上海交通大学
材料科学与工程学院
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MSE6701H, Multiscale Materials Modeling and Simulation

- ✓ Electronic DFT
- ✓ Atomistic MD
- • Mesoscale PF

Lecture 11

Applications of PFM (I): Interface & Spinodal decomposition

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Contents

1D interface: numerical solution

- **Solid-liquid in equilibrium**

$$f[\phi(x,t)] = 4U\left(-\frac{1}{2}\phi^2 + \frac{1}{4}\phi^4\right)$$

To model the **phenomenological** behavior of a system with two phases of equal energy

- **Finite difference method:**

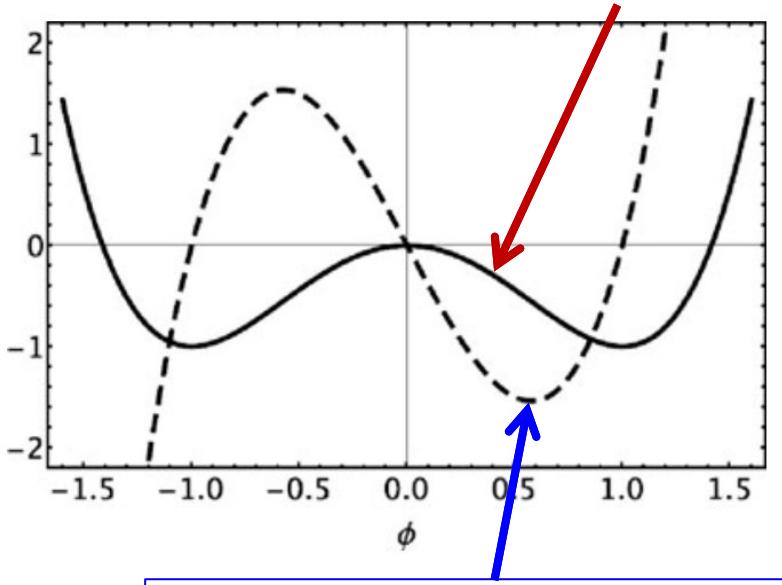
$$\frac{d\phi_i}{dx} = \frac{\phi_{i+1} - \phi_{i-1}}{2a}, \quad \frac{d^2\phi_i}{dx^2} = \frac{\phi_{i+1} + \phi_{i-1} - 2\phi_i}{a^2}$$

$$\Rightarrow \frac{\partial \phi_i}{\partial t} = -M\left[4U(-\phi_i + \phi_i^3) - \alpha\left(\frac{\phi_{i+1} + \phi_{i-1} - 2\phi_i}{a^2}\right)\right]$$

Numerical methods: Finite difference/element method, Fast Fourier Transformation method

$$\frac{\partial \phi(\boldsymbol{x},t)}{\partial t} = -M\left[\frac{\partial f(\phi)}{\partial \phi} - \alpha\nabla^2\phi(\boldsymbol{x},t)\right]$$

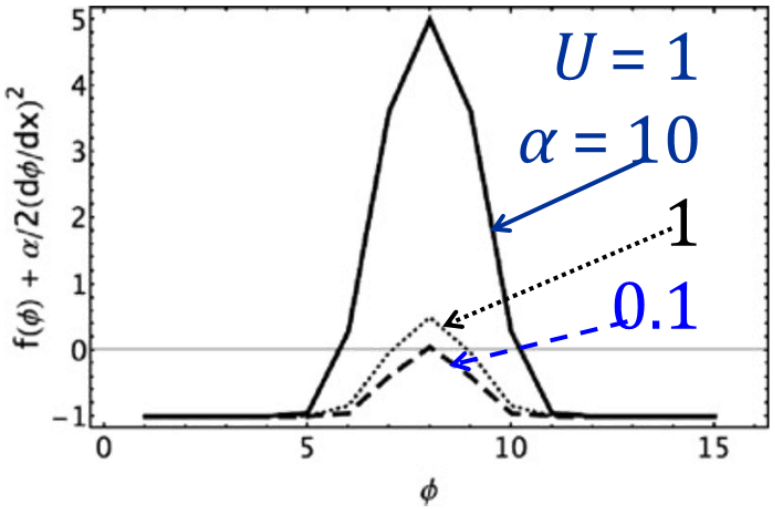
Double well chemical energy density $f(\phi)$



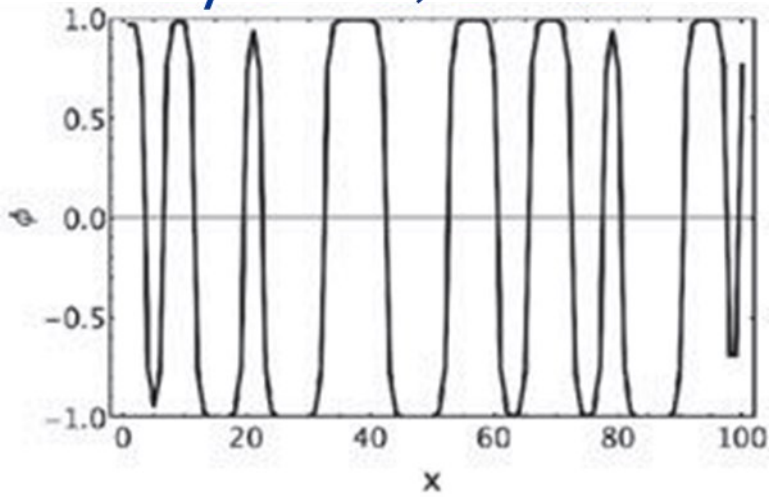
$$\frac{\partial f(\phi)}{\partial \phi} = 4U(-\phi + \phi^3), U = 1$$

1D interface: discussion

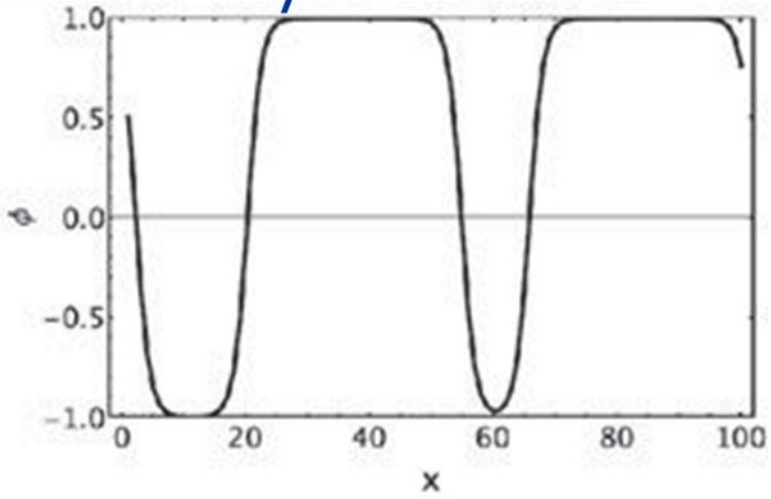
- **Influence of interface energy?**



$\alpha/U = 1, U = 1$



$\alpha/U = 10$



$d\phi_i/dt \approx 0$, **but not at equilibrium**

- **Equilibrium: no interfaces to minimize the interface energy**
- **Q: α = 0?**

1D interface: analytical solution

(for simple interface model)

- Condition for minimum total energy (equilibrium)

$$\Leftrightarrow \frac{\delta F[\phi(\boldsymbol{x},t)]}{\delta\phi(\boldsymbol{x},t)} = 0 \Rightarrow \frac{\partial f(\phi)}{\partial\phi} - \alpha\nabla^2\phi(\boldsymbol{x},t) = 0$$

- Interface located in yz plane at x = 0, with $f[\phi(x,t)] = 4U\left(-\frac{1}{2}\phi^2 + \frac{1}{4}\phi^4\right)$

- Free energy per unit area $\frac{F}{A} = \int_x \left[4U\left(-\frac{1}{2}\phi^2 + \frac{1}{4}\phi^4\right) + \frac{\alpha}{2}\left(\frac{\partial\phi}{\partial x}\right)^2\right]dx$

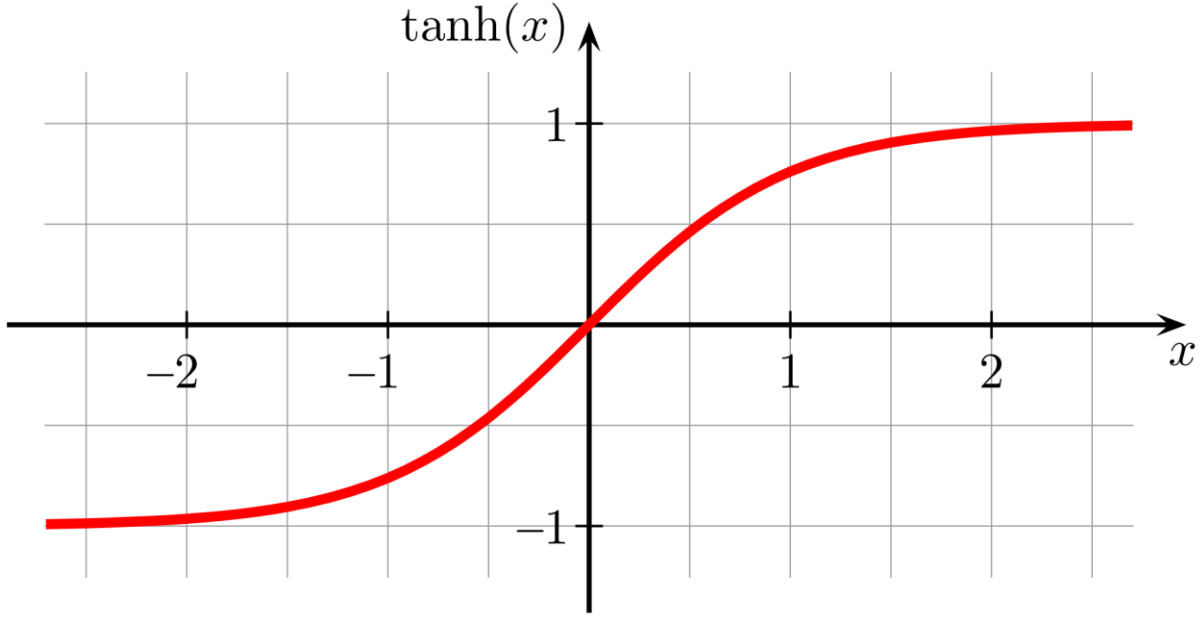
- $\frac{\delta(F/A)}{\delta\phi} = 0 \Rightarrow 4U[-\phi(x) + \phi^3(x)] - \alpha\left[\frac{\partial^2\phi(x)}{\partial x^2}\right] = 0$

