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MSE6701H, Multiscale Materials Modeling and Simulation

Hands-on PF

Equilibrium interface, Dendritic Crystal Growth, Grain growth

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2022.1.5

Review: Phase field method for microstructure evolution

- Microstructure in PFM
- Driving forces for microstructure evolution
- Governing equation for microstructure evolution
- Solve the governing equation to obtain microstructure

Contents

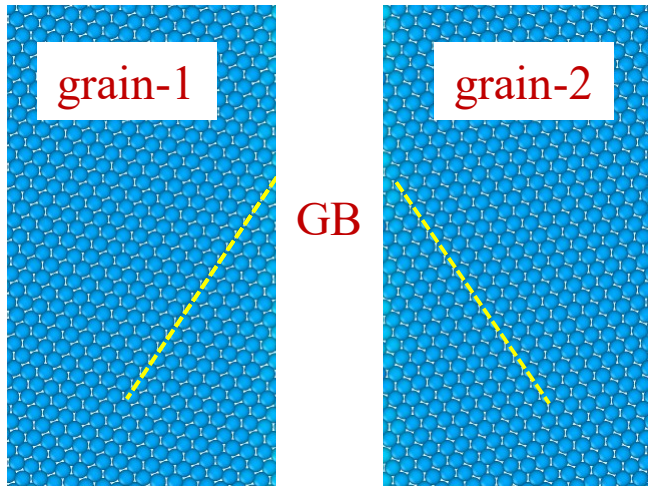
- **Case study**
  - **I. One dimensional interface: structure & energy**
  - **II. Dendritic crystal growth: effects of temperature & anisotropic interface energy**
  - **III. Grain growth of polycrystal: multi-phase field method**

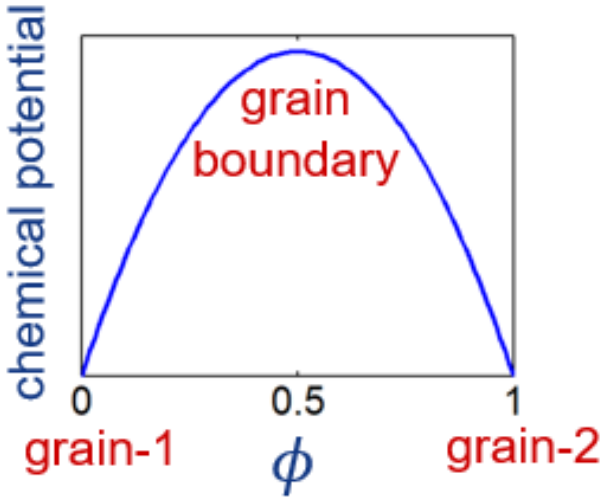
- Goals
  - ✓ understand
    - How equilibrium interface structure is determined by energy minimization
    - How crystal growth is determined by decrease of total free energy
  - ✓ perform PF simulation by solving evolution equation with MATLAB

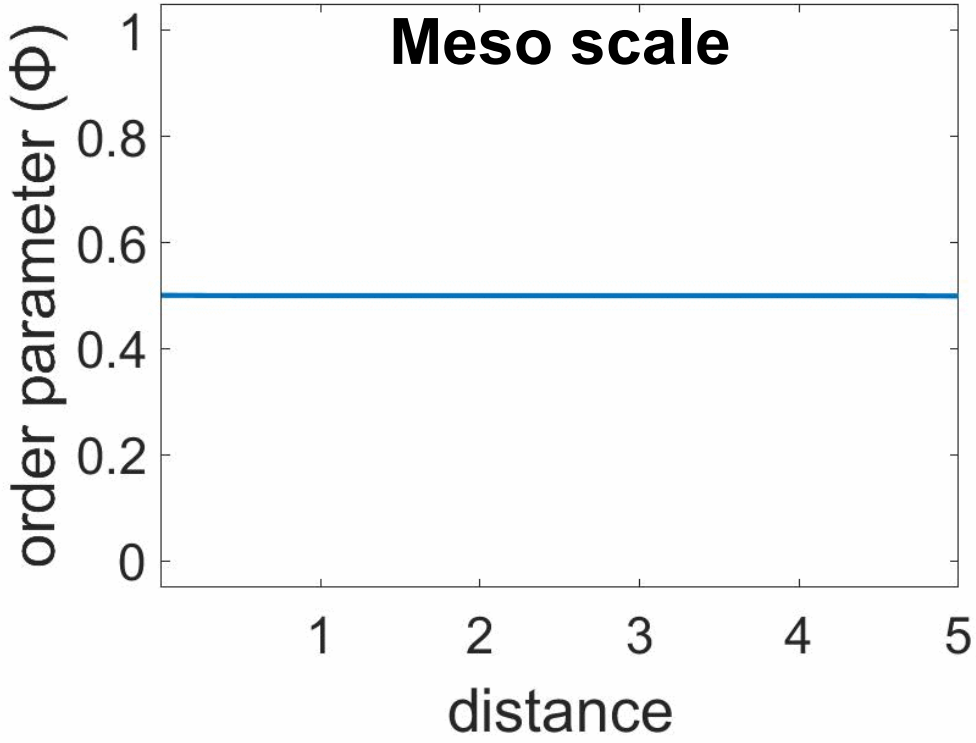
I. 1D interface structure

- 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





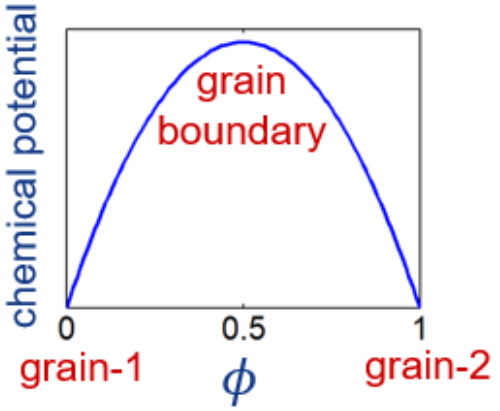


I. 1D interface structure

- Free energy density

$$f[\phi(x)] = U \cdot \phi(1-\phi) + \frac{k}{2}|\nabla\phi|^2$$

$$f_{\text{che}} \quad + \quad f_{\text{grad}}$$



- Evolution equation

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

- Equilibrium state

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

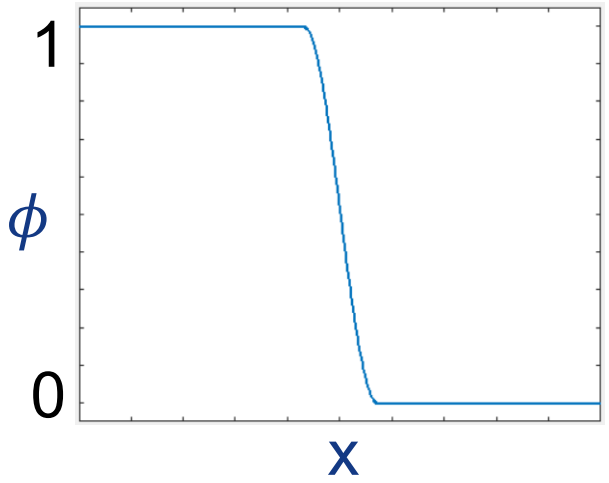
solve the 2nd order ordinary differential equation

➔ equilibrium distribution $\phi[x]$

I. 1D interface structure: analytical solution

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

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

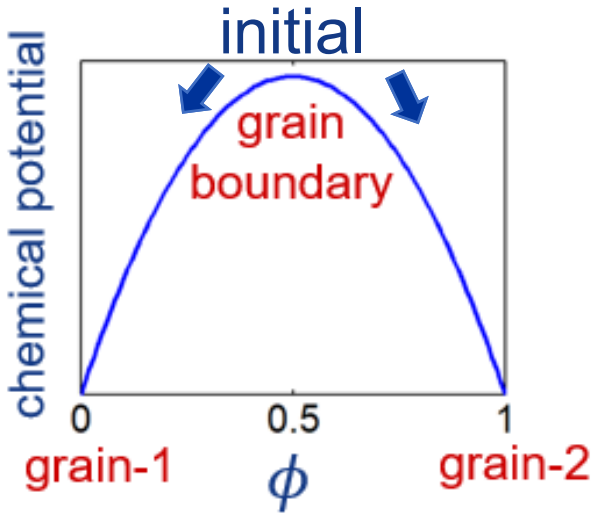


- Analytical solution to the equilibrium interface: $\phi(x) = ?$
  - Interface thickness: $\pi\sqrt{\frac{k}{2U}}$
  - Total energy: $\int_{-\infty}^{+\infty} f[\phi(x)]dx = \frac{\pi}{4\sqrt{2}}\sqrt{kU}$

