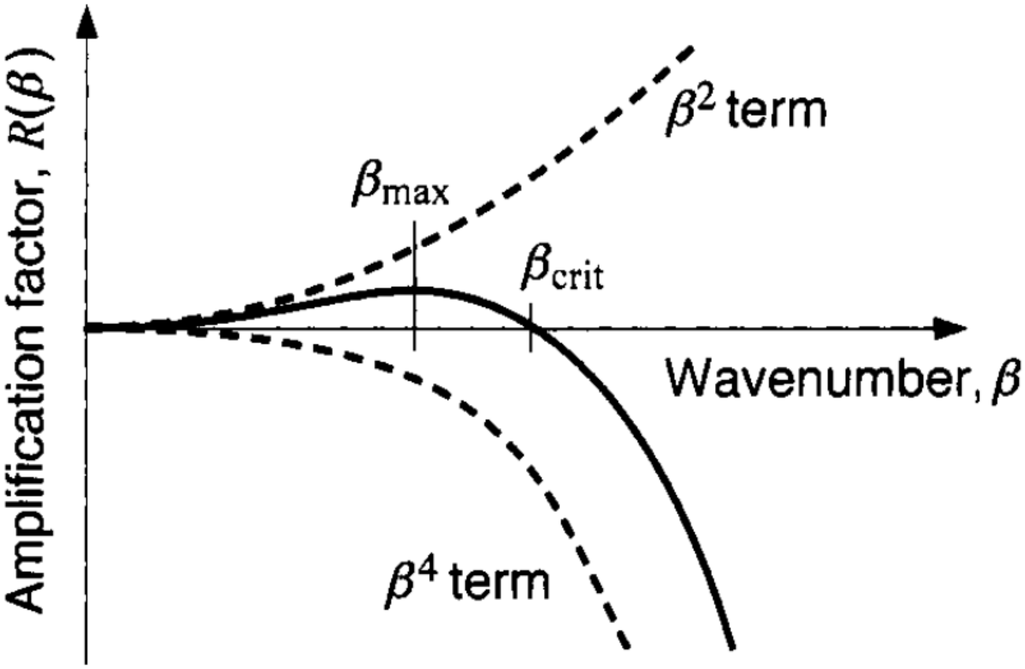
How will the amplitude change?

$$\frac{dA(t)}{dt} = \frac{M_0\beta^2}{(c^\beta - c^\alpha)}\left[16f^m - 2\kappa\beta^2(c^\beta - c^\alpha)\right]A(t)$$

Amplification factor $R(\beta)$ in Cahn-Hilliard equation

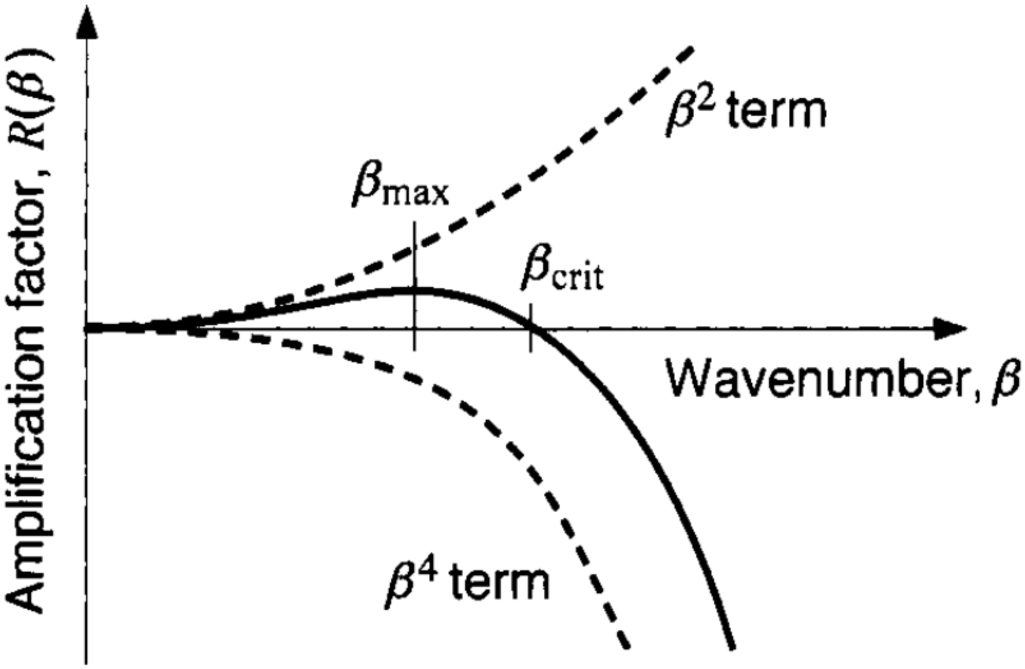
$$R(\beta) = -M_0\left(\frac{\partial^2 f}{\partial c_B^2}\beta^2 + 2\kappa\beta^4\right)$$

The β^4 term now stablizes $R(\beta)$!