Analytical solution for equilibrium interface

$$\frac{\delta(F/A)}{\delta\phi}=0\Rightarrow 4U[-\phi(x)+\phi^3(x)]-\alpha\left[\frac{\partial^2\phi(x)}{\partial x^2}\right]=0$$

$$\Rightarrow \phi(x)=\tanh\left(x\sqrt{2U/\alpha}\right)$$

$$b.c.\begin{cases}\phi|_{x=-\infty}=-1\\ \phi|_{x=+\infty}=1\\ -1\leqslant\phi\leqslant 1\end{cases}$$



- Minimum interface energy?

$$\frac{F}{A}=\frac{4\sqrt{2}}{3}\sqrt{U\alpha}$$

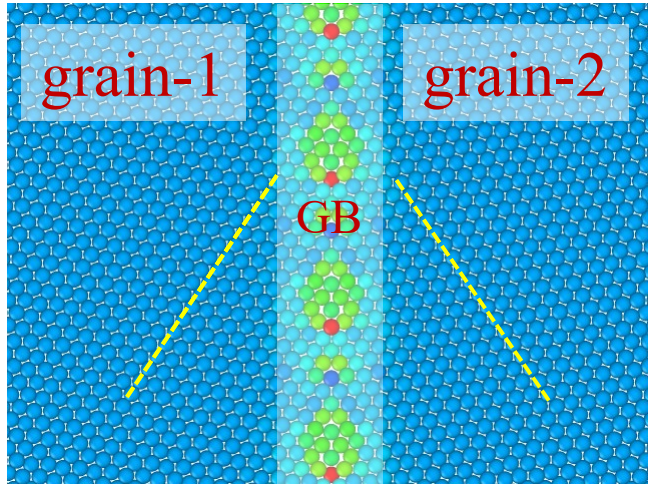
- Interface width?

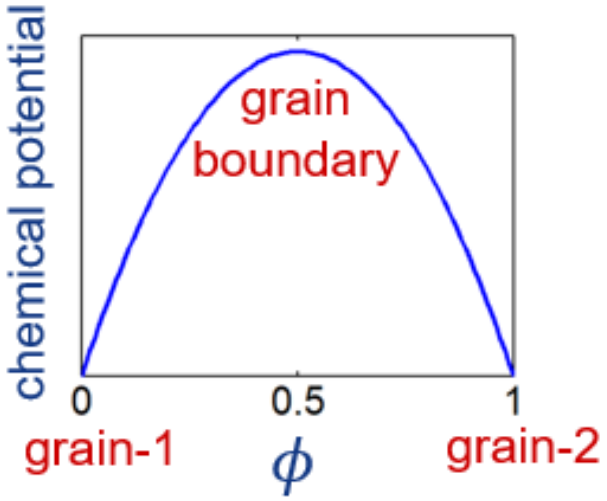
$$w\propto\sqrt{\alpha/U}$$

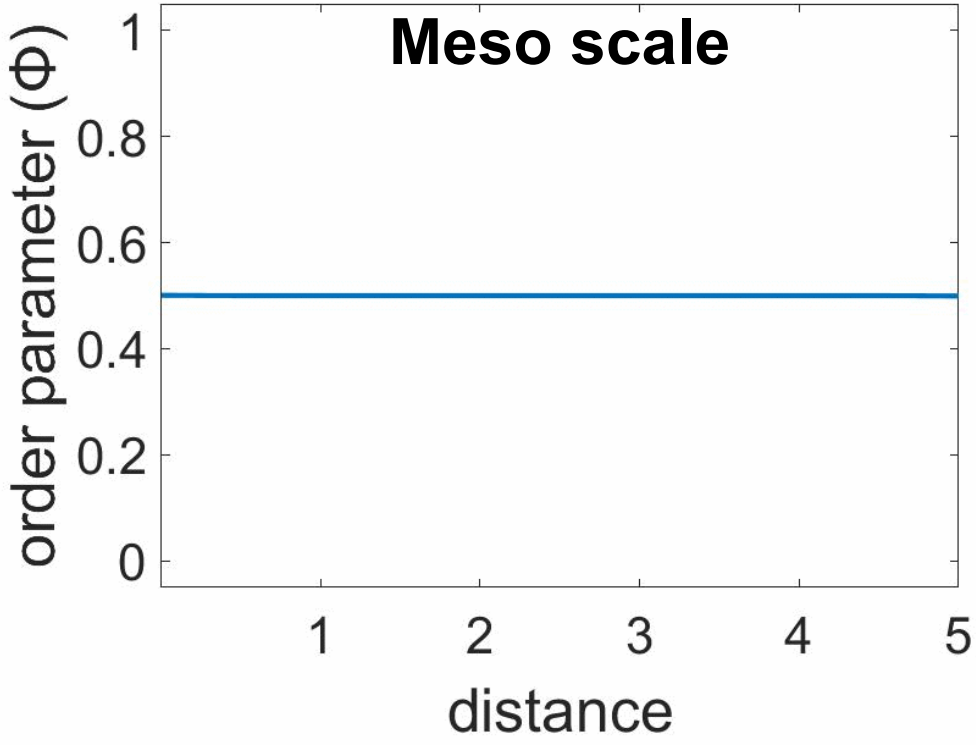
1D interface structure

- With given chemical energy and interface energy,
  - what is structure of the equilibrium interface, i.e. thickness?
  - what is the total energy for the equilibrium interface structure?

Atomic scale



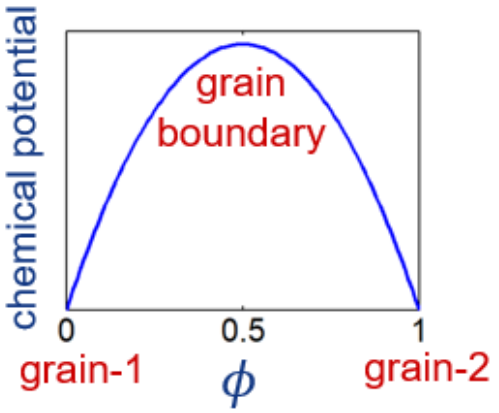




Free energy functional→ interface

- Free energy functional

$$F[\phi(x),\nabla\phi]=\int_{\Omega} U\cdot|\phi(1-\phi)|+\frac{k}{2}|\nabla\phi|^{2}dV$$



- Evolution equation

$$\dot{\phi}=-M\frac{\delta F}{\delta\phi}=-M[U(1-2\phi)-k\nabla^{2}\phi]$$

- Equilibrium state

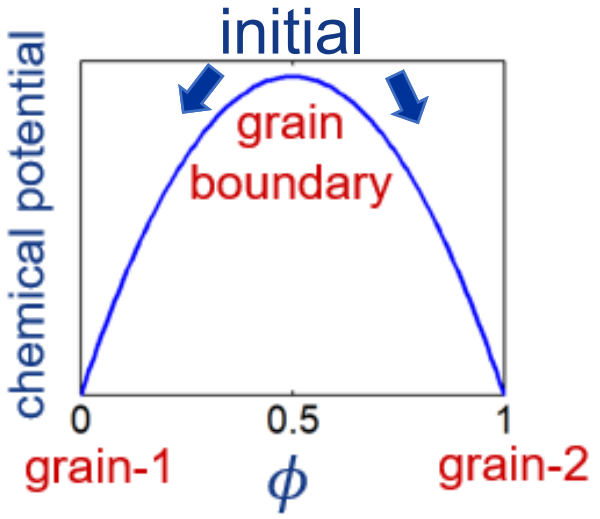
$$\dot{\phi}=0\Longrightarrow U(1-2\phi)-k\nabla^{2}\phi=0$$

solve the 2nd order ordinary differential equation
➔ equilibrium distribution $\phi[x]$

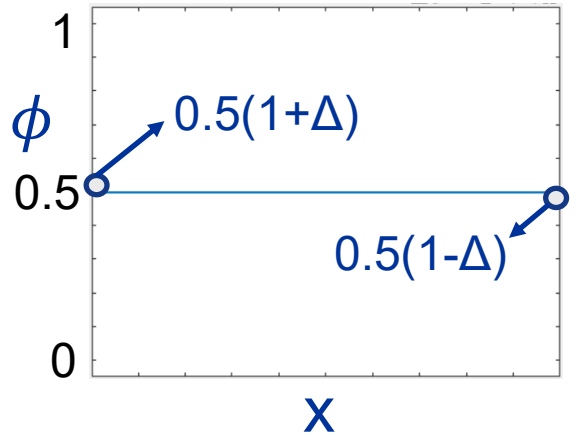
1D interface: Numerical solution

- System evolves following the control equation.
- Initialize: initial high energy state + slight perturbation at left and right boundary

$$\begin{cases} F = \int_x \left[U \cdot \phi(1-\phi) + \frac{k}{2} |\nabla \phi|^2 \right] dx \\ \dot{\phi} = -M \frac{\delta F}{\delta \phi} = -M \left[U(1-2\phi) - k\nabla^2 \phi \right] \\ \phi_{t+\Delta t} = \phi_t + \dot{\phi} \Delta t \end{cases}$$



- discrete spacing Δx
- discrete time step Δt
- The **gradient** and **Laplacian** operators are computed using **finite difference method**:



$$\nabla \phi(x) = \frac{\phi(x+\Delta x) - \phi(x-\Delta x)}{2\Delta x};\ \nabla^2 \phi(x) = \frac{\phi(x+\Delta x) + \phi(x-\Delta x) - 2\phi(x)}{(\Delta x)^2}$$

1D interface: numerical solution

- numerical solution (using finite differential method in MATLAB)
  - **Initialization**

```
% compute the interface thickness and the i
clear all; clc;

nx = 1000;  % x range
dx = 0.005; % grid spacing of x
L = 0.01;   % mobility
k = 20;     % interface energy coefficient
u = 200;    % chemical energy coefficient

% max dt to ensure numerical stablity
dt = 1 / (2*L) / (2*u + k/dx^2) ;

% total time steps (should be large enough
total_step = 50000;

phi = zeros(nx,1);
grad_phi = zeros(nx,1);
lap_phi = zeros(nx,1);
x = zeros(nx,1);
```