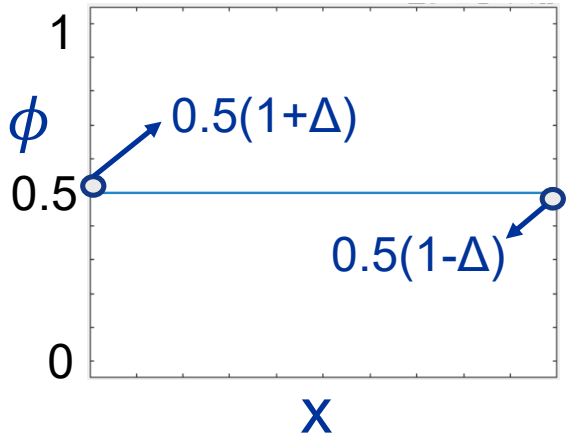
I. 1D interface structure: numerical solution

- 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**:



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

I. 1D interface structure： 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**

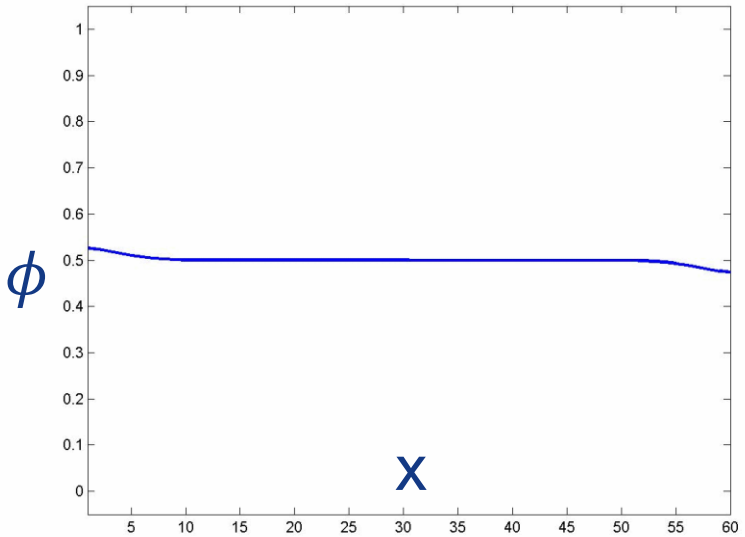
```
%gradient
grad_phi(i) = (phi(ip) - phi(im))/(2*dx);

%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
```

I. 1D interface structure : numerical solution

- Equilibrium $\phi(x)$

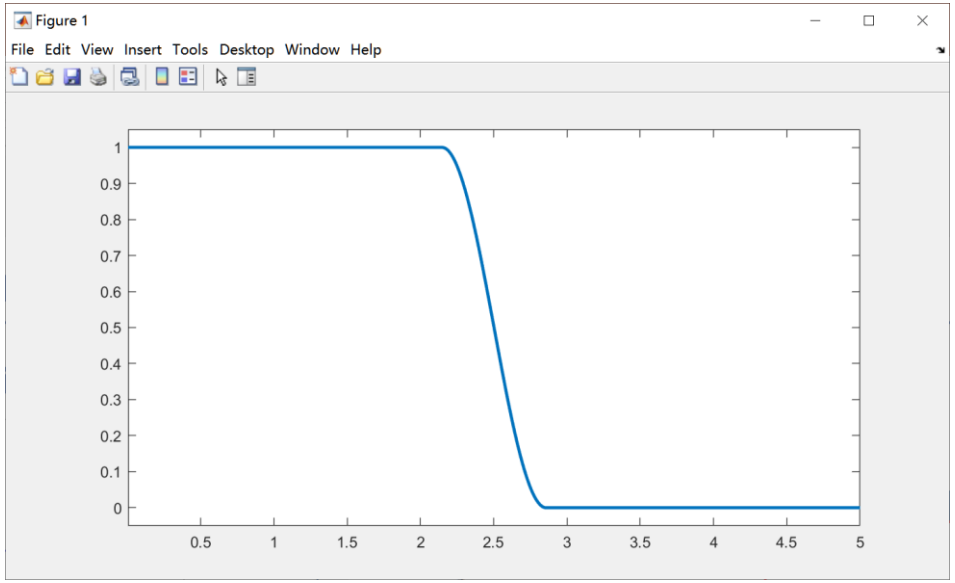


- Interface **width (w)**

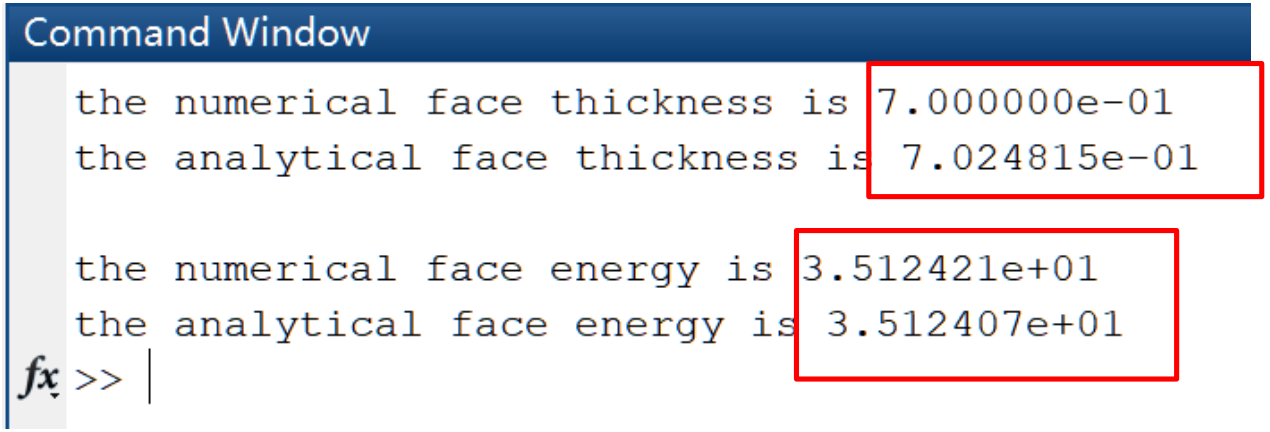
$$w = x_2 - x_1$$

$$\phi(x_2) = 0.9999$$

$$\phi(x_1) = 0.0001$$



Numerical v.s. analytical (w & energy)

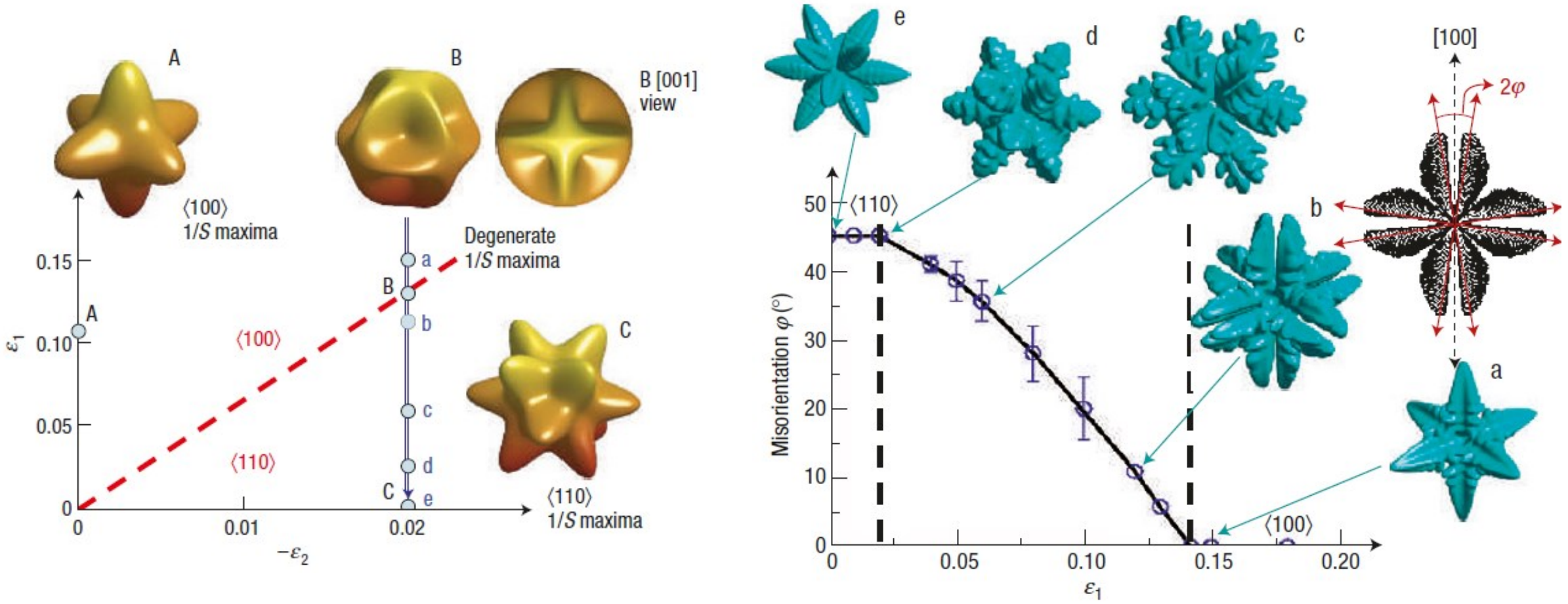


II. Dendritic crystal growth

- the beautiful snowflake always shows dendritic and fractal structure, why?

