Phase-Field Modeling of Freezing and Freeze Concentration

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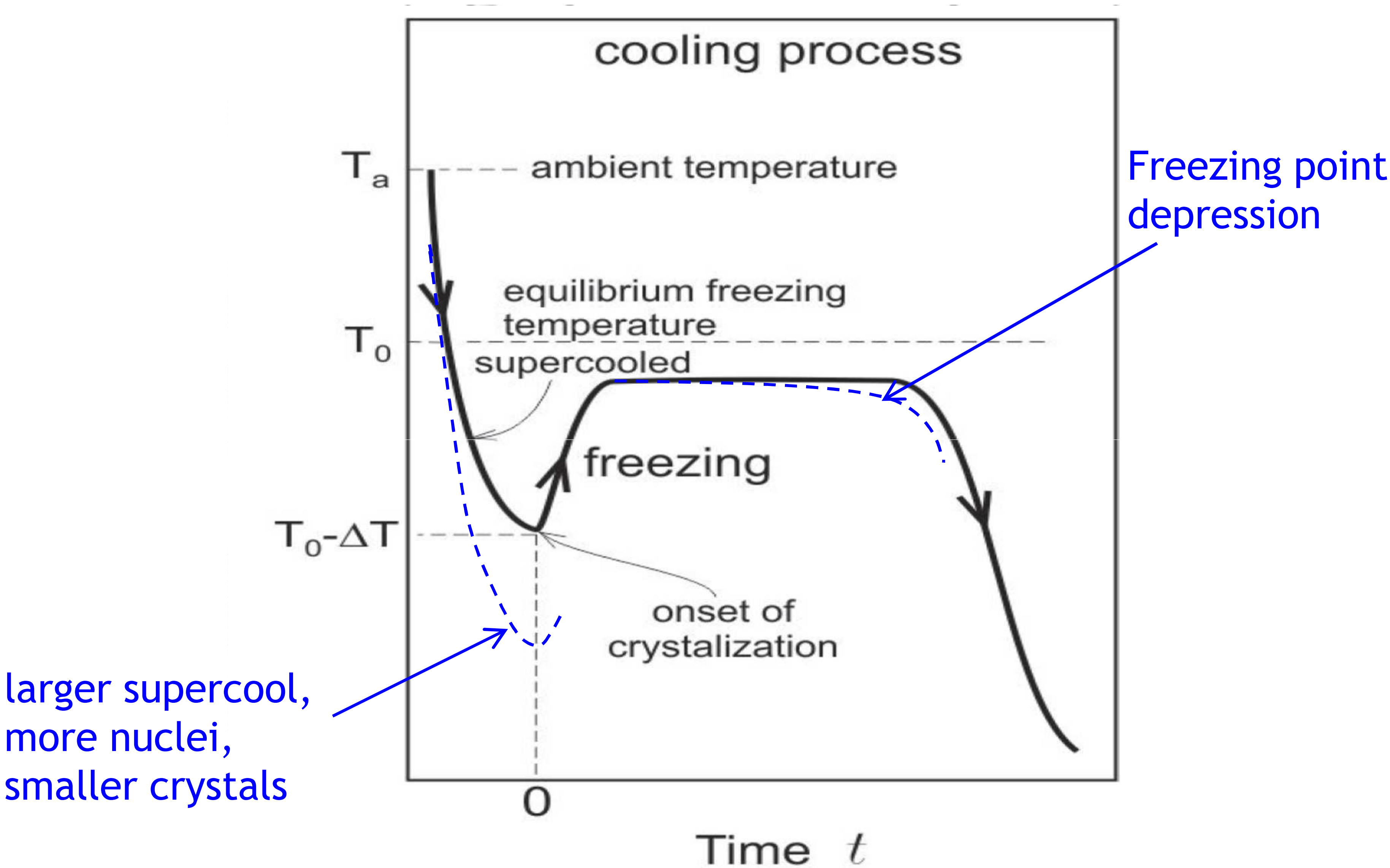
Motivation

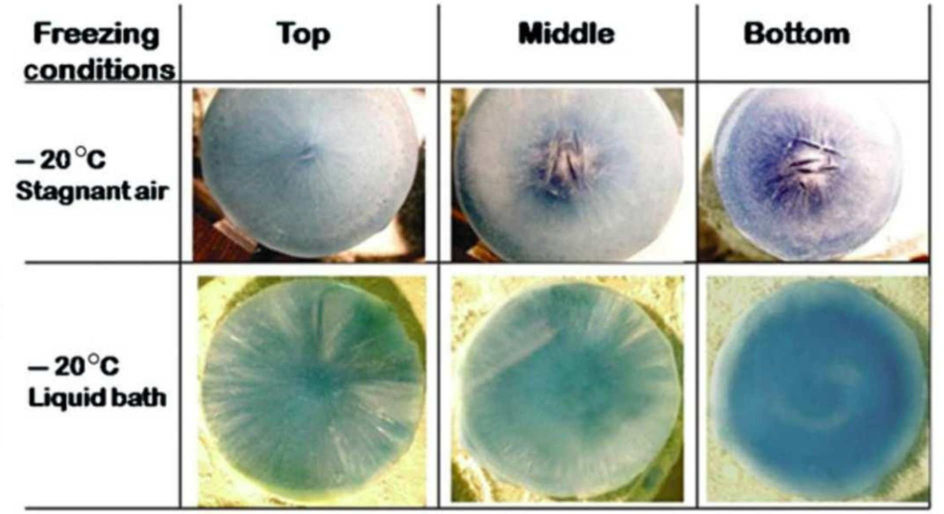
Better understanding, quantitative analysis, computational tool for rapid process design

(freezing, freeze thawing, freeze concentration, freeze drying of biologics, issues about stability …)