Δx → dx
k → k
U → u
Δt → dt
ϕ → phi

  - **initial value of ϕ**

```
%==============initial value of phi ======================
for i = 1:nx
    x(i) = i * dx;
    phi(i) = 0.5;
end
%==============setting the initial disturbance=============
f = 0.02;
phi(1) = phi(1)*(1+f);  phi(nx) = phi(nx)*(1-f);
phi(2) = phi(2)*(1+f);  phi(nx-1) = phi(nx-1)*(1-f);
```

  - **gradient and Laplacian of ϕ**

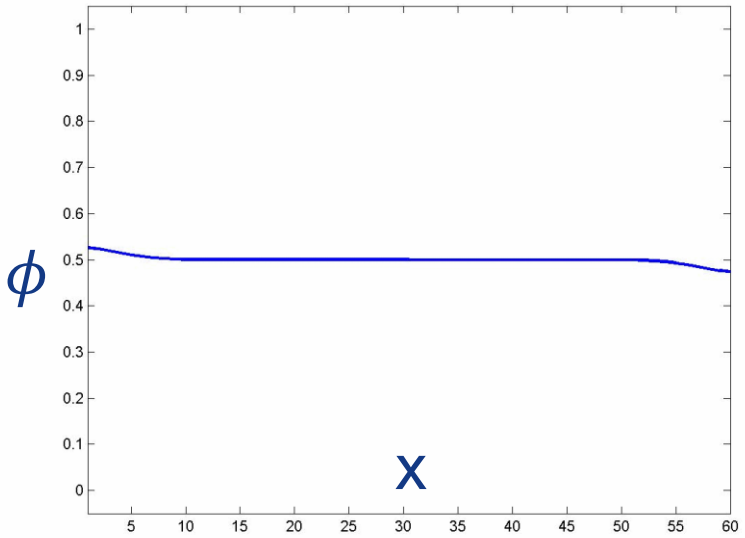
```
%gradient
grad_phi(i) = (phi(ip) - phi(im))/(2*dx);

%laplacian
lap_phi(i) = ( phi(ip)-2*phi(i)+phi(im) )/(dx^2);
```

  - **update ϕ by evolution equation**

```
%time evolution
phii=phi(i);
term1 = u*(1-2*phii);   % driving force of chemical energy
term2 = -k*lap_phi(i);  % driving force of gradient energy
term = term1 + term2;
phi(i) = phii - L*term*dt;% update phi
```

Equilibrium interface structure

- Equilibrium $\phi(x)$

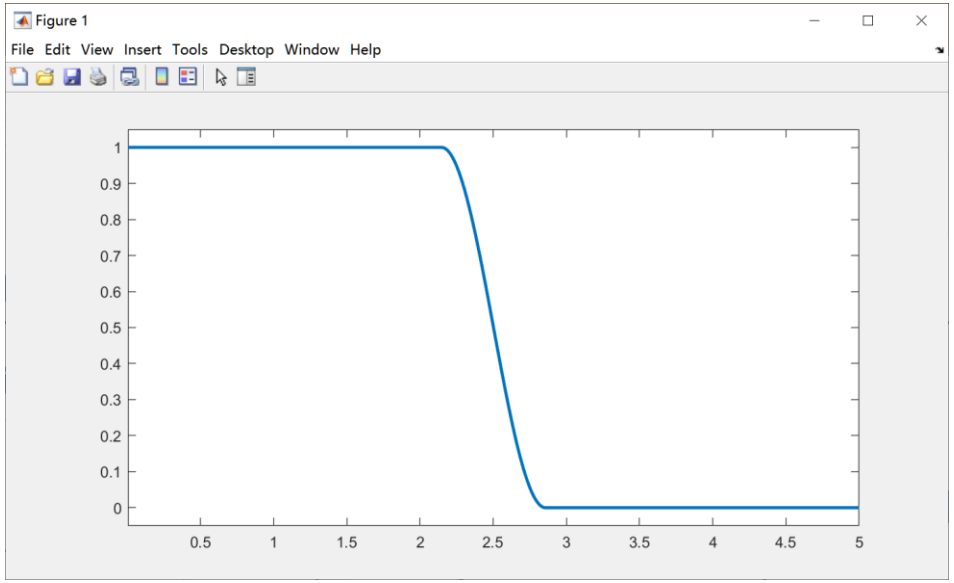


- Interface **width (w)**

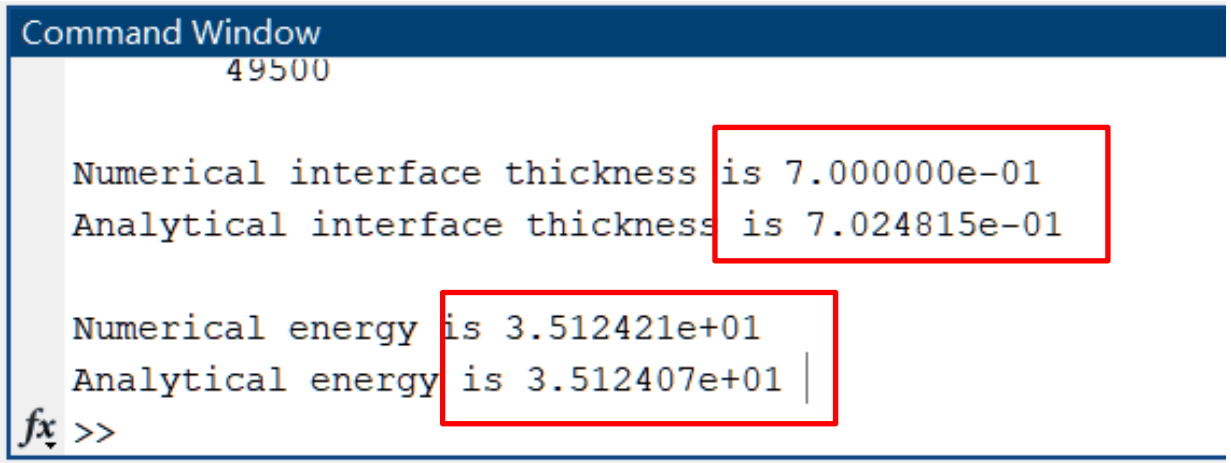
$$w = x_2 - x_1$$

$$\phi(x_2) = 0.9999$$

$$\phi(x_1) = 0.0001$$



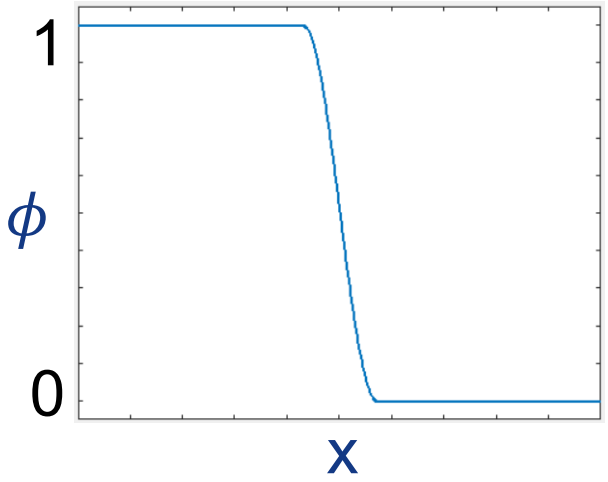
Interface thickness & energy: Numerical vs. analytical solution



1D interface: Analytical solution

- Solve the equilibrium interface structure i.e. order parameter $\phi(x)$

$$\begin{cases} U(1-2\phi) - k\nabla^2\phi = 0 \\ \phi|_{x<0} = 1 \\ \phi|_{x>w} = 0 \\ 0 \leqslant \phi \leqslant 1 \end{cases}$$



- Analytical solution to the equilibrium interface: $\phi(x) = ?$
  - Interface thickness: $\pi\sqrt{\frac{k}{2U}}$
  - Total energy: $\int_{-\infty}^{+\infty} f[\phi(x)]dx = \frac{\pi}{4\sqrt{2}}\sqrt{kU}$

Contents

1. Cahn-Hilliard equation for evolution of conserved field variables: **Spinodal decomposition**
2. Allen-Cahn equation for evolution of non-conserved field variables: One-dimensional interface
3. **Discussion, outlook and summary**
   - **Advantages & Limitations of PFM**

Spinodal decomposition

- Cooling from T_1 ($>T_c$) to T_2($<T_c$)

- **Spontaneous decomposition**
- **"Uphill" diffusion**
- **Always reach equilibrium**

Porter, David A, and Kenneth E Easterling. 2009. *Phase transformations in metals and alloys.* pp 304-305.