II. Dendritic evolution: orientation selection

$$\gamma(\theta,\varphi)=\gamma_0[1+\varepsilon_1 K_1(\theta,\varphi)+\varepsilon_2 K_2(\theta,\varphi)+\cdots]$$



Orientation selection in dendritic evolution, *Nature Materials* **5**:660–664(2006).

II. Dendritic crystal growth

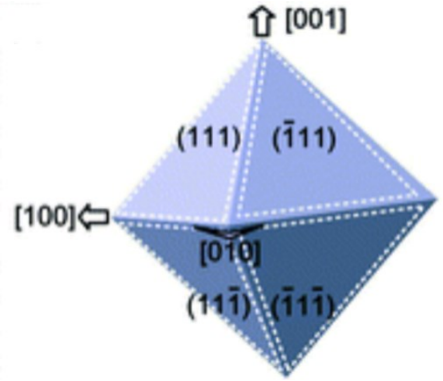
- Where do these beautiful dendritic structures come?
- Is it a common phenomenon in solidification?
- How to predict and control of microstructure in solidification?
  (based on mechanism)

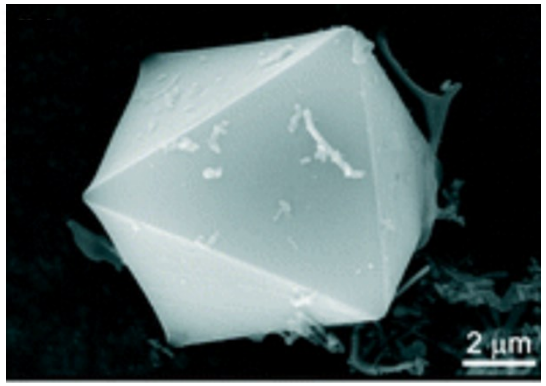
- **Two main factors**
  - the anisotropic interface energy
  - latent heat / solute redistribution

II. Dendritic crystal growth

- **Factor 1: anisotropic interface energy**
  - crystals tend to be bounded by low energy surfaces (interfaces), such as

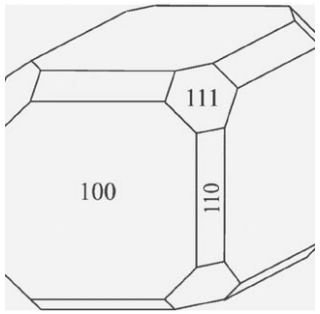
- **{111} planes in FCC crystal**





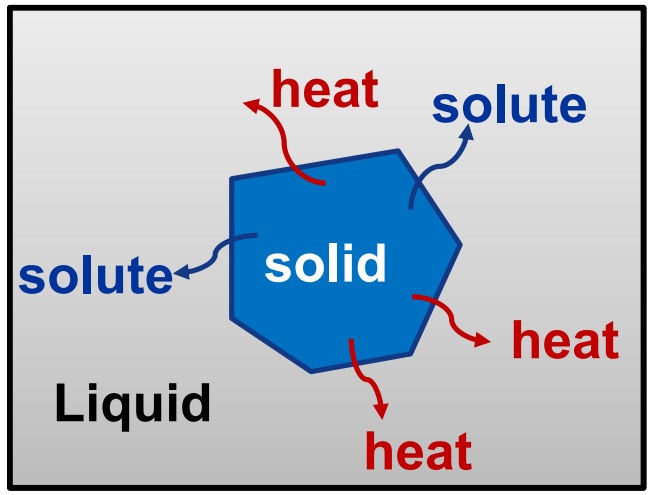
Lei Chen, et al. CrystEngComm, 2014, 16, 448-454

- **{100} planes in simple cubic**

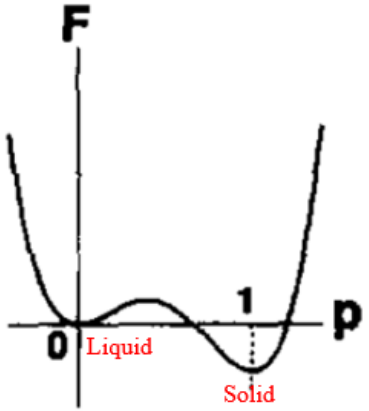


II. Dendritic crystal growth

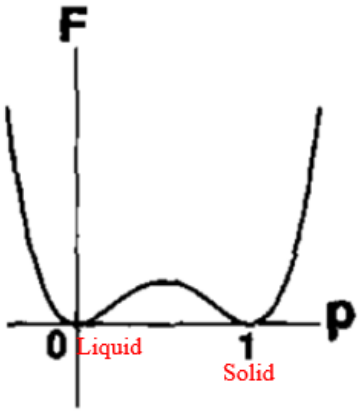
- **Factor 2: latent heat or solute redistribution**
  - the transformation from liquid to solid may release some heat or solute to the surrounding liquid



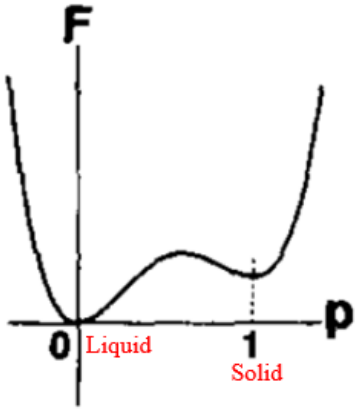
- **The chemical energy density is dependent on temperature (or solute concentration)**



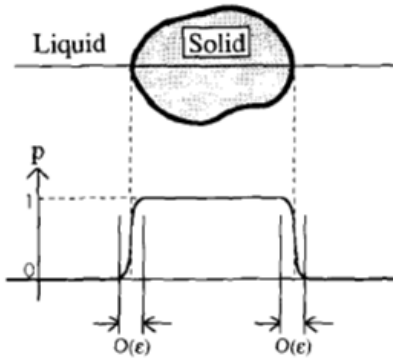
T<T_c



T=T_c

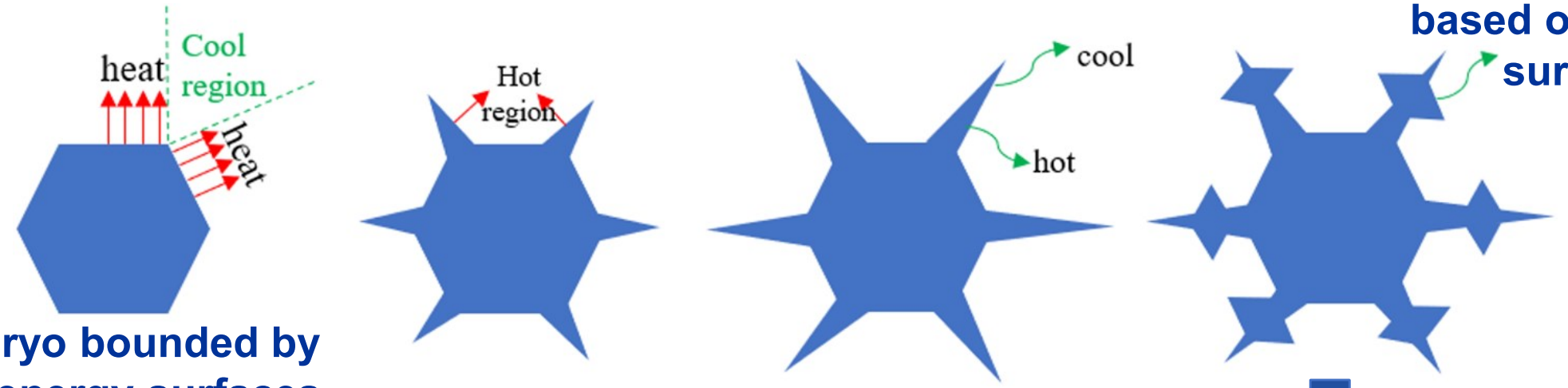


T>T_c



II. Dendritic crystal growth

➢ the explanation of dendritic crystal growth



- **Repeat the processes of new embryos and new dendrites**
  ➔ the fractal morphologies