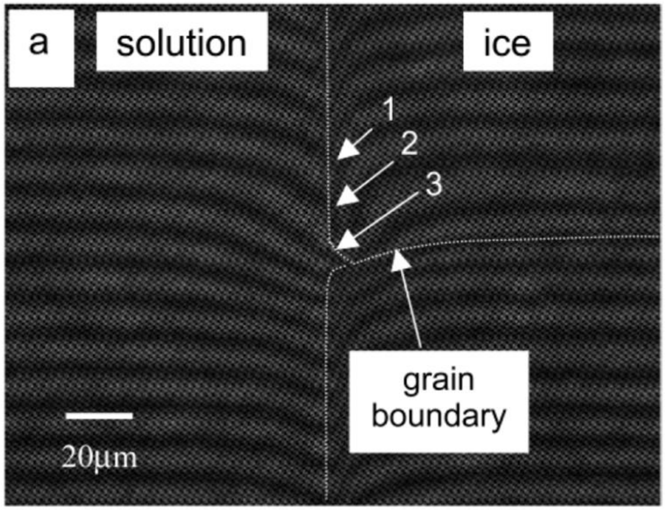
Typical cooling and freezing curve



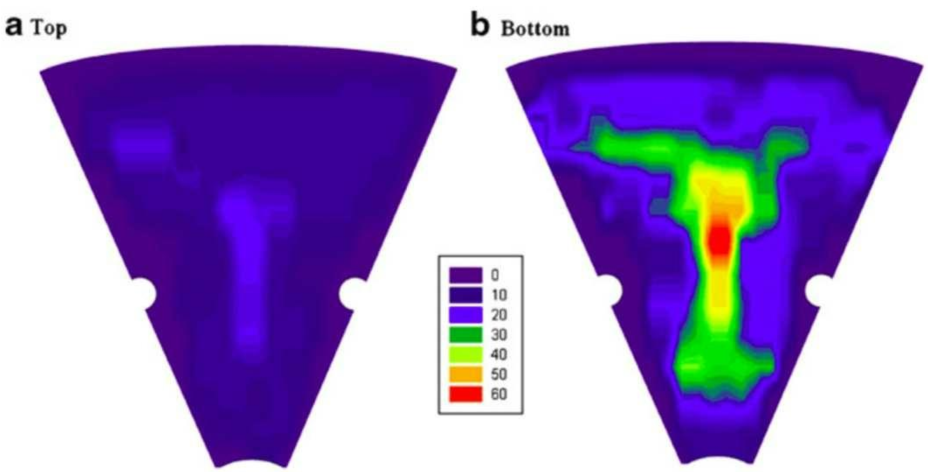
Slow vs fast, large- vs small-scale phenomena



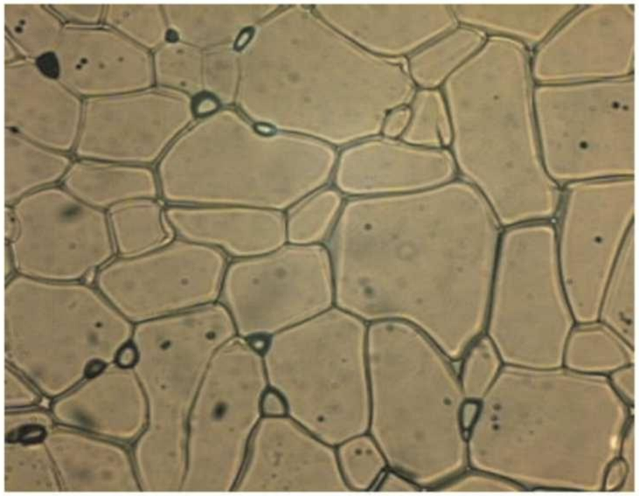
M.A. Rodrigues et al., *J. Pharm. Sci.*, 2011