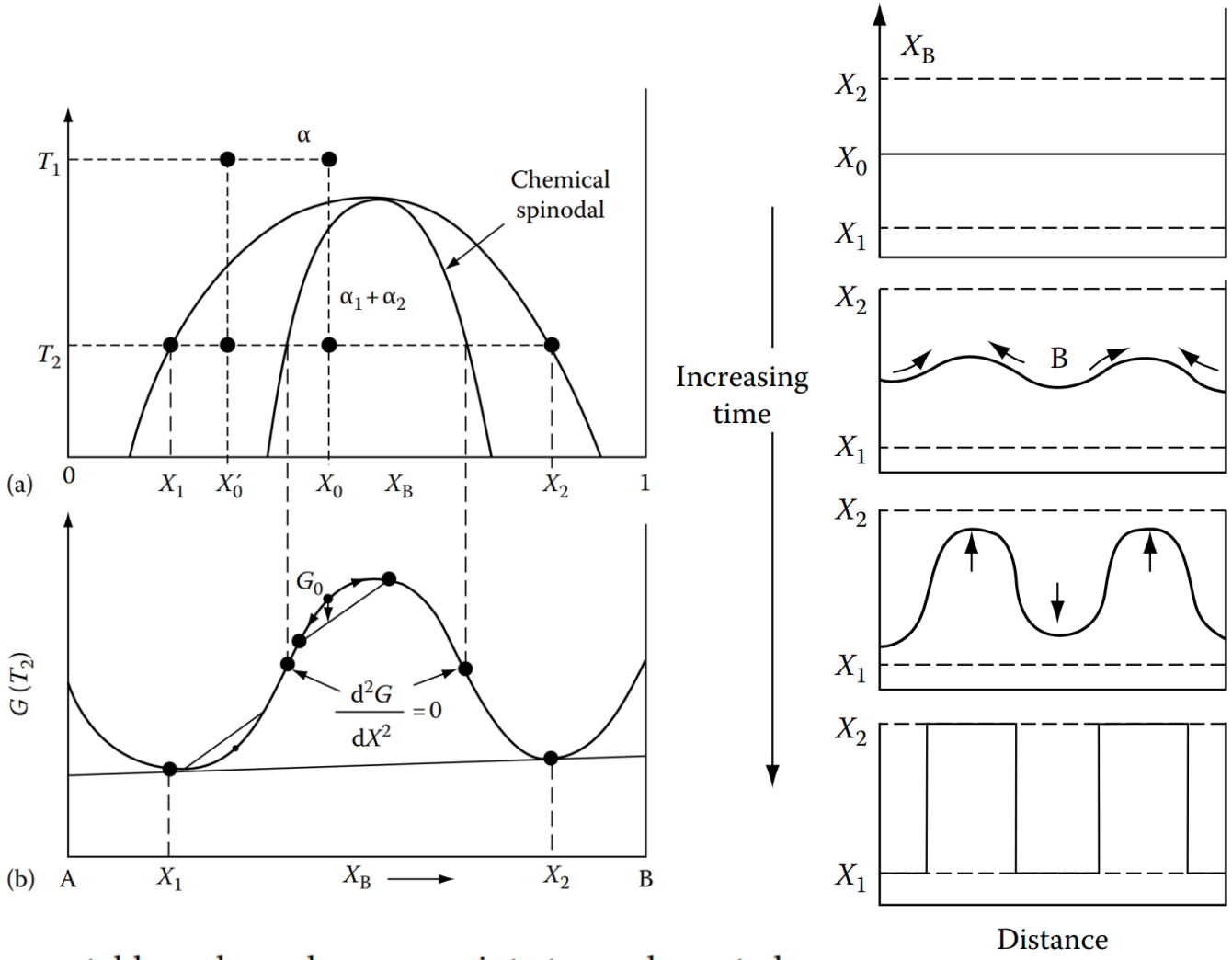
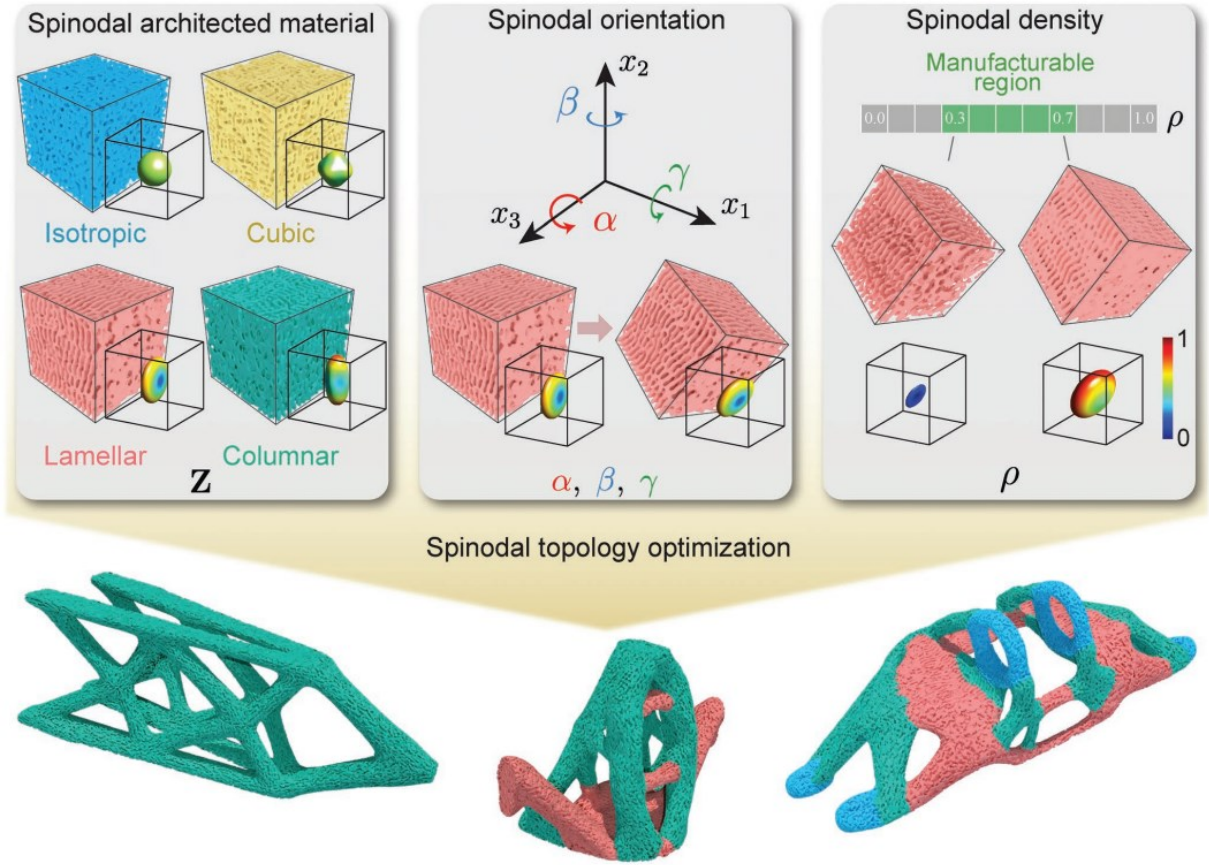
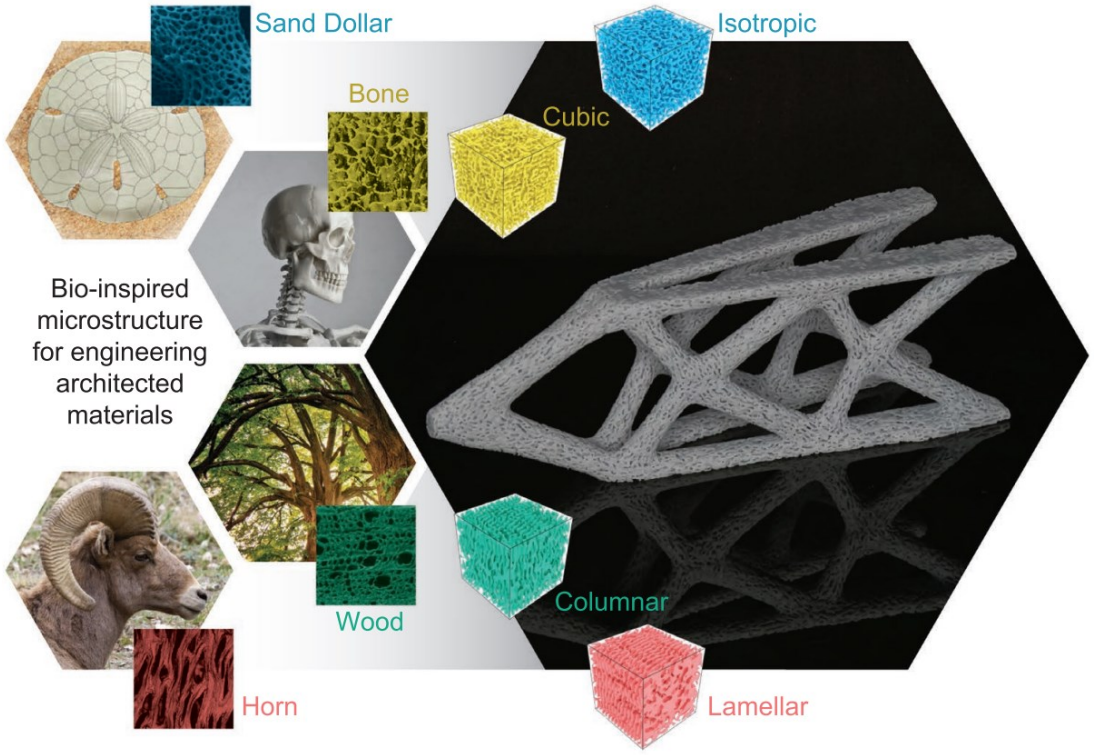


FIGURE 5.38
Alloys between the spinodai points are unstable and can decompose into two coherent phases α_1 and α_2 without overcoming an activation energy barrier. Alloys between the coherent miscibility gaps and the spinodai are metastable and can decompose only after nucleation of the other phase.

Spinodal architected materials

- **Spinodal architected materials with tunable anisotropy enable biomimicry of mechanical and biological function in engineered systems.**