- anisotropic interface energy
- latent heat / solute redistribution

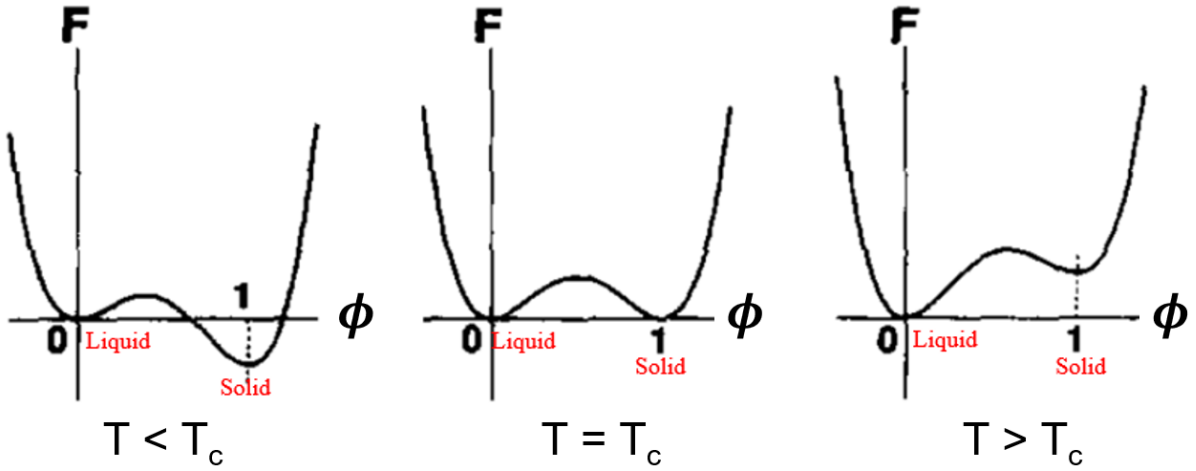
➡ dendritic crystal

II. Dendritic crystal growth in phase field model

- **Phase description: ϕ = 0 for liquid and ϕ = 1 for solid**
- **Free energy (chemical energy & interface energy)**
  - **chemical energy density,** varies with temperature *or solute concentration*)

$$f_{che}(\phi,T)=\frac{1}{4}\phi^4-\left(\frac{1}{2}-\frac{m}{3}\right)\phi^3+\left(\frac{1}{4}-\frac{m}{2}\right)\phi^2$$

$$\text{with } m(T)=\frac{\alpha}{\pi}\arctan[\gamma(T_e-T)]$$



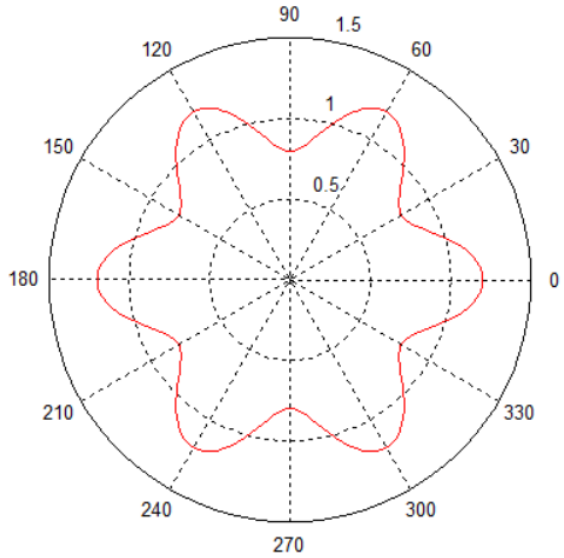
  - **interface energy density**

R. Kobayashi, Physica D 63(3-4) (1993) 410-423

II. Dendritic crystal growth in phase field model

- **Free energy (chemical energy & interface energy)**
  - **chemical energy density**
  - **interface energy density** (anisotropic, varies with crystalline structure)

interface energy vs. orientation



$$f_{int} = \frac{1}{2}(\varepsilon_\theta \nabla\phi)^2, \text{ with } \varepsilon_\theta = \bar{\varepsilon}\{1 + \delta\cos[j(\theta - \theta_0)]\}$$

- **Driving force: temperature change (or solute diffusion)**

$$\frac{\partial T}{\partial t} = c_1 \nabla^2 T + \mathrm{LH} \cdot \frac{\partial \phi}{\partial t}$$

← **latent heat**

heat conduction

R. Kobayashi, Physica D 63(3-4) (1993) 410-423

II. Dendritic crystal growth in phase field model

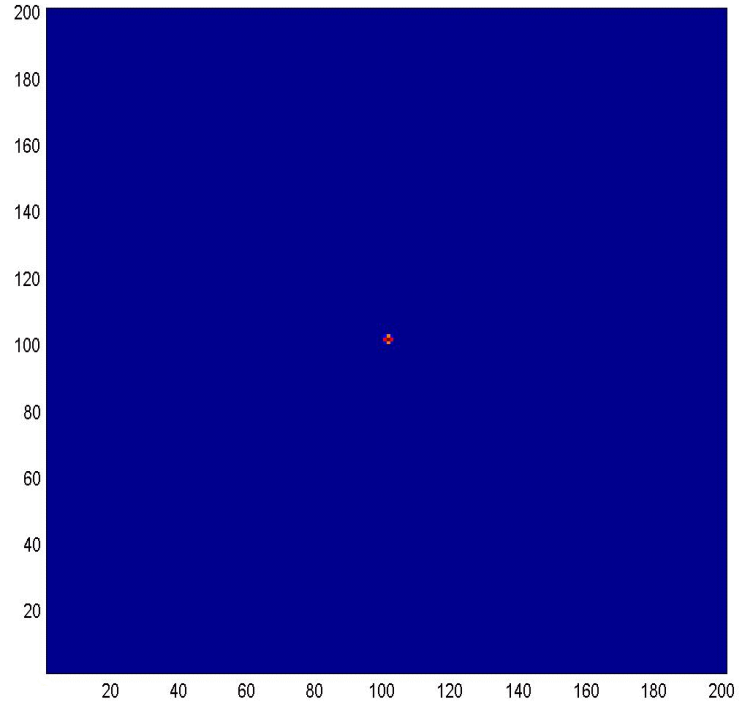
- Phase Field: solve the order parameter field and temperature field at each time increment Δt

$$\phi_{t+\Delta t} = \phi_t + \frac{\partial \phi}{\partial t}\Delta t,\ T_{t+\Delta t} = T_t + \frac{\partial T}{\partial t}\Delta t$$

$$\frac{\partial \phi}{\partial t} = -M\frac{\delta F[\phi, \nabla\phi, T]}{\delta \phi}$$

Allen-Cahn equation (Ginzburg-Landau)

$$c_1 \nabla^2 T + \mathrm{LH} \cdot \frac{\partial \phi}{\partial t} = \frac{\partial T}{\partial t}$$



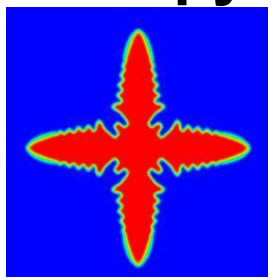
heat conduction + latent heat → temperature ch

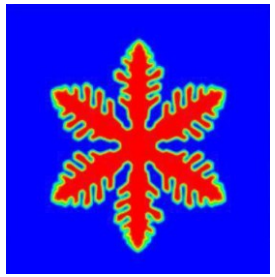
Results in your PF report

- Effects of anisotropic mode & latent heat on dendritic crystal growth
  1. **Vary anisotropic mode**
  2. **Vary the latent heat (can dendrites form without latent heat?)**
  3. **Other factors?**

```
%====================== material parameters========
epsilonbar = 0.005; % gradient energy coefficient
mu = 1.0;
delta = 0.02; % the strength of anisotropy
LH = 1.5;      % latent heat coefficient
anisotropy = 6.0 ;  % mode number of anisotropy
alpha = 0.9;
gamma = 10.0;
teq = 1.0 ;
```