M.F. Butler, *Cryst. Growth Des.*, 2002

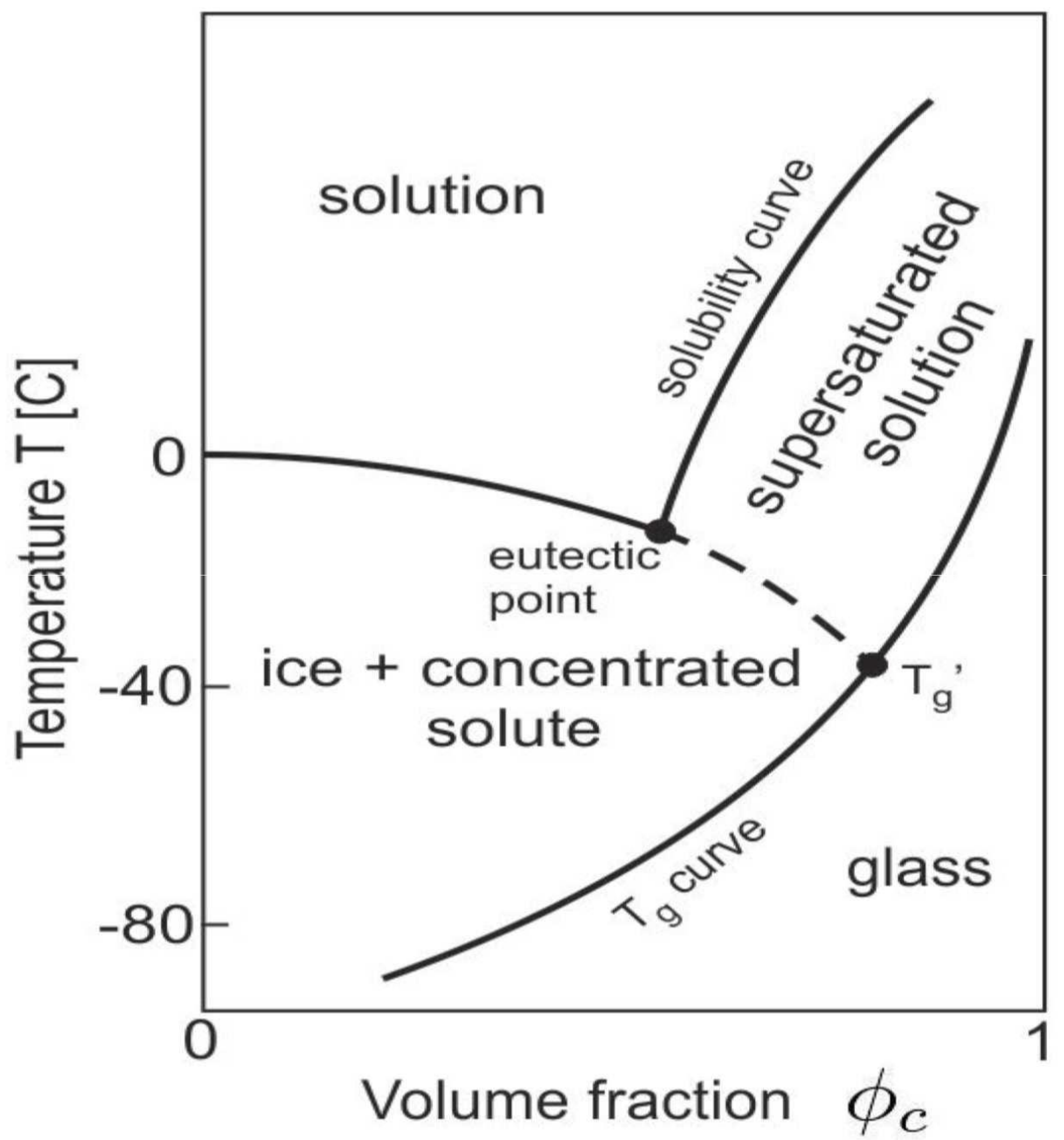


S.K. Singh et al., *Pharm. Res.*, 2011



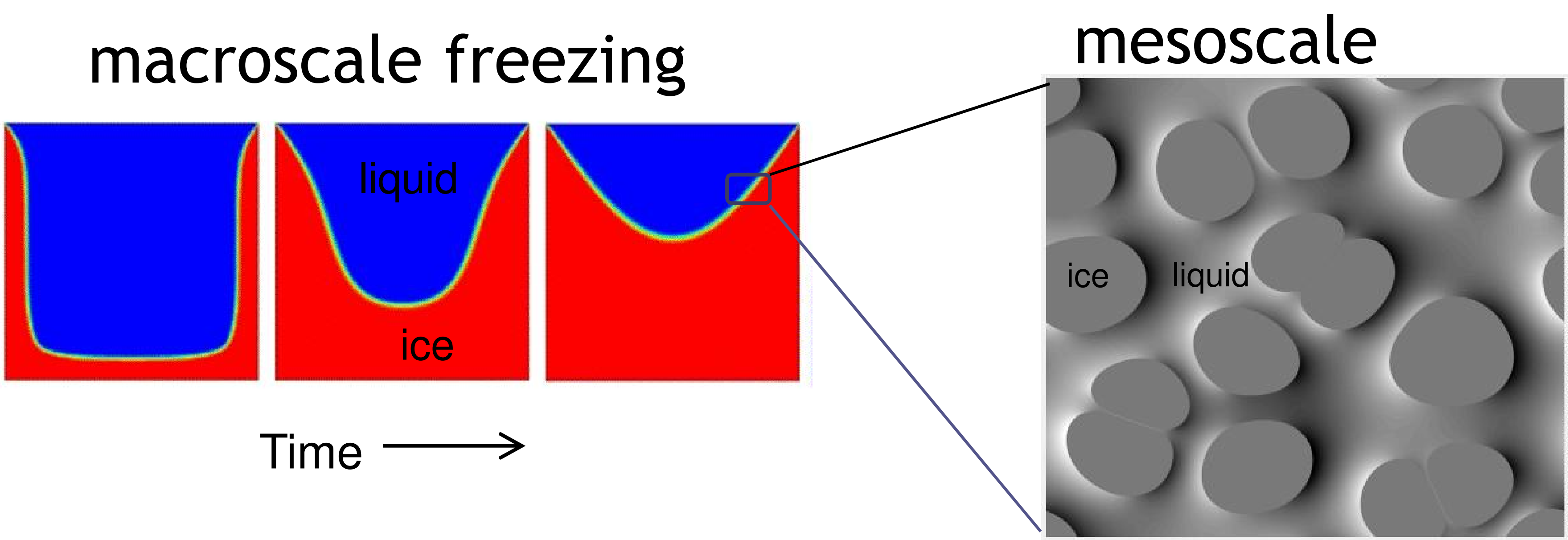
J.J. Schwegman, et al., *J. Pharm. Sci.*, 2009

Phase diagram (e.g. water + sucrose + …)



Fully coupled transport phenomena

- Multiscale, multiphase flow, T-dep local properties
- Heat transfer (conduction + convection + radiation?)
- Multi-component mass transfer, thermodynamics
- Phase transition, freeze concentration dynamics

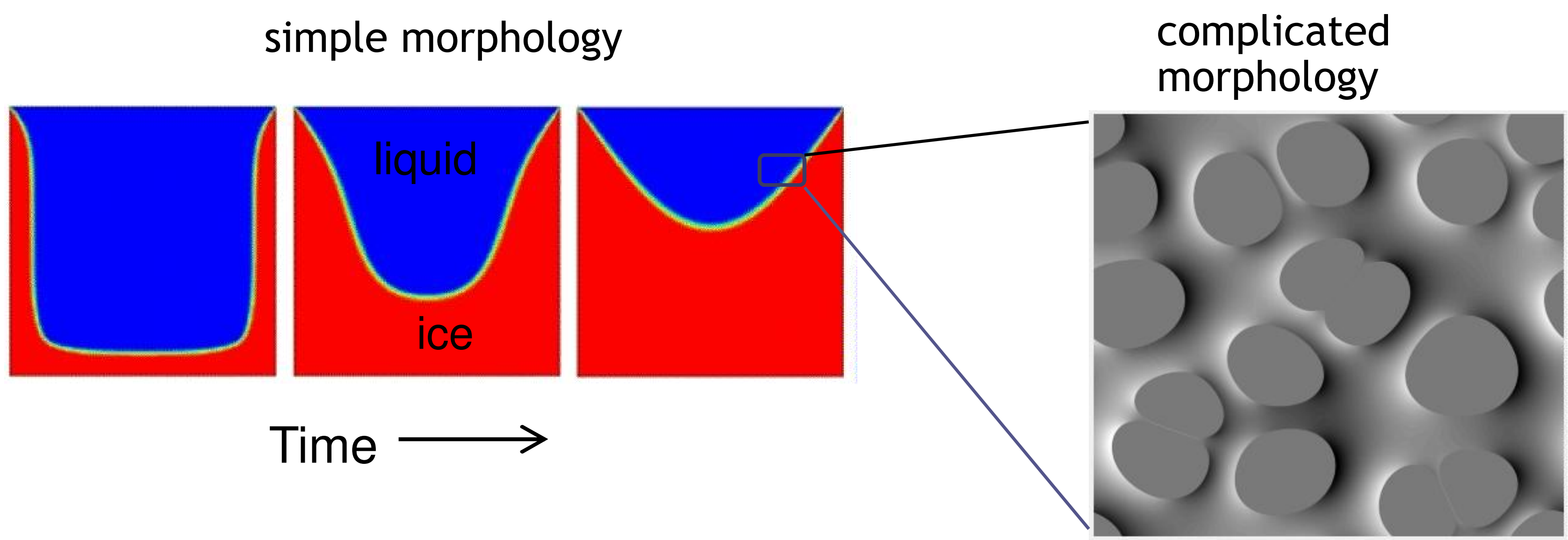


How to deal with moving boundary problem ?

(i) *Lagrangian* or *Eulerian* description ?