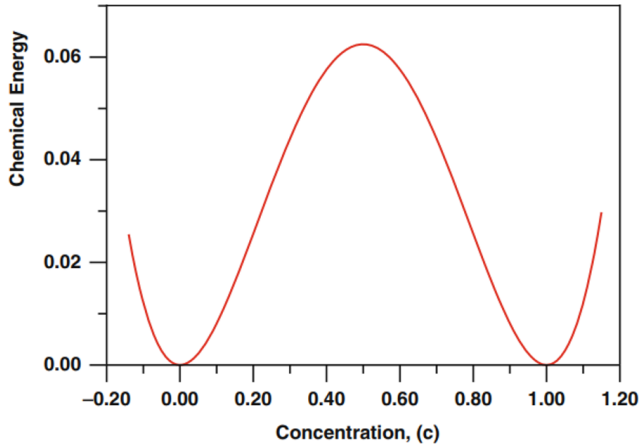
https://doi.org/10.1002/adma.202109304

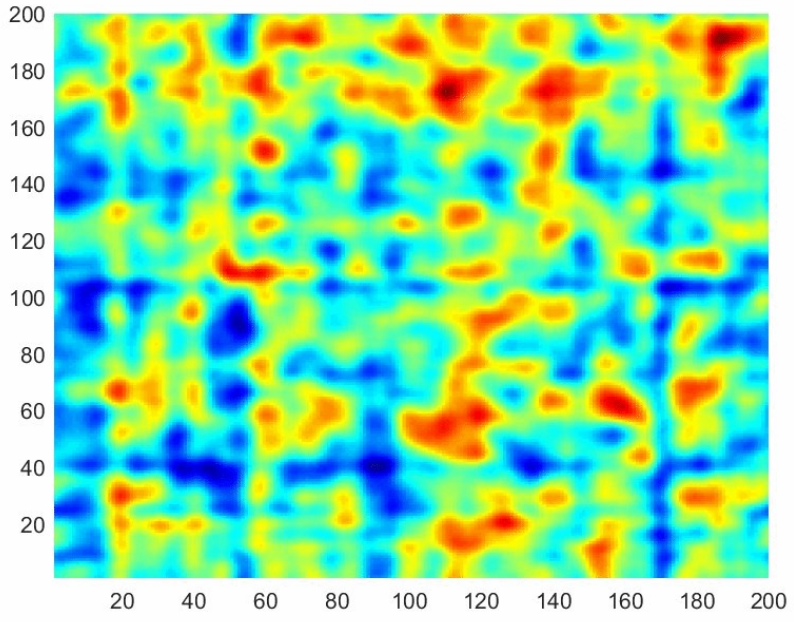
PF simulation of Spinodal decomposition

- Free energy functional

$$F = \int_{\Omega} \left[Uc^2(1-c)^2 + \frac{k}{2}|\nabla c|^2 \right] dV$$

$$f_{\text{chemical/Bulk}} \quad + \quad f_{\text{grad}}$$





$$\frac{\delta F}{\delta c} = 2Uc(2c^2 - 3c + 1) - k\nabla^2 c$$

$$\frac{\partial c(\boldsymbol{x},t)}{\partial t} = M\nabla^2\left(\frac{\delta F}{\delta c}\right)$$

Numerical solution

$$\frac{c(\boldsymbol{x},t+dt)-c(\boldsymbol{x},t)}{dt}=M\cdot\left[\nabla^2\left(\frac{\delta F[c(\boldsymbol{x},t)]}{\delta c(\boldsymbol{x},t)}\right)\right]$$

$$\text{Laplacian: } \nabla^2 c(x_i,y_j)=\frac{c(x_{i+1},y_j)+c(x_{i-1},y_j)+c(x_i,y_{j+1})+c(x_i,y_{j-1})-4c(x_i,y_j)}{dx\cdot dy}$$

$$dFdc_{ij}=\frac{\delta F[c(\boldsymbol{x},t)]}{\delta c(\boldsymbol{x},t)}=2Uc(2c^2-3c+1)-k\nabla^2 c(x_i,y_j)$$

$$c(\boldsymbol{x},t+dt)=c(\boldsymbol{x},t)+dt\cdot M\left[\nabla^2\left(\frac{\delta F[c(\boldsymbol{x},t)]}{\delta c(\boldsymbol{x},t)}\right)\right]$$

$$=c(\boldsymbol{x},t)+dt\cdot M\nabla^2(dFdc_{ij})$$

Numerical Solution (1)


```
nx = 200;   % number of gricreatecond in x-dire
ny = 200;   % number of grid in y-direction
dx = 1.;  % grid size in x-direction
dy = 1.; % grid size in y-direction

Ub = 1; % energy barrier
kgra = 5; %gradient coefficient
Mob = 1; % mobiility

con= 0.5+0.01*(0.5-rand(nx,ny)); %concentratio
grad_con2 = zeros(nx,ny); % abs(gradient_con)^
lap_con = zeros(nx,ny); %laplacian_c
dfdc = zeros(nx,ny); %functional derivative of
lap_dfdc = zeros(nx,ny);

nstep=3000;
Nfreq=50;
dt = 0.002 ; % 0.0003 time increment
% store energy with time
file_eng = fopen('TotalEnergy.txt', 'w');
```

```
for times = 1:nstep
    % laplacian_con, and dF/dc
    for i=1:nx
        for j=1:ny
            %periodic boundary condition
            jp = j+1; jm = j-1; ip = i+1; im = i-1;
            if (im==0)
                im=nx;
            end
            if (ip==nx+1)
                ip=1;
            end
            if (jm==0)
                jm=ny;
            end
            if (jp==ny+1)
                jp=1;
            end
            lap_con(i,j) =((con(ip,j)+con(im,j) ...
                +con(i,jp) + con(i,jm)) - 4.0*con(i,j))/(dx*dy);
            dfdc(i,j) = 2*Ub*con(i,j)*(2*con(i,j)^2-3*con(i,j)+1) ...
            -kgra*lap_con(i,j);
            grad_con2(i,j)=((con(ip,j)-con(i,j))/dx)^2 ...
                + ((con(i,jp)-con(i,j))/dy)^2;
        end
    end
```

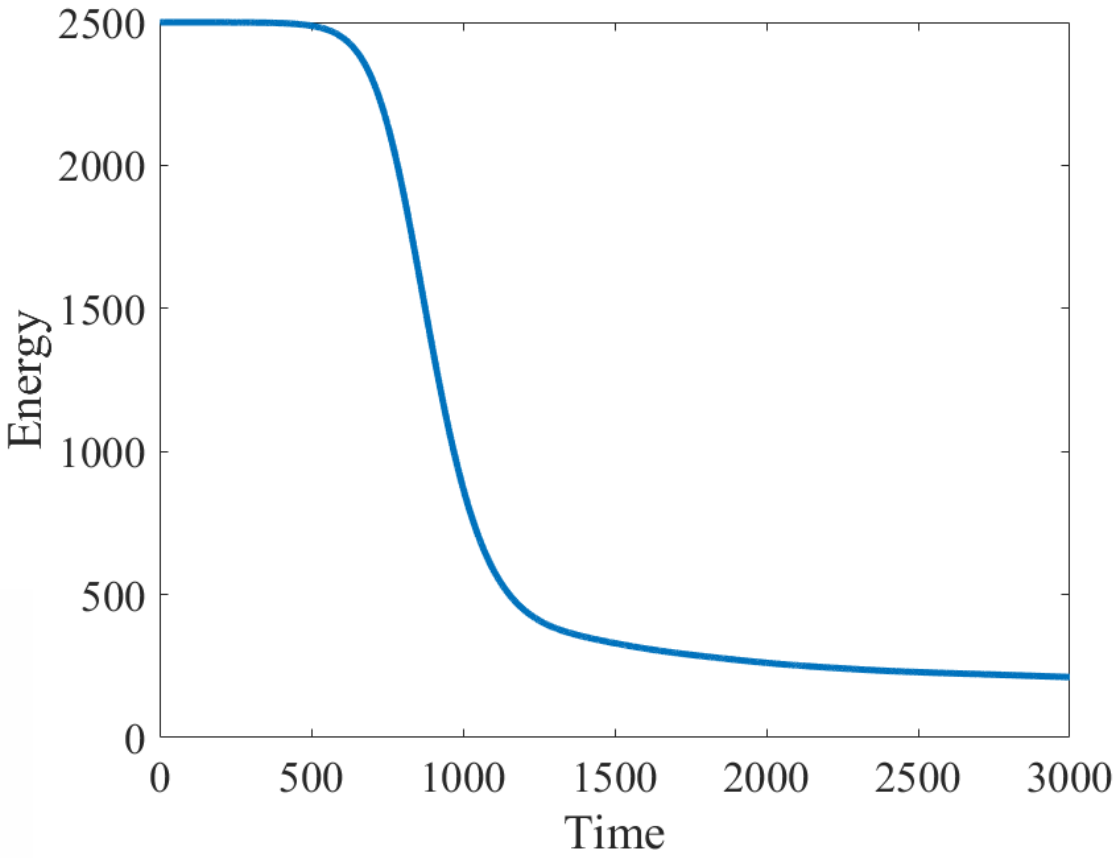
Numerical Solution (2)


```
lap_dfdc(i,j) = (dfdc(ip,j)+dfdc(im,j)+dfdc(i,jp) + ...
    dfdc(i,jm) - 4*dfdc(i,j))/(dx*dy);

con(i,j) = con(i,j) + dt*Mob*lap_dfdc(i,j);

% trunction
if (con(i,j)>1)
    con(i,j)=1.;
end
if (con(i,j)<0)
    con(i,j)=0.;
end
```

```
% ouput the energy evolution with time
ener=0.; % energy of the system
for i=1:nx
    for j=1:ny
        ener=ener+dx*dy*Ub*con(i,j)*con(i,j)*(1-con(i,j))^2 ...
            +kgra*0.5*grad_con2(i,j);
    end
end
fprintf(file_eng, '%d    %d \n', times, ener);

% visualize the concentration c(xi,yj);
if mod(times,Nfreq)==0
    figure(1);
    image(con,'CDataMapping','scaled');
    colormap('jet(64)'); pcolor(con);shading flat; axis ('xy');
    times
    picname = ['./', num2str(times) '.jpg']; % the saved file name
    saveas(gcf, picname);
end
```

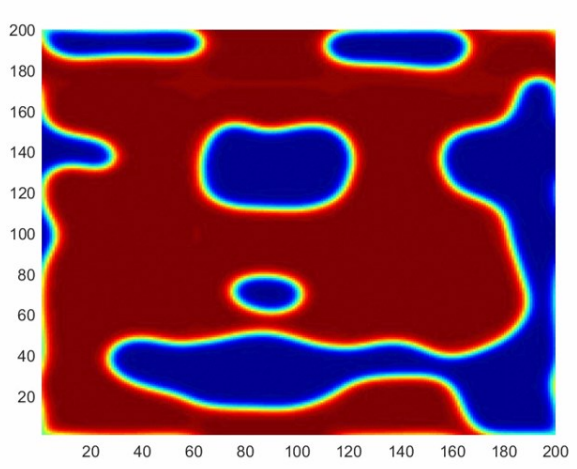
Discussion

- Energy evolution with time?

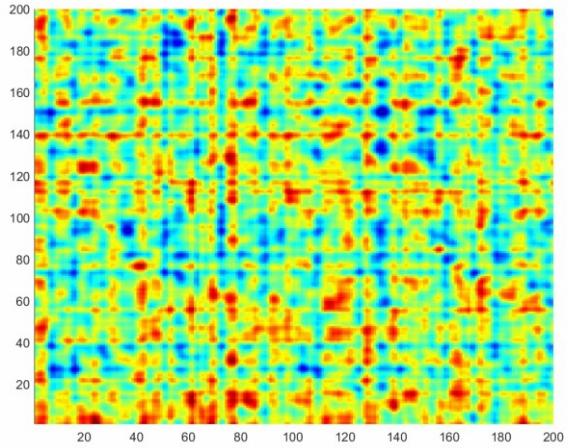


- Influence of gradient energy?