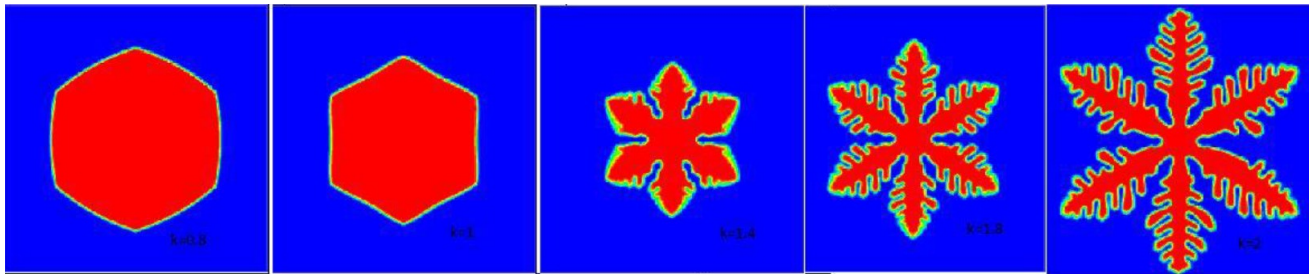
anisotropy = 4



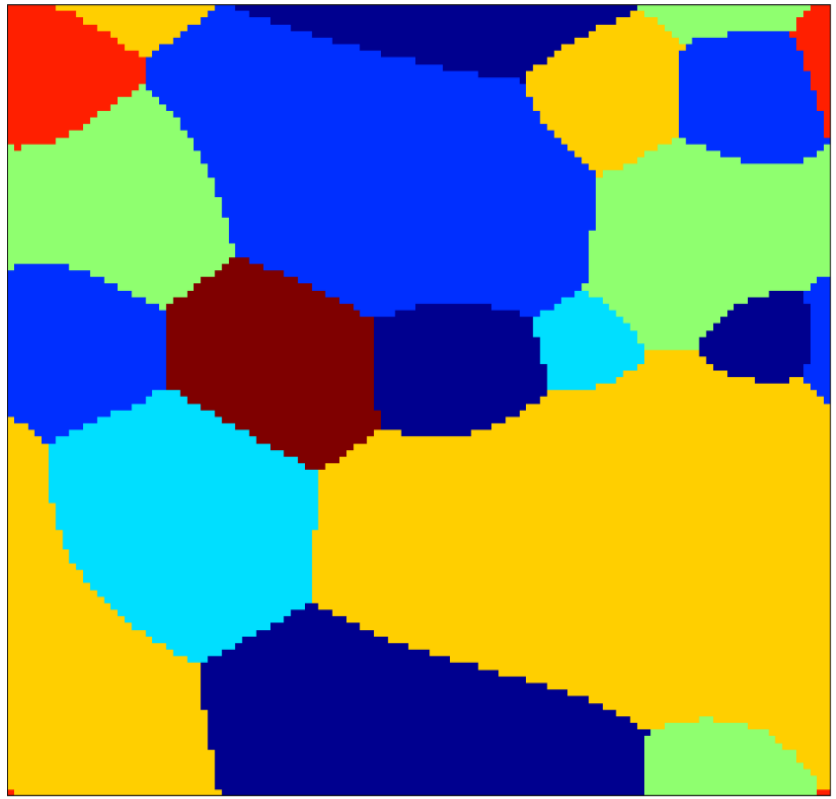


anisotropy = 6

LH = 0.8 **1.0** **1.4** **1.8** **2.0**



III. Polycrystal: formation and evolution



how to describe the formation and evolution of polycrystal by Phase Field method ?

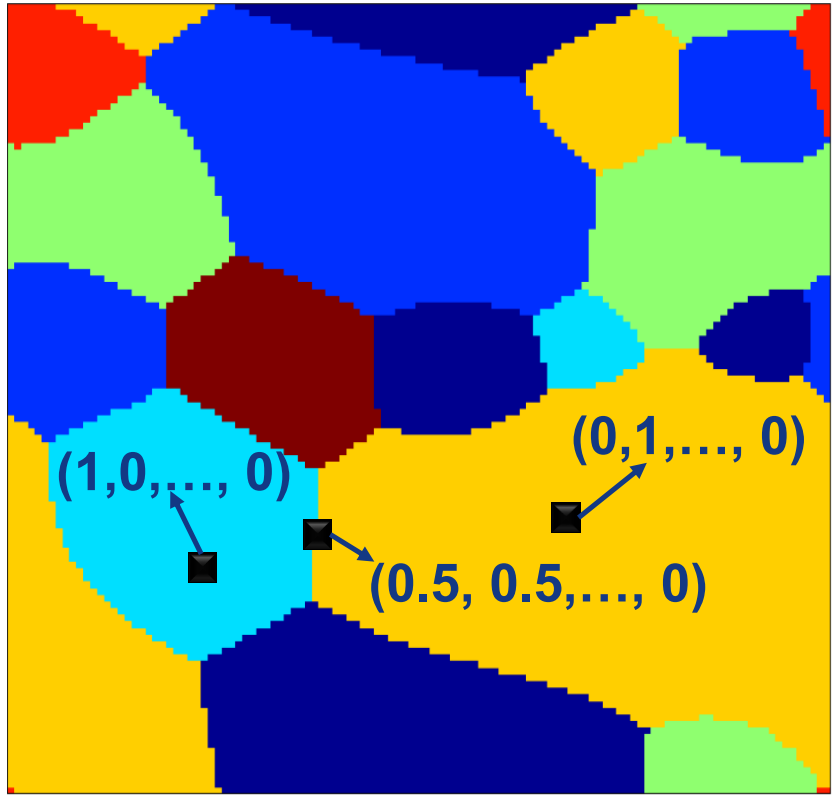
III. Polycrystal: microstructure

- How to describe different grains in PF ?
- Grains of different orientations can be represented by different phases,
- Each phase will be assigned an OP