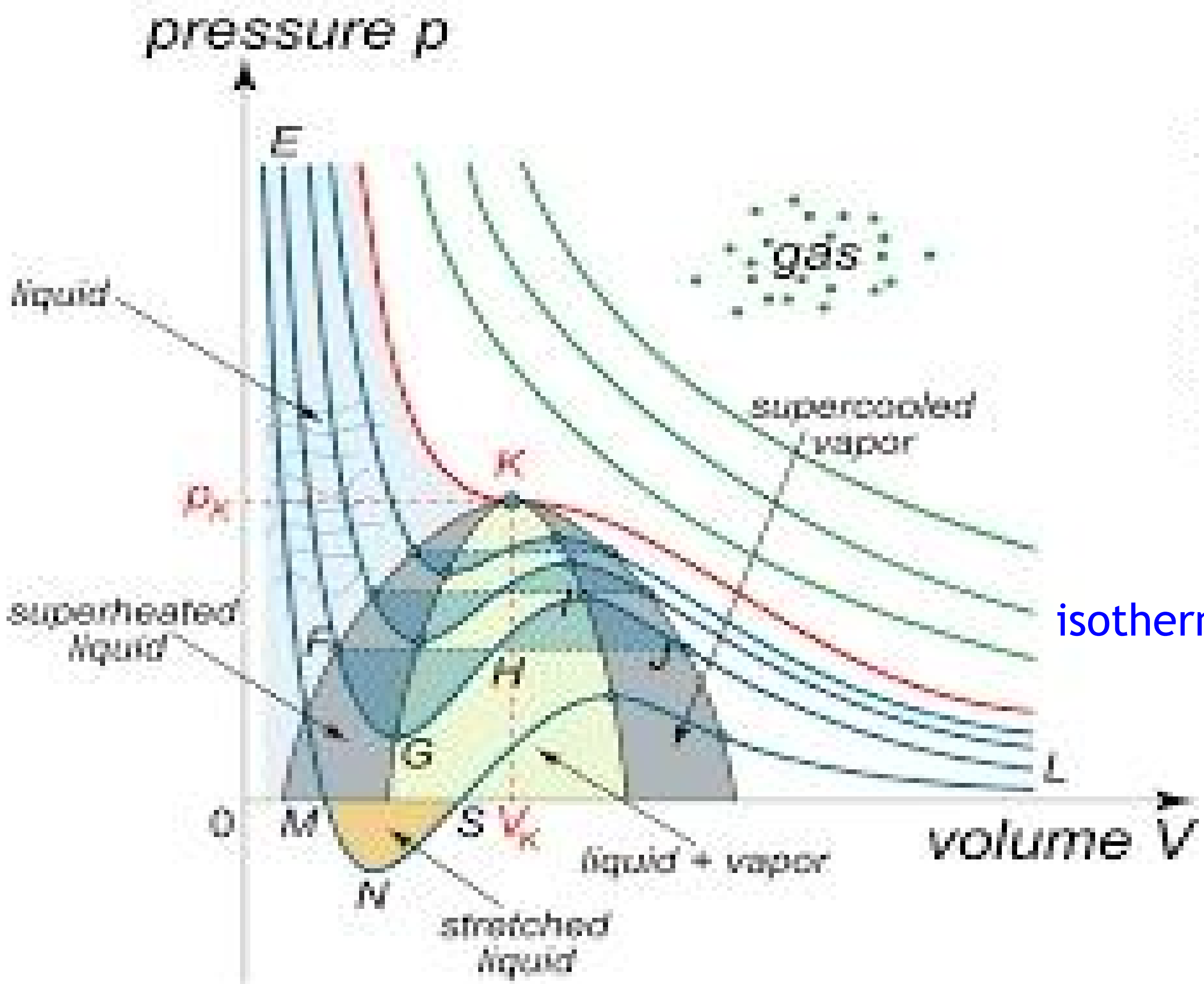
(ii) Sharp or smooth but thin interface ?

(iii) Interfacial thickness/mobility/energy/kinetics ?



Phase field approach

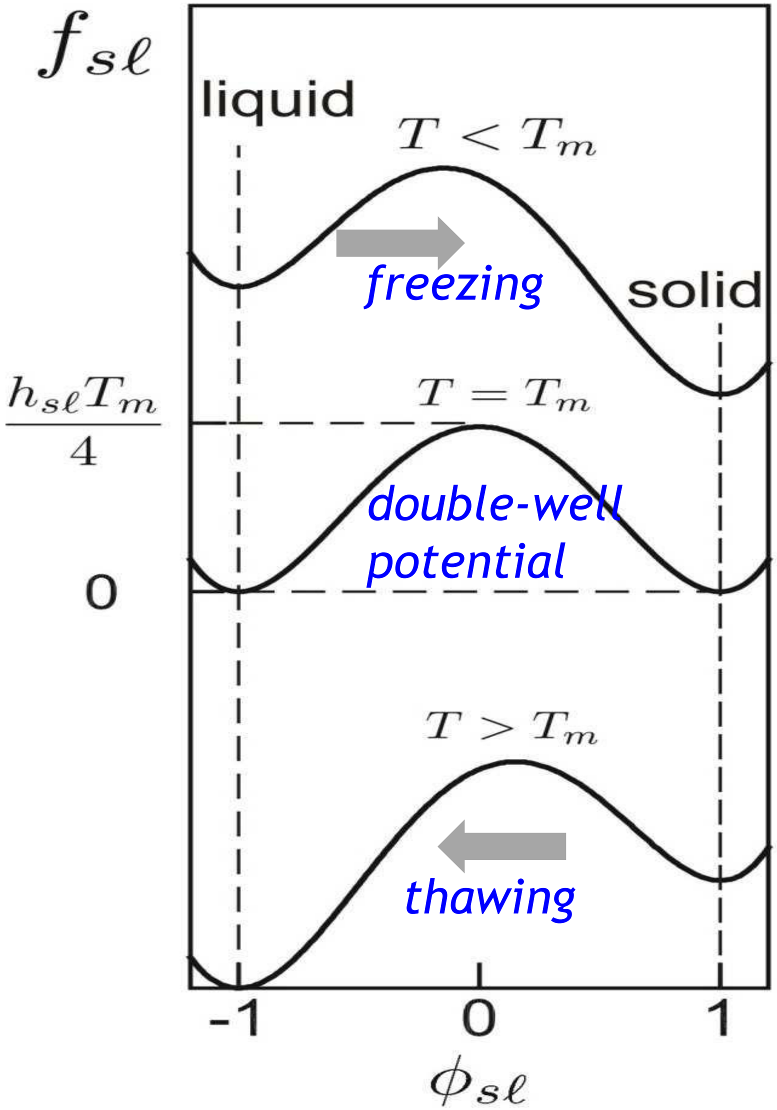
Idea from van der Waals equation of state (smooth phase transition)