$k = 1$



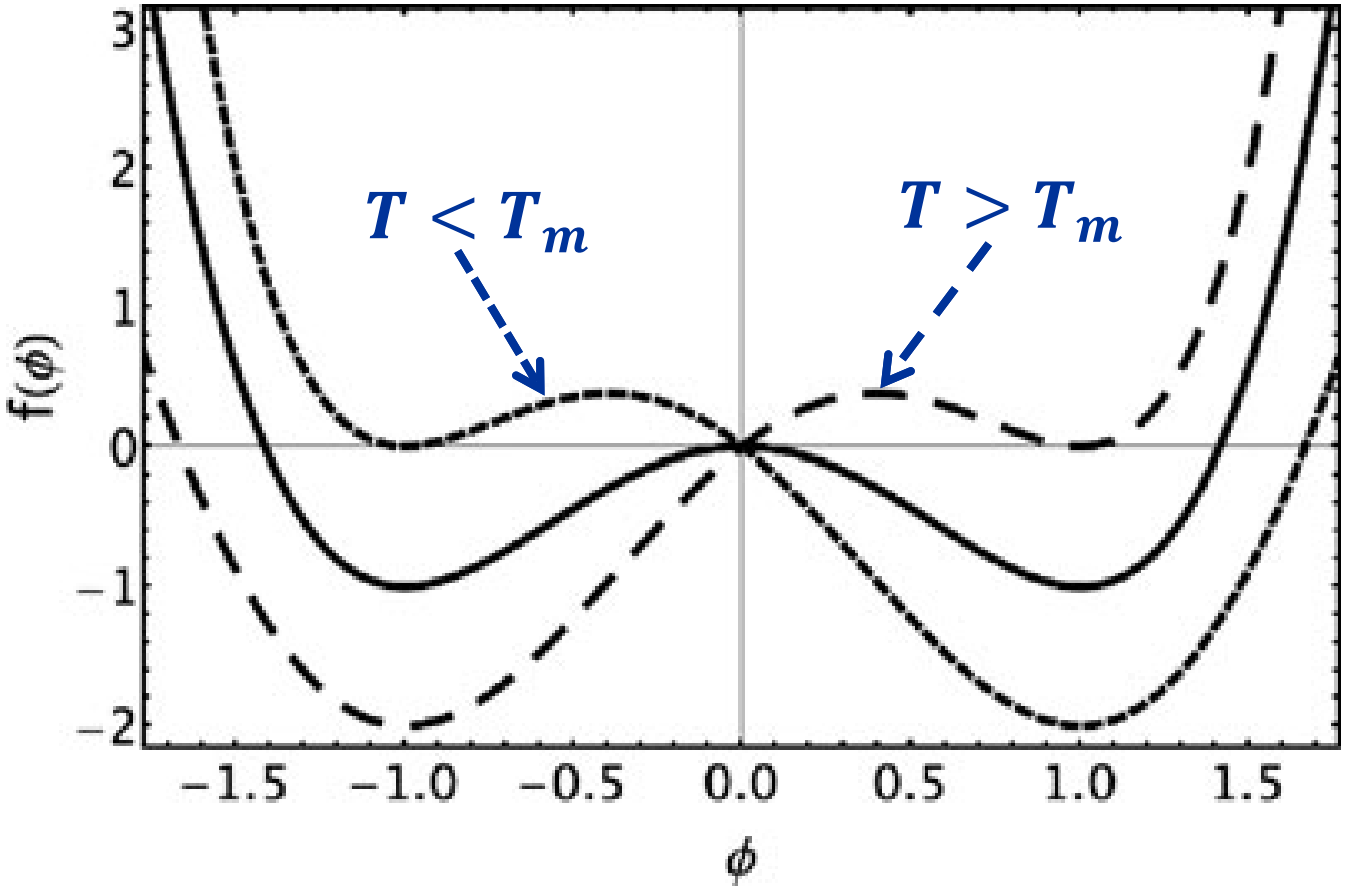
$k = 5$



Contents

3.1 Phase preference

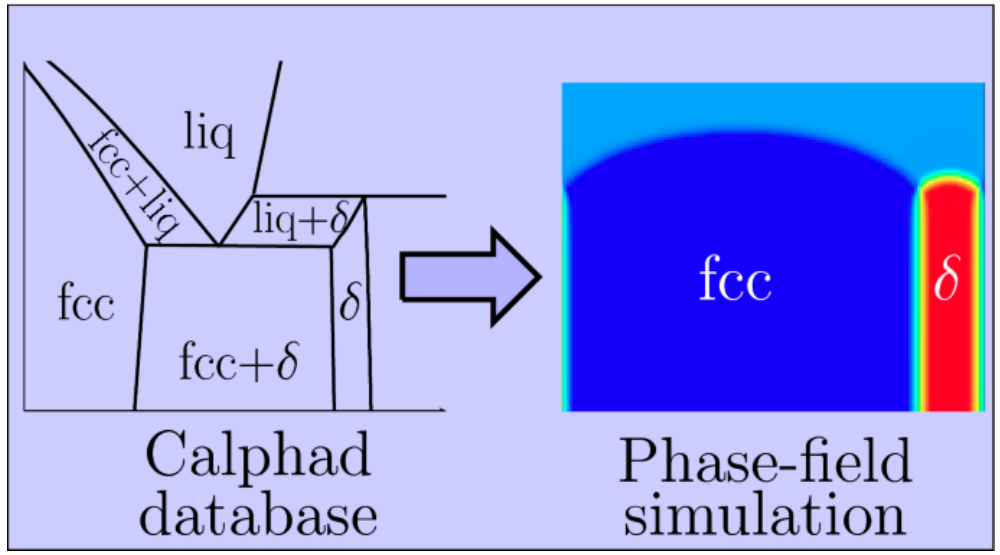
$$f[\phi] = 4U\left(-\frac{1}{2}\phi^2 + \frac{1}{4}\phi^4\right) + \frac{15\gamma}{8}\left(\phi - \frac{2}{3}\phi^3 + \frac{1}{5}\phi^5\right)(T - T_m), \gamma > 0.$$

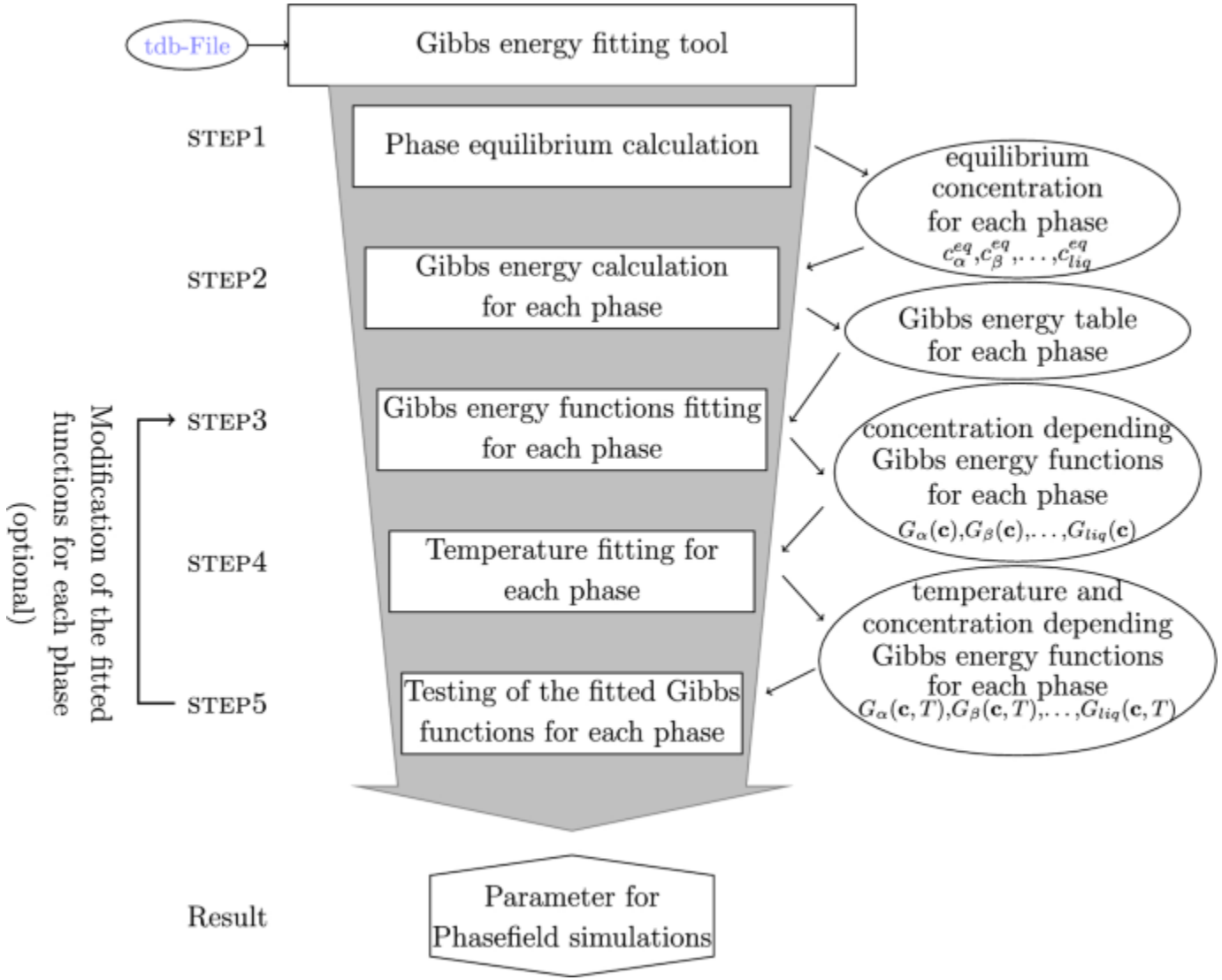


- $T = T_m$: $f[\phi = 1] = f[\phi = -1]$
  solid liquid
- $T \neq T_m$: one phase is preferred