Cahn-Hilliard equation: critical wavelength

- Critical wavelength $\lambda_c = \frac{\pi}{2}(c^\beta - c^\alpha)\sqrt{\frac{\kappa}{f^m}}$
- $\lambda > \lambda_c$ –> Growth
- Fastest growing wavelength $\lambda_{\max} = \sqrt{2}\lambda_c$



Applications of spinodal decomposition: pattern formation

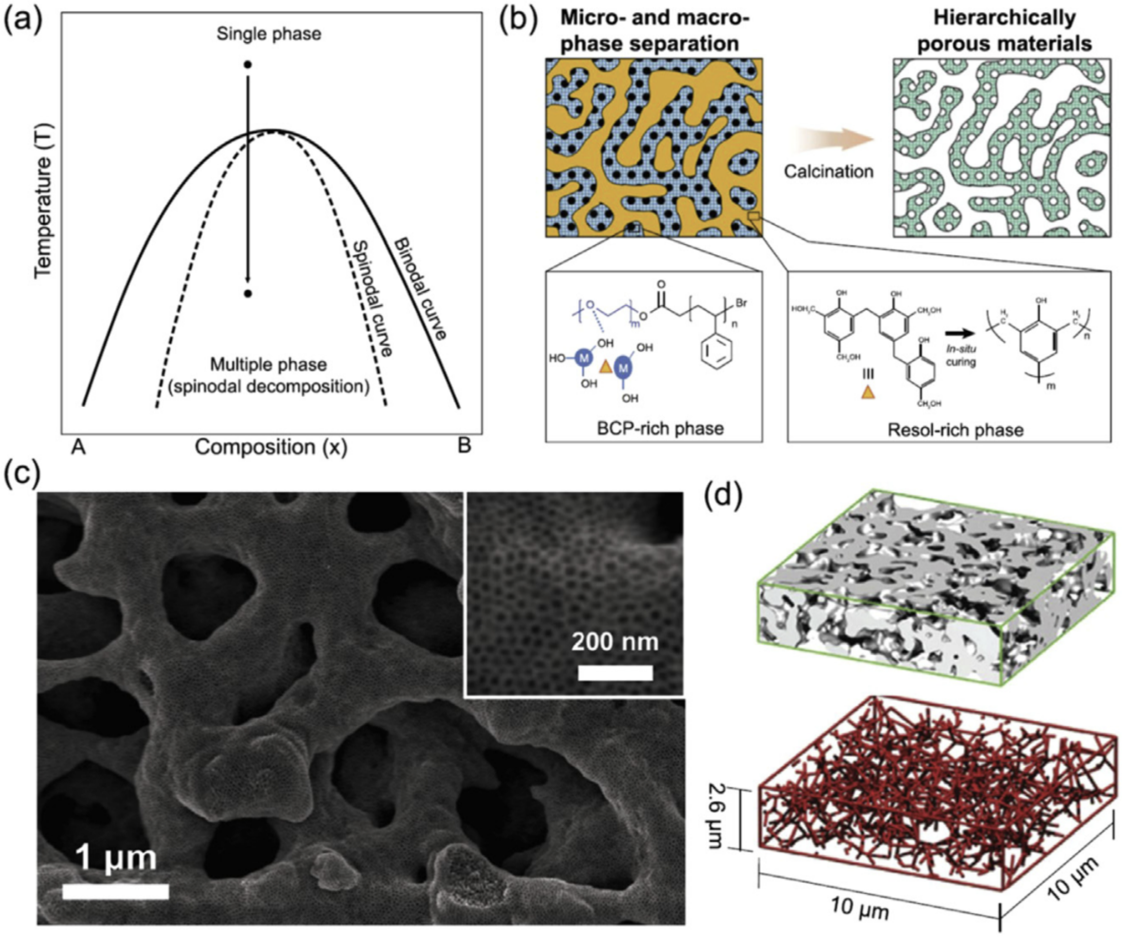


Figure 13.9 (a) Schematic phase diagram showing immiscibility and spinodal domes. (b) Fabrication of a hierarchically porous material via curing of an organic additive in the porous inorganic spinodal microstructure. (c) Scanning electron microscopy (SEM) image of the porous $TiNb_2O_7$ skeleton structure. (d) Isosurface imaging from 3D tomography of the porous material. *(Reproduced with permission from Ref. [9]).*

Summary

- Continuous phase transformation is caused by initial composition inside the spinodal line (unstable region)
- Negative $\tilde{D}$ causes spatial fluctuation to amplify
- Cahn-Hilliard equation describes the driving force

- Continuous phase separation occurs in many material systems and give rise to rich phase separation patterns