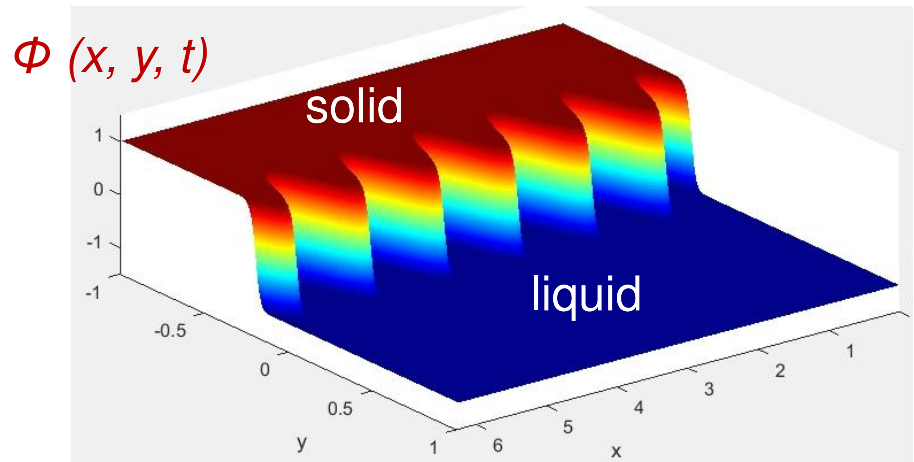


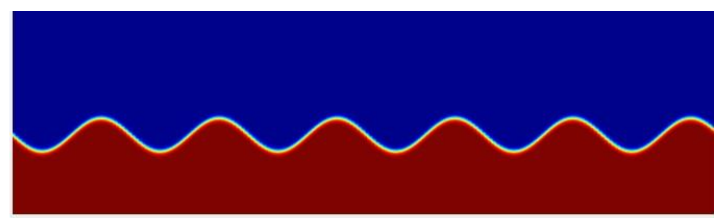
isotherms

source: math24.net

Connection of phase-field variable *Φ* with free energy *f*







Evolving dynamics of a non-equilibrium system

(Landau-Ginzburg, Allen-Cahn, Cahn-Hilliard, Models A/B/C/H, Penrose-Fife, …)

(i) Minimize the free energy functional

$$\mathcal{F} = \int_\Omega \left[\rho f(e, \phi, \rho) + \frac{1}{2} \xi_{\mathcal{F}}^2 |\nabla \phi|^2 \right] dV$$

local f.e. of bulk phases

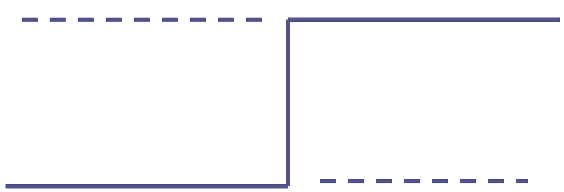
nonlocal, gradient energy

system evolves as

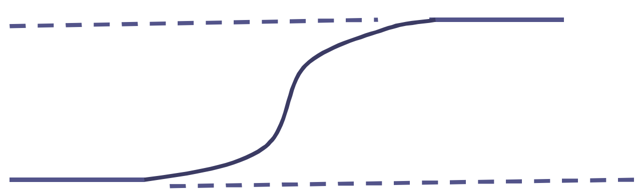
$$\frac{\partial \phi}{\partial t} \propto \frac{\delta \mathcal{F}}{\delta \phi}$$

functional derivative

separated phases



diffuse interface



(ii) Maximize the entropy functional

$$\mathcal{S} = \int_\Omega \left[\rho s(e, \phi, \rho) - \frac{1}{2}\xi_s^2 |\nabla \phi|^2 \right] dV$$

bulk phases — gradient effect

system evolves as

$$\frac{\partial \phi}{\partial t} \propto -T \frac{\delta \mathcal{S}}{\delta \phi}$$

quadratic term in the functional is often associated with net flux of something

Further connections with conservation laws, thermodynamics laws …

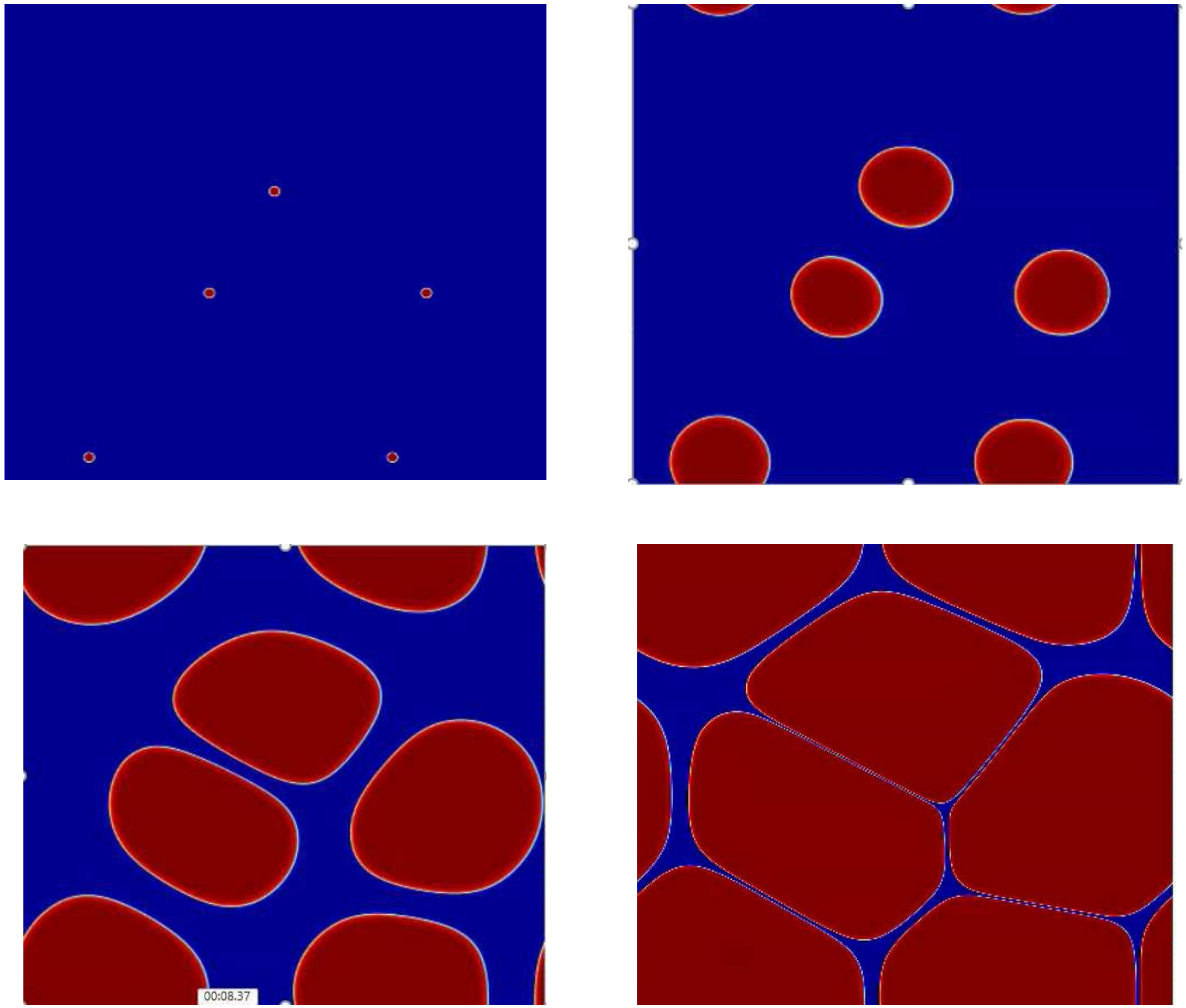
Advantages and challenges

- Phase field defines local state (order parameter) of the material, distinguishes material interface, interacts with other fields (ρ, v, p, T, u, c_i, θ …).
- Insights into non-equilibrium thermodynamics, good at describing microstructure evolution, dendrite and grain growth problems, including thermal fluctuation and nucleation.
- *Challenge*: Integration of material sciences with thermal fluid sciences, multi-phase transition, thermo-viscoelastic-plastic or fracture mechanics.
- *Challenge*: maintaining thermodynamic consistency, expensive 3d computation, high resolution for interfacial kinetics and dynamics ...