- **Accurate free energy model?**
  - **thermodynamic calculations such as CALPHAD**
  - **database**

Coupling CALPHAD databases with PF models



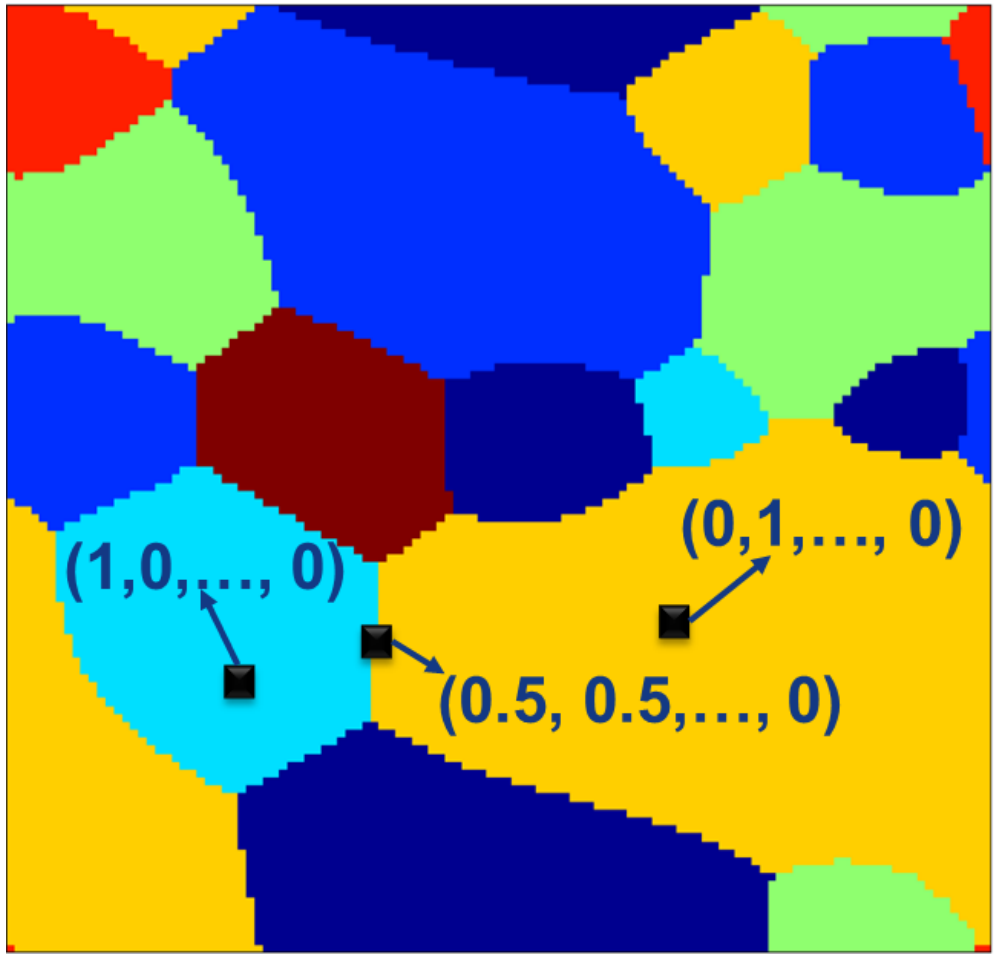


https://link.springer.com/article/10.1007/s10853-021-06033-7

3.2 Multi-phase system

- Example: grain growth--many “phases” with same composition, each phase (ϕ_i) represents a grain with a different orientation.

$$(\phi_1, \phi_2, \cdots, \phi_n) = (1, 0, \cdots, 0)$$



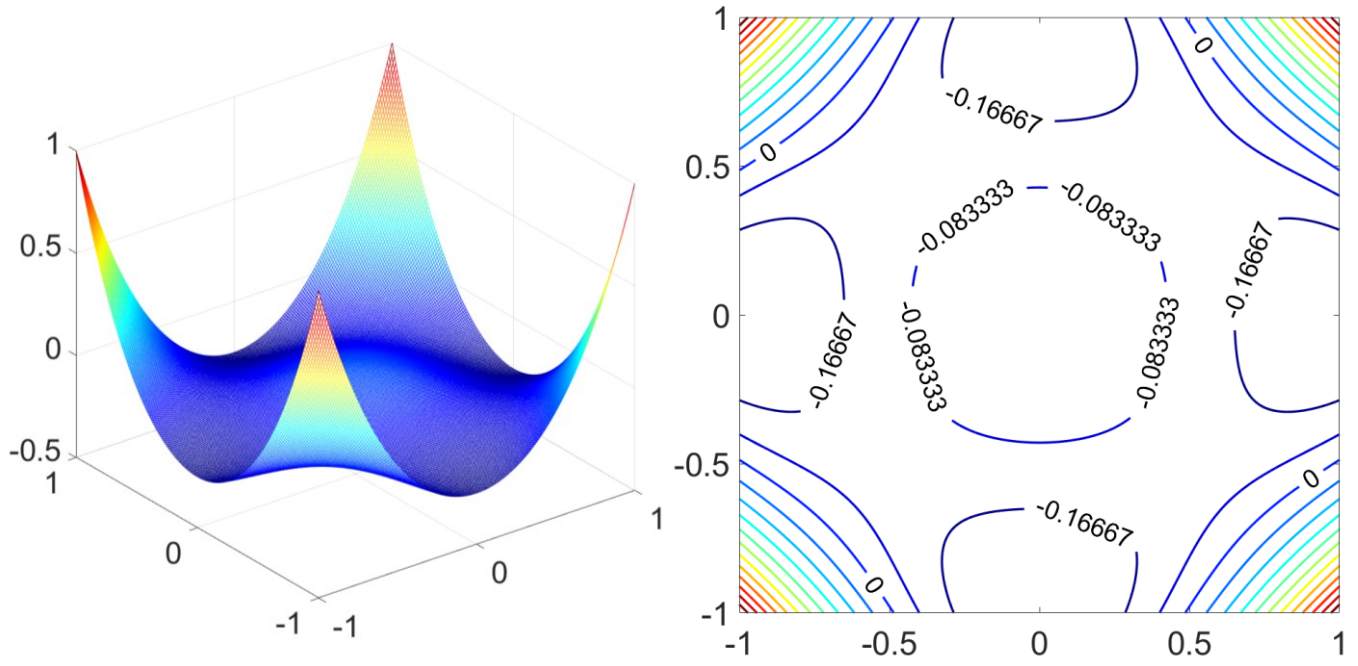
3.2 Multi-phase system (1)

- Free energy
  - arbitrary # of order parameters for different orientations
  - Distinct minima, each has only one ϕ_i is non-zero.

$$f[\{\phi_i\}] = -\frac{\alpha}{2}\sum_{i=1}^{P}\phi_i^2 + \frac{\beta}{4}\left(\sum_{i=1}^{P}\phi_i^2\right)^2 + \left(\gamma - \frac{\beta}{2}\right)\sum_{i=1}^{P}\sum_{j\neq i=1}^{P}\phi_i^2\phi_j^2$$

$$P = 2,\ \alpha = \beta = \gamma = 1$$

other options?

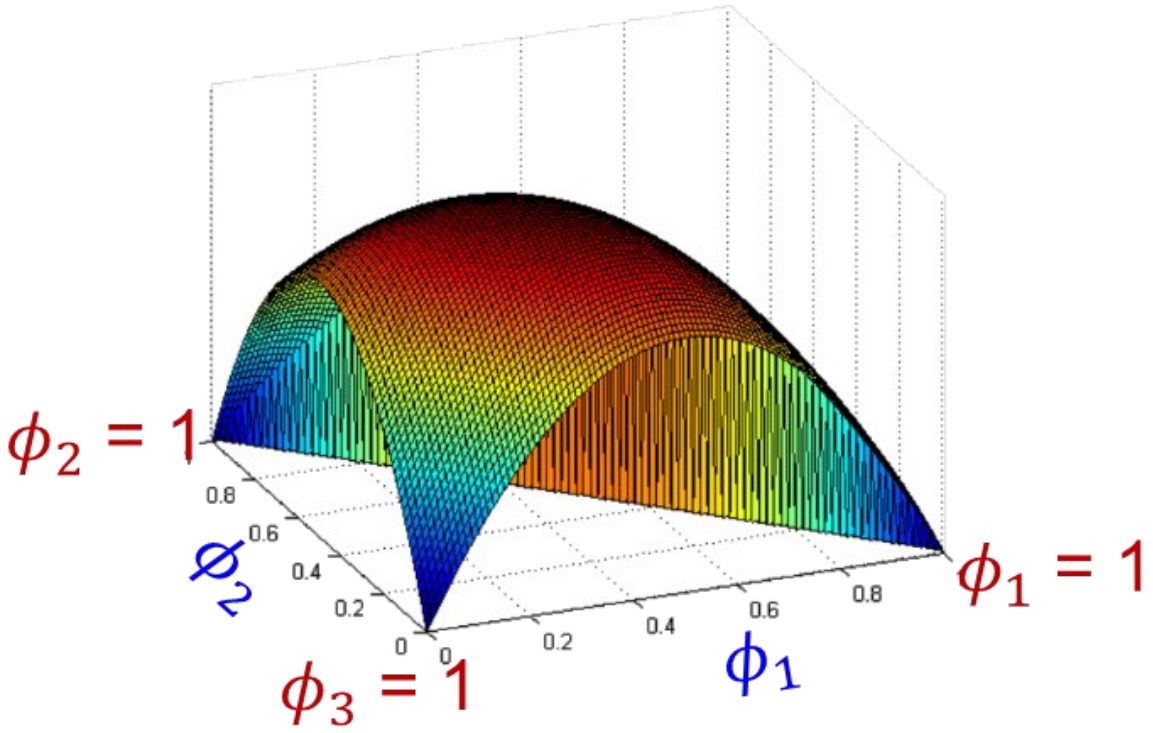


V. Tikare, E. A. Holm, D. Fan and L. Q. Chen, Acta Materialia 47(1998) 363-371

3.2 Multi-phase system (2)

- Free energy: Distinct minima, each has only one ϕ_i approaching unity or zero (pure phase)

$$f[\{\phi_i\}] = U\left(|\phi_1\phi_2| + |\phi_2\phi_3| + |\phi_3\phi_1|\right)$$