$$\boldsymbol{\phi} = (\phi_1, \phi_2, \cdots, \phi_n)$$

grain-1 grain-2 grain-n

ϕ_i represents the volume fraction of grain-i

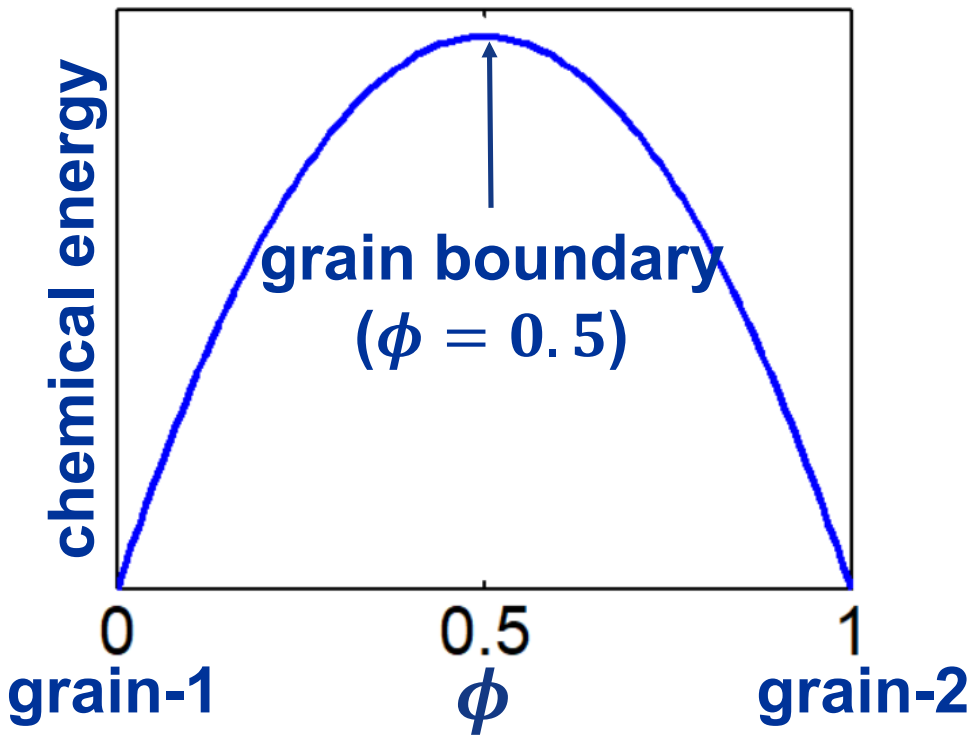


III. Polycrystal: free energy

- **Free energy**
  1. **chemical energy**
  2. **interface or gradient energy**

- **For two grains, chemical energy density**

$$f_{che} = U\left|\phi(1-\phi)\right|$$



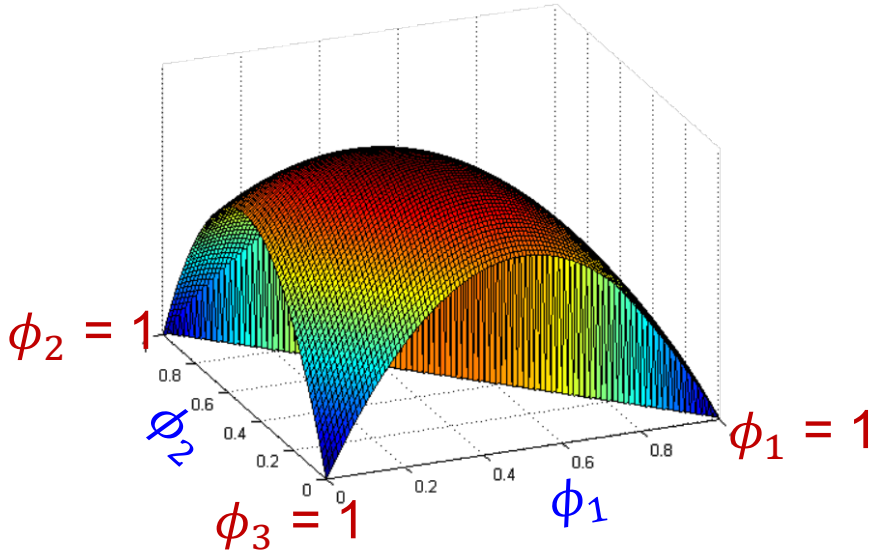
III. Polycrystal: chemical energy (1)

- **For many grains, how to construct the chemical energy potential?**
  - **each grain corresponds to the ground state energy**
  - **the grain boundary corresponds to a higher energy**

$$f_{che} = U \cdot \sum\nolimits_{p<q} |\phi_p \phi_q|$$

- 3 phases?

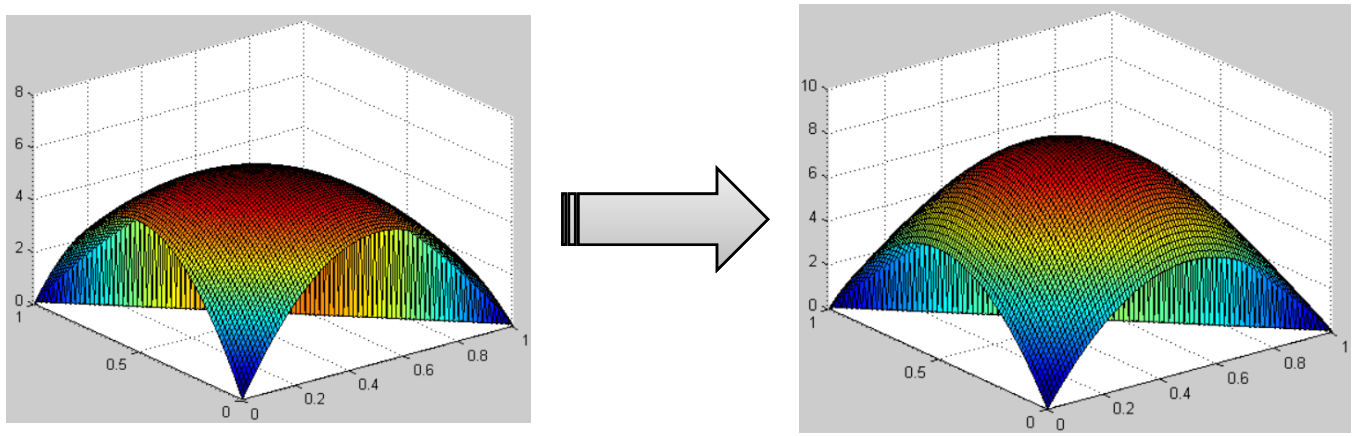
$$f_{che}[\{\phi_i\}] = U\left(|\phi_1\phi_2| + |\phi_2\phi_3| + |\phi_3\phi_1|\right)$$



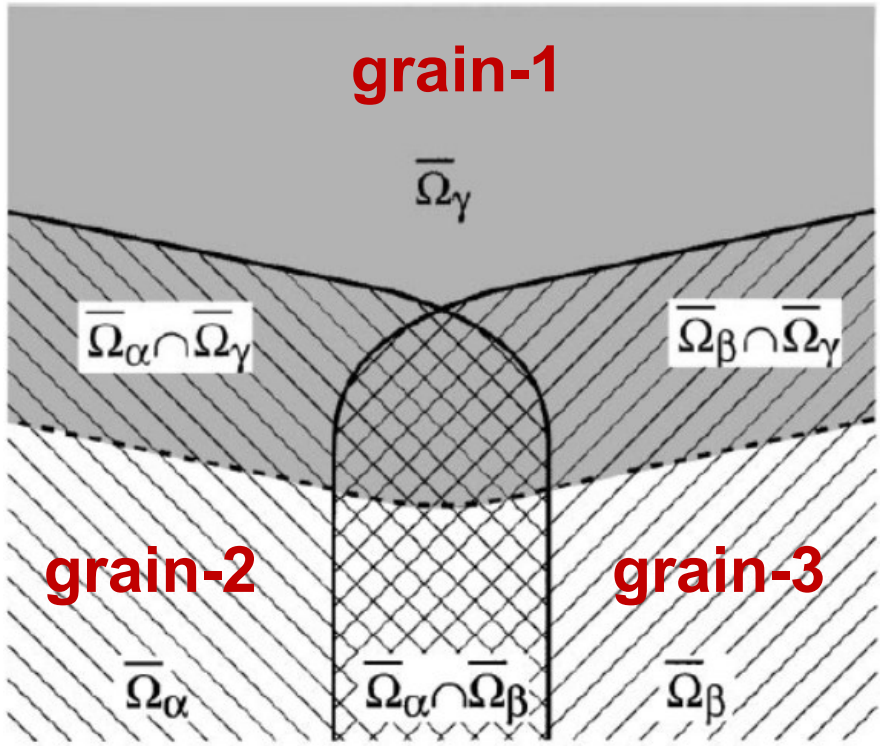
III. Polycrystal: chemical energy (2)

- Triple grain boundary: 3 phases coexist
- **Energy penalty term**

$$f_{penalty} = \tilde{U} \cdot \sum_{p<q<r} |\phi_p \phi_q \phi_r|$$



$$f_{che} + f_{penalty} \Longrightarrow F_{che}$$

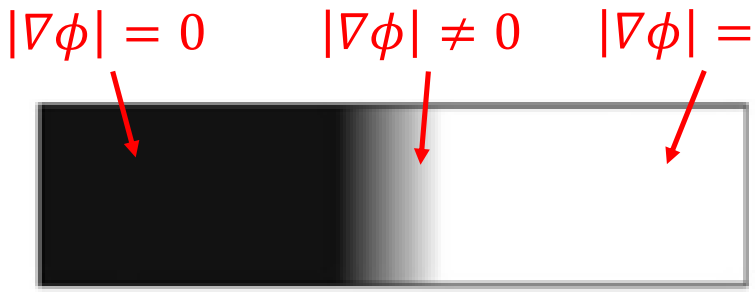


III. Polycrystal: free energy

➢ Free energy

1. chemical energy
2. **Interface or gradient energy**

at interface, the gradient $|\nabla\phi| \neq 0$



- interface energy density

$$f_{int} = \frac{k}{2}\sum\nolimits_p |\nabla\phi_p|^2$$

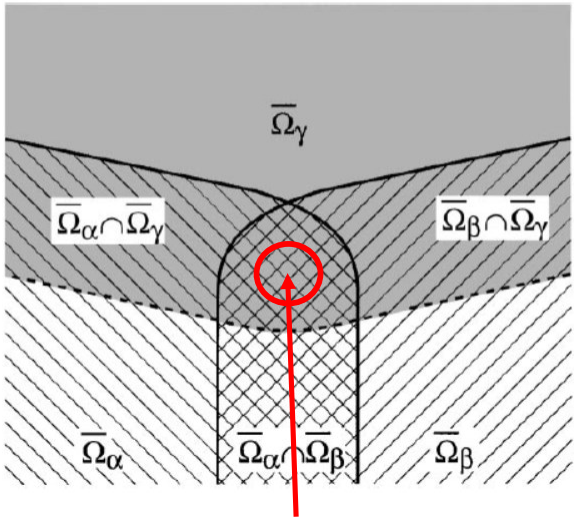
➢ Total free energy

$$\begin{aligned} F &= f_{che} + f_{penalty} + f_{int} \\ &= U \cdot \sum\nolimits_{p<q} |\phi_p \phi_q| \\ &+ \tilde{U} \cdot \sum\nolimits_{p<q<r} |\phi_p \phi_q \phi_r| \\ &+ \frac{k}{2}\sum\nolimits_p |\nabla\phi_p|^2 \end{aligned}$$