Result: growth of ice crystals (ice nuclei in sucrose solution)

time scale ~ 1 s
domain size ~ 60 x 60 µm
supercooled at -10 ºC

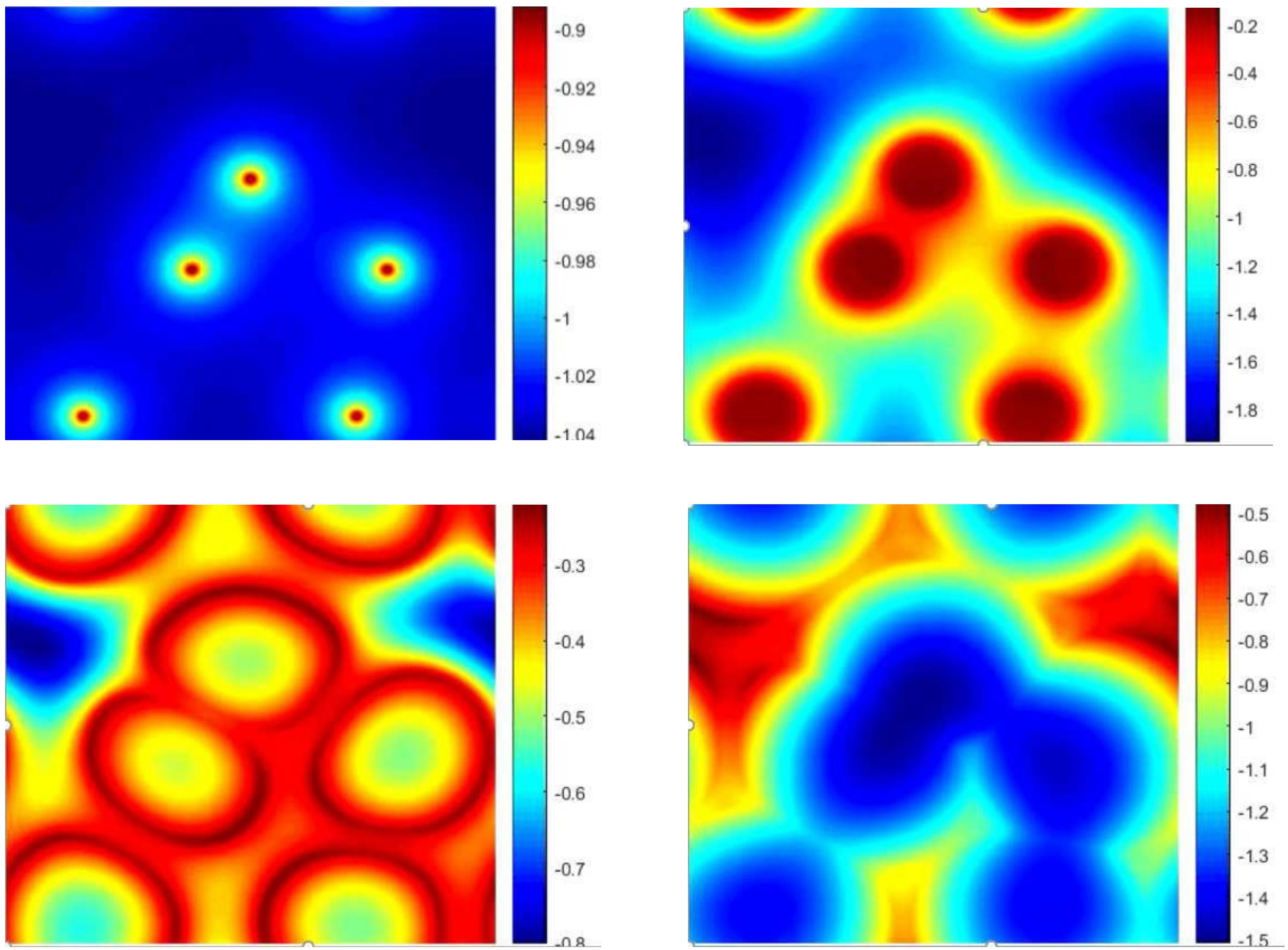
$\phi_{s\ell}$



Result: temperature

time scale ~ 1 s, temperature scale 10 ºC
domain size ~ 60 x 60 µm
initially supercooled at -10 ºC