3.3 Current state of Phase Field Modeling

- Modeling meso-(micro-) scale microstructure
  - **Based on thermodynamic principles**

- Current topics
  - Realistic, complex, multi component systems

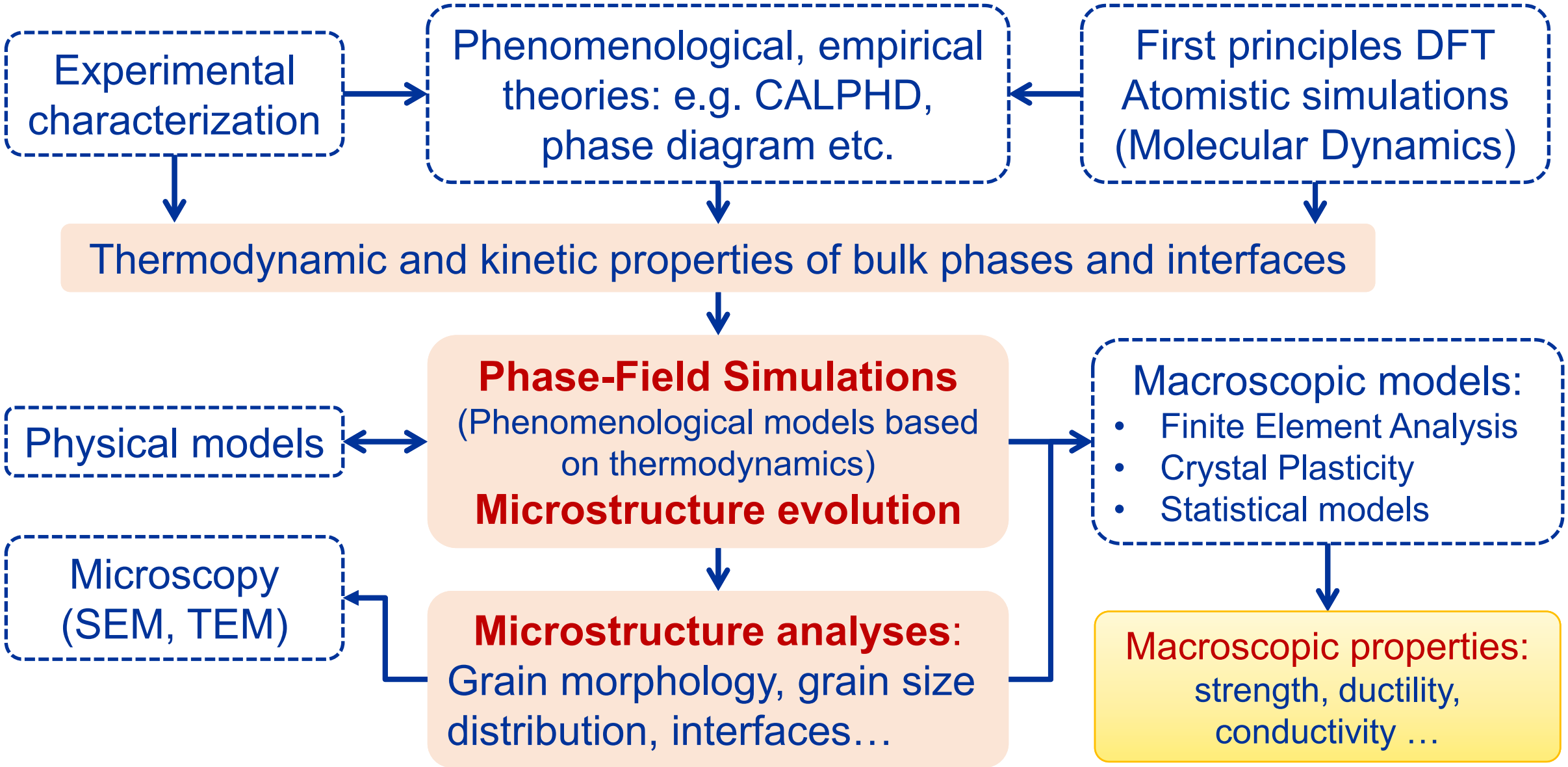
    More realistic description of free energy

  - **Quantitative aspects**

3.4 Quantitative PFM (1)

- Accurately reproduce bulk properties, and interfaces as observed
  - Effective model description and parameters
  - Numerical issues
- Provide insights into evolution of complex morphologies (i.e. grain assemblies, twin evolution etc.)
  - Effect of individual bulk and interface properties on results
- Predictive ability ?
  - **Depends on availability and accuracy of input data**
  - Requires composition and orientation dependence

3.4 Quantitative PFM (2)

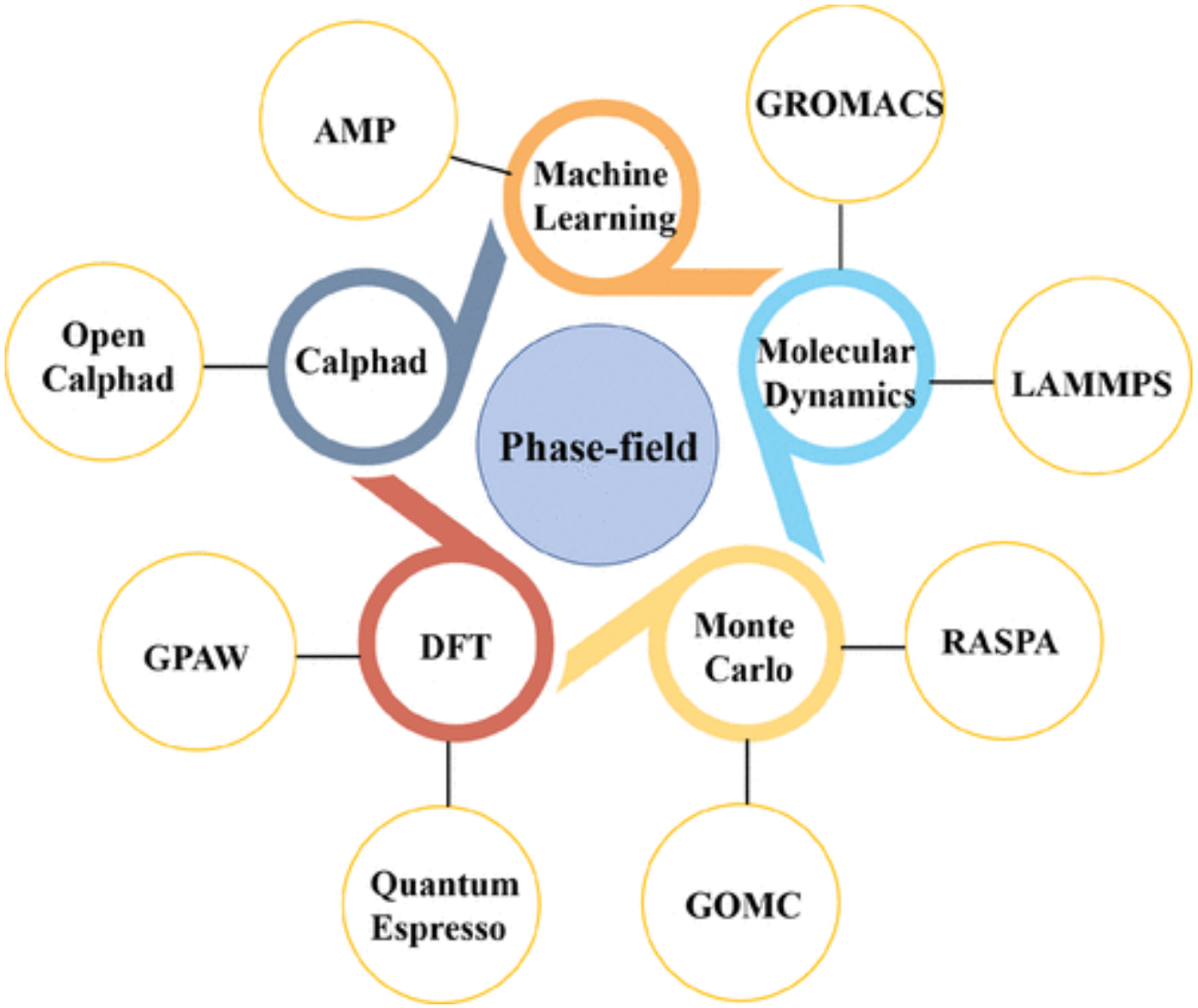


3.5 Parameter assessment

- Different kinds of input data
  - Bulk phase stabilities, bulk phase diagram information (CALPHAD)
  - Interfacial energy and mobility
  - Elastic properties, crystal structure, lattice parameters
  - Diffusion mobilities/coefficients (DICTRA mobilities)
- Orientation and composition dependence
  - Anisotropy, segregation, solute drag
  - Very important for microstructure evolution, but difficult to measure/calculate

Coupling phase-field with thermodynamic databases

Integrating Phase-Field Simulations with DFT, MD, …



https://doi.org/10.1021/acsenergylett.0c01904

Summary for PFM

- **Microstructure in PFM**
  - Field variables (conserved, non-conserved)
- **Driving forces for microstructure evolution**
  - Decrease of free energy
  - Free energy
- **Governing equation for microstructure evolution**
  - Conserved variable (Cahn-Hilliard Equation)
  - Non-conserved (Allen-Cahn equation)
- **Solve the governing equation to obtain microstructure**
  - Determine parameters (atomic scale models, experiments)
  - Initialize variables, apply boundary conditions
  - Numerical solutions

Homework for PF (3)

1. For a one dimensional interface with the following free energy,

$$F[\phi]=\int_{\Omega}\left[f_0\left(-\frac{1}{2}\phi^2+\frac{1}{4}\phi^4\right)+\frac{\alpha}{2}|\nabla\phi|^2\right]dV$$

   1) Numerically solve the evolution of interface structure and system energy using **fixed** boundary condition.
   2) Discuss the influence of energy barrier f_0 and the gradient coefficient α on the results.

- Due: 2022.12.25

Next Week:

Hands-On Phase Filed Method: dendric crystal growth & grain growth