III. Polycrystal: grain evolution

- **Extra constraint for multi-phase field variables**

$$\sum_p \phi_p = 1,\ i.e.\ \sum_p \dot{\phi}_p = 0$$



$$\phi_1 = 0.4$$
$$\phi_2 = 0.3$$
$$\phi_3 = 0.3$$

- **Allen-Cahn equation does not automatically satisfy this constraint**

$$\sum_p \dot{\phi}_p = \sum_p \left(-M \frac{\delta F}{\delta \phi_p} \right) \neq 0$$

- **A new evolution equation is required**

III. Polycrystal: evolution equation

➢ **Constraint:** volume fractions of multiple phases should be conserved

$$\sum_p \phi_p = 1,\ i.e.\ \sum_p \dot{\phi}_p = 0$$

- **phase field**

$$\dot{\phi} = -M\frac{\delta F}{\delta \phi}$$

- **multi-phase field method[1] (*n* phases, *n* > 2)**

$$\dot{\phi}_p = -\frac{1}{n}\sum_q^n M_{pq}\left(\frac{\delta F}{\delta \phi_p} - \frac{\delta F}{\delta \phi_q}\right)$$

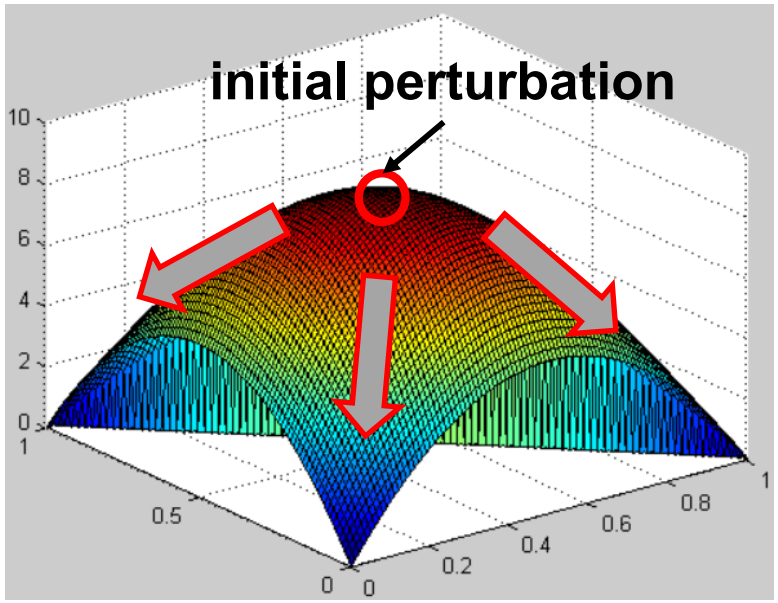
It automatically satisfies

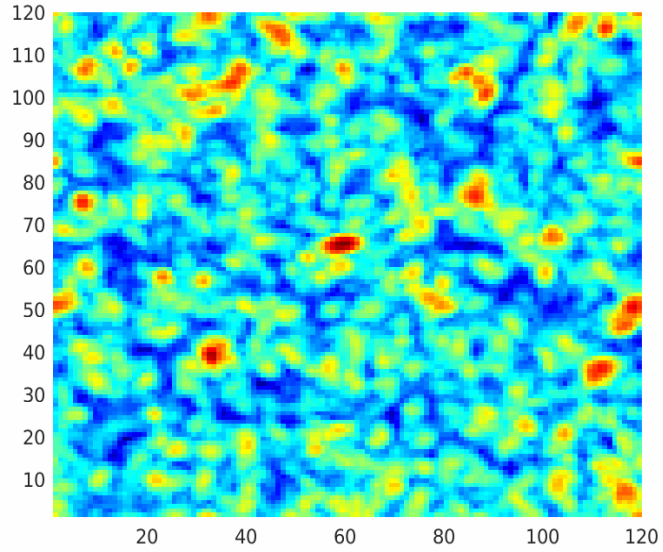
- $\text{multi}-\text{phase conservation}\ \sum_p \dot{\phi}_p = 0$
- $\text{free energy density decreases}\ \dot{f} = \sum_p \frac{\delta F}{\delta \phi_p}\dot{\phi}_p < 0$

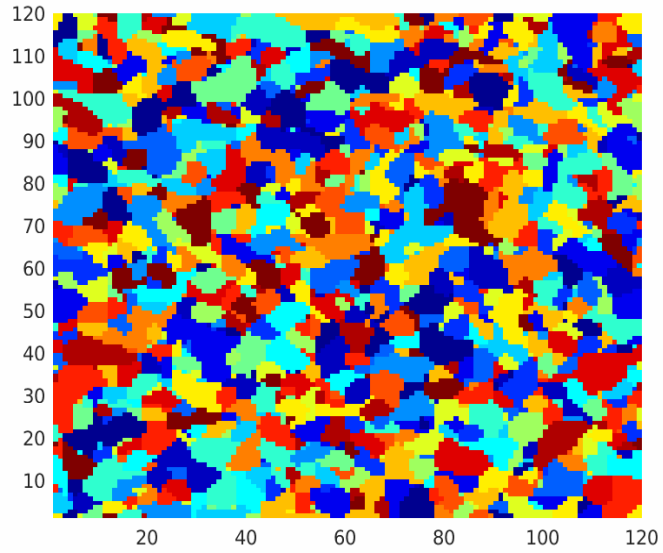
[1] I. Steinbach, F. Pezzolla. Physica D 134 (1999) 385–393

III. Polycrystal: formation and evolution

- Initialization
  - Initial state: initial perturbation around $1/n$, n being the number of grains (ϕ_i), grain nuclei
  - all grains are mixed together, considered as the amorphous liquid phase