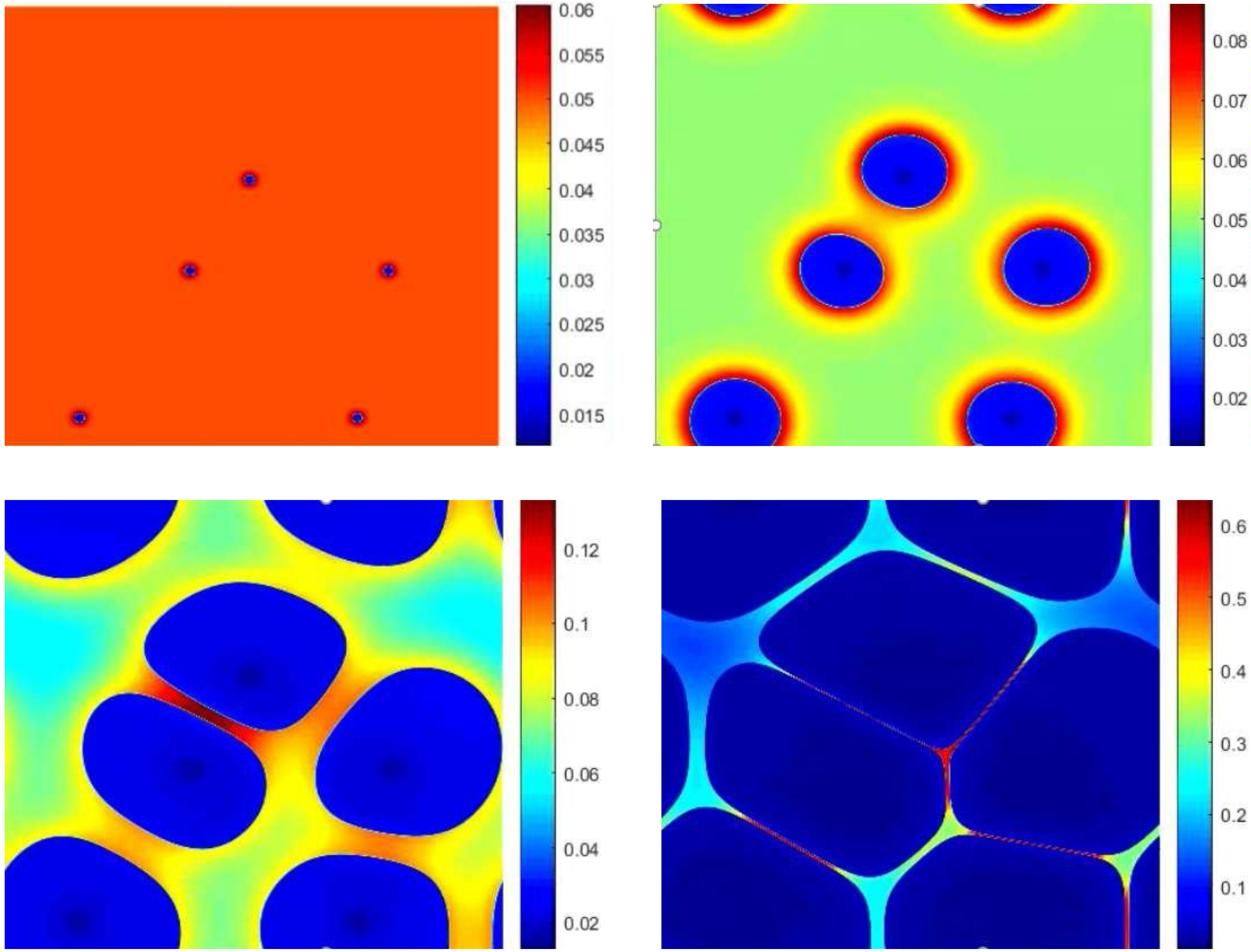
T



Result: solute concentration

Initial volume fraction
~ 0.05 in liquid solution, 0 in ice

ϕ_c



More details on thermodynamic consistency

Entropy functional

need two phase fields

$$\mathcal{S} = \int_\Omega \left[\rho s(e, \phi_{s\ell}, \phi_c) - \frac{1}{2}\xi_{s\ell}^2 |\nabla \phi_{s\ell}|^2 - \frac{1}{2}\xi_c^2 |\nabla \phi_c|^2 \right] dV;$$

bulk phase — non-local or gradient effect

Reynolds transport theorem + entropy balance

Entropy transport eq.

$$\rho \frac{\mathrm{D}s}{\mathrm{D}t} - \frac{1}{2}\xi_{s\ell}^2 \frac{\mathrm{D}}{\mathrm{D}t}|\nabla \phi_{s\ell}|^2 - \frac{1}{2}\xi_c^2 \frac{\mathrm{D}}{\mathrm{D}t}|\nabla \phi_c|^2 = -\nabla \cdot \mathbf{J}_\mathrm{s} + \dot{\Gamma} - \frac{\dot{\Omega}}{T}$$

entropy production

Gibbs eq.

$$\frac{\mathrm{D}s}{\mathrm{D}t} = \frac{1}{T}\frac{\mathrm{D}e}{\mathrm{D}t} - \frac{1}{T}\frac{\partial e}{\partial \phi_{s\ell}}\frac{\mathrm{D}\phi_{s\ell}}{\mathrm{D}t} - \frac{1}{T}\frac{\partial e}{\partial \phi_g}\frac{\mathrm{D}\phi_g}{\mathrm{D}t}$$

2nd law of thermodynamics, positive entropy production

heat conduction — phase transition

$$\dot{\Gamma} = \dot{\boldsymbol{q}} \cdot \nabla \left(\frac{1}{T} \right) + \left[\xi_{s\ell}^2 \nabla^2 \phi_{s\ell} - \frac{\rho}{T} \frac{\partial e}{\partial \phi_{s\ell}} \right] \frac{D\phi_{s\ell}}{Dt}$$

$$+ \left[\xi_c^2 \nabla^2 \phi_c - \frac{\rho}{T} \frac{\partial e}{\partial \phi_c} \right] \frac{D\phi_c}{Dt} \geq 0$$

solute redistribution

Allen-Cahn

$$\frac{D\phi_{s\ell}}{Dt} = M_{s\ell} \left[\xi_{s\ell}^2 \nabla^2 \phi_{s\ell} - \frac{\rho}{T} \frac{\partial e}{\partial \phi_{s\ell}} \right]$$

interface evolving dynamics — interfacial mobility

Cahn-Hilliard

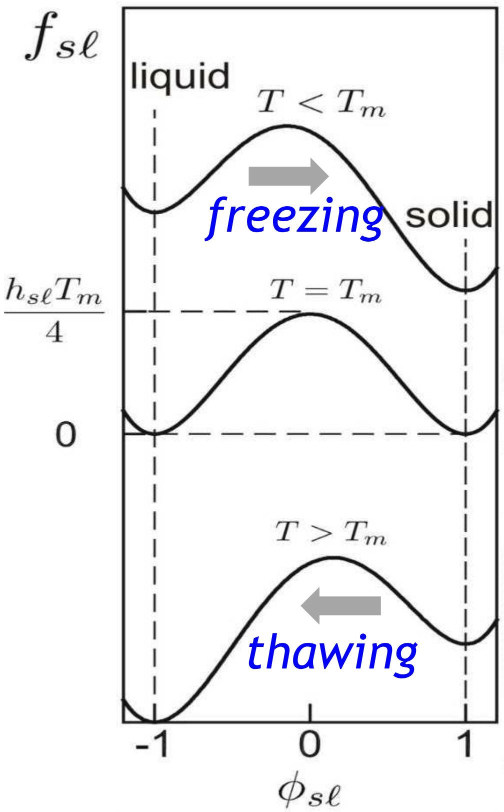
$$\frac{D\phi_c}{Dt} = -\nabla \cdot \boldsymbol{J}_{\phi_c} = -\nabla \cdot \left[M_c(\phi_{s\ell}, \phi_c) \nabla \frac{\delta \mathcal{S}}{\delta \phi_c} \right]$$

$$M_c = \frac{D(\phi_c, \phi_{s\ell}, T)}{\rho R} \phi_c (1 - \phi_c)$$

Free energy including Flory-Huggins regular solution model

$$f(T,\phi_{s\ell},\phi_c) = (1-\phi_c) f_{s\ell} + \phi_c f_c + RT\left[\frac{1}{N}\phi_c \ln(\phi_c) + (1-\phi_c)\ln(1-\phi_c) + \chi(\phi_{s\ell})G(\phi_c)\right]$$