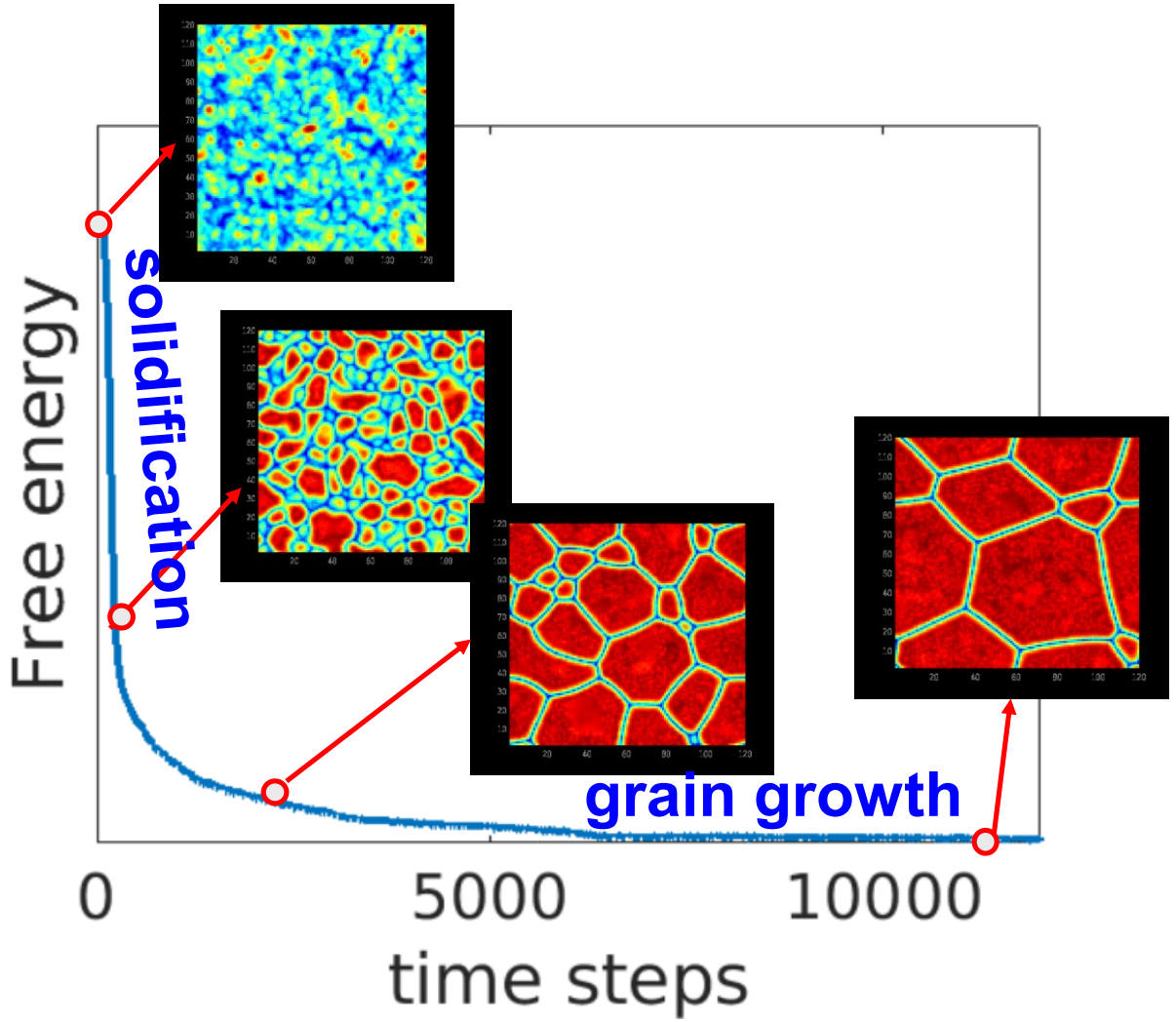






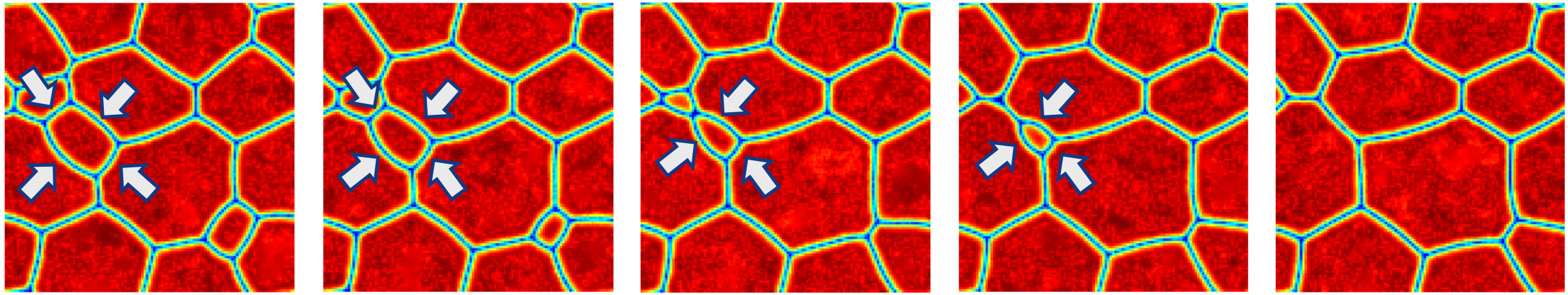
III. Polycrystal: evolution

- Total free energy
  - **Rapidly decreases during solidification**
  - **Slowly decreases during grain growth by the migration of grain boundary**



III. Polycrystal: formation and evolution

- Grain growth
  - **grain boundary moves toward the center of curvature**
  - **big grains eat small grains**
  - **interface area decreases → lower the interface energy**



III. Polycrystal: formation and evolution

- **Geometry model setup**

```
4   %=========== parameters for geometric model==
5   am = 0;
6   Q = 20;          % number of different phases
7   nx = 120;        % number of grid in x-direction
8   ny = 120;        % number of grid in y-direction
9   dx = 0.1;
10  dy = 0.1;
11  dt = 0.01;  % time step
```

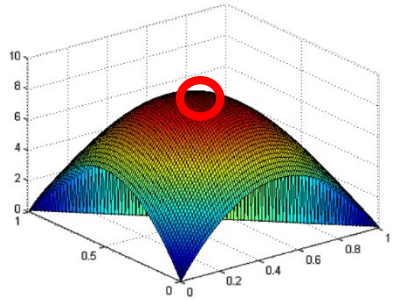
20 grains with different orientations

- **Initial order parameter phi(p, xi, yj)**

```
41  %==========initialize parameters for phase field====
42  for i = 1:nx
43      for j = 1:ny
44          for p = 1:Q
45              phi(p,i,j) = 1 / Q;
46          end
47      end
48      x(i)=i;
49  end
```

- **initial perturbation**

```
50  %==========set the initial perturbatiom==================
51  f = 0.01;   %relative proportion for perturbation
52  for i=1:nx
53      for j=1:ny
54          for p=1:Q
55              phi(p,i,j) = phi(p,i,j) - f + 2*f*rand(1,1);
56          end
57          % total phases
58          am = 0;
59          for p = 1:Q
60              am = am + phi(p,i,j);
61          end
62          % normalization
63          for p = 1:Q
64              phi(p,i,j) = phi(p,i,j)/am;
65          end
66          % verify
67          AMphi = 0;
68          for p = 1:Q
69              AMphi = AMphi + phi(p,i,j);
70          end
71          if abs(AMphi-1) > 0.0001
72              AMphi
73              error('error, total phi does not equal 1');
74          end
75      end
76  end
```



III. Polycrystal: formation and evolution

- **Evolution equation**

$$\dot{\phi}_p = -\frac{1}{n}\sum_q^n M_{pq}\left(\frac{\delta F}{\delta \phi_p} - \frac{\delta F}{\delta \phi_q}\right)$$

```
AMphi = 0;
for p = 1:Q
    AMphi = AMphi + abs( phi(p,i,j) );
end

% compute variational derivative
AMva = 0;
for p = 1:Q

    term2 = 0; % the penalty term
    for m = 1:Q
        if m ~= p
            for n = (m+1):Q
                if n ~= p
                    term2 = term2 + abs(phi(m,i,j)) * abs(phi(n,i,j));
                end
            end
        end
    end
    term2 = term2 * sign(phi(p,i,j));
    term2 = term2 * u_p;
    phii = phi(p,i,j);

    % variational derivative of chemical potential,
    varia(p) = u * sign(phii) * (AMphi-abs(phii)) ...
        + term2 - k * lap_phi(p,i,j); % variation derivative of penalty term, & gradient energy,
    AMva = AMva + varia(p);
end
% update order parameter
for p = 1:Q
    term = varia(p) - AMva / Q;
    phi(p,i,j) = phi(p,i,j) - L*term*dt;
end
% total phases
am = 0;
for p = 1:Q
    am = am + phi(p,i,j);
end
% normalization
for p = 1:Q
    phi(p,i,j) = phi(p,i,j) / am;
end

% verify
AMphi = 0;
for p = 1 : Q
    AMphi = AMphi + phi(p,i,j);
end
if abs(AMphi-1) > 0.001
    AMphi
    error('error, total phi does not equal 1');
end
```

- **Energy & microstructure**

```
% ================== the energy ==============
eng(i, j) = 0;
for p1 = 1:Q
    for p2 = (p1 + 1):Q
        eng(i, j) = eng(i, j) + u * abs(phi(p1, i, j) ...
            * phi(p2, i, j)); % chemical potential term
    end
end
for p1 = 1:Q
    for p2 = (p1 + 1):Q
        for p3 = (p2 + 1):Q
            eng(i, j) = eng(i, j) + u_p * abs(phi(p1, i, j)...
                * phi(p2, i, j) * phi(p3, i, j));
                % penalty term of 3 phases coexistence
        end
    end
end
for p = 1:Q
    eng(i, j) = eng(i, j) + k / 2 * ((grad_phi(p,i,j,1))^2 ...
        + (grad_phi(p,i,j,2))^2); % gradient energy term
end

% ============= grain boundary ================
gap(i, j) = max(phi(:,i,j)) - min(phi(:,i,j));

% === different grains in different colors ====
[aa, bb] = max(phi(:,i,j));
polyCrys(i, j) = bb; % show different grains
```

Report for Phase Field Method

- **Key factors in your report**
  1. Introduction (Task, purpose)
  2. Method (model and simulation details, step by step)
  3. Results (figures, tables, analyses)
  4. Full discussion (not limited to the following aspects)
     - How does the input influence simulation results and why
     - How to determine input parameters like energy barrier, gradient coefficient, mobility for specific problems
     - The role of simulation results in multi-scale modeling
       - Further analyses: how to analyze distribution and evolution of grain size …
       - Further application, implication, against experiments …
  5. Conclusion and outlook (e.g. apply PFM results in multi-scale modeling)

- Due: Jan 16, 2021

Final exam: 18:00-20:00, Jan 12

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