Flory's parameter, partition effect $\chi_s > \chi_\ell$



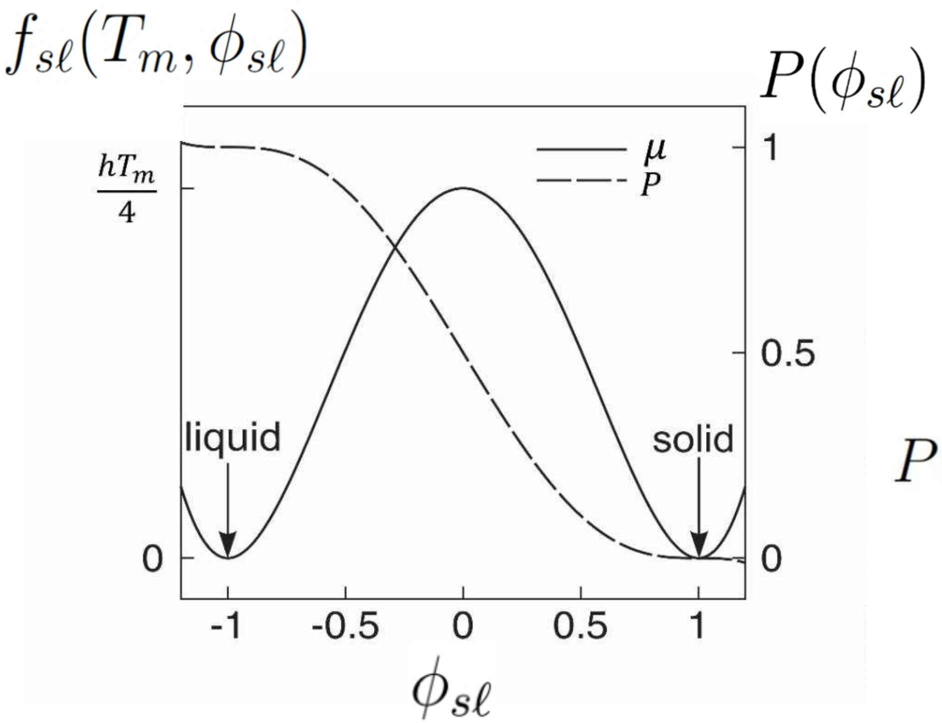
driving force for freezing/melting

$$f_{s\ell}(T,\phi_{s\ell}) = -T\int_{T_{eq}}^{T} \frac{e_{s\ell}}{T'^2} dT' + \frac{T f_{s\ell}(T_{eq},\phi_{s\ell})}{T_{eq}}$$

$$\frac{1}{4} h_{s\ell} T_m (1-\phi_{s\ell}^2)^2.$$

Internal energy and latent heat

$$e(T,\phi_{s\ell},\phi_c) = \underbrace{e_{s\ell}(T,\phi_{s\ell})}_{\text{phase change}} + \underbrace{RT\chi(\phi_{s\ell})\,4\phi_c^2(1-\phi_c)^2}_{\text{mixing}}$$



$$e_s(T) + P(\phi_{s\ell})L_a$$

$$P(\phi_{s\ell}) = \frac{1}{2} - \frac{15}{16}\left(\frac{1}{5}\phi_{s\ell}^5 - \frac{2}{3}\phi_{s\ell}^3 + \phi_{s\ell}\right)$$

(Wang et al., 1993)

smooth transition of internal energy between solid and liquid phases

Thermophysical properties

P-function for interpolation of thermophysical properties: *density, specific heat, thermal conductivity, dynamic viscosity, diffusivity, and Flory's interaction parameter …*

e.g., *thermal conductivity* and *viscosity* in supercooled regime:

$$k_T(T, \phi_{s\ell}, \phi_c) \simeq k_{T0}\left[P(\phi_{s\ell})\widetilde{k_{T\ell}}(T, \phi_c) + (1-P)\widetilde{k_{Ts}}(T)\right]$$

$$\eta_\ell(T, \phi_c) \simeq \underbrace{4.442 \times 10^{-5} \exp\left(\frac{2.288 \times 168.9}{T - 168.9}\right)}_{\text{Vogel-Fulcher-Tamman}} \underbrace{\exp\left(\frac{6.3\phi_c}{1 - 0.85\phi_c}\right)}_{\text{Mooney}}$$

Temperature field

$$\rho c_p \frac{\mathrm{D}T}{\mathrm{D}t} = \nabla \cdot \left(k_T \nabla T \right) - \rho \left[L_a P' + RT\chi' G \right] \frac{\mathrm{D}\phi_{s\ell}}{\mathrm{D}t} - \rho RT \chi G' \frac{\mathrm{D}\phi_c}{\mathrm{D}t} - \dot{\Omega}$$

coupling with phase transition and mixing energy

simplified cooling

Fluid motion (buoyant effect & density variation, capillarity, osmosis, viscoelastic stress …)

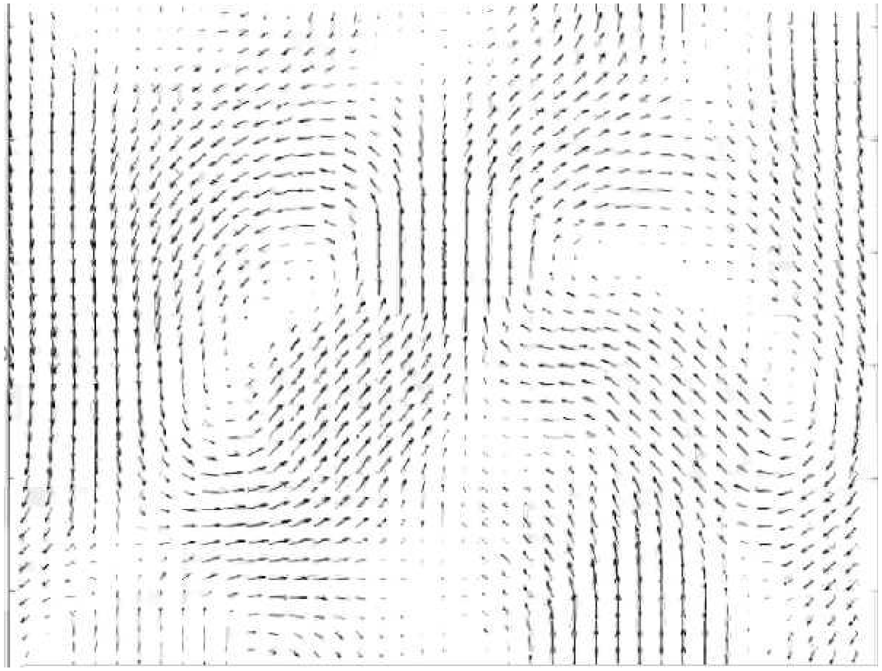
Scaling …

Fan, T.-H., Li, J.-Q., Minatovicz, B., Soha, E., Sun, L., Patel, S., Chaudhuri, B., Bogner, R., Phase-Field Modeling of Freeze Concentration of Protein Solutions, *Polymers* **11**, 10, 2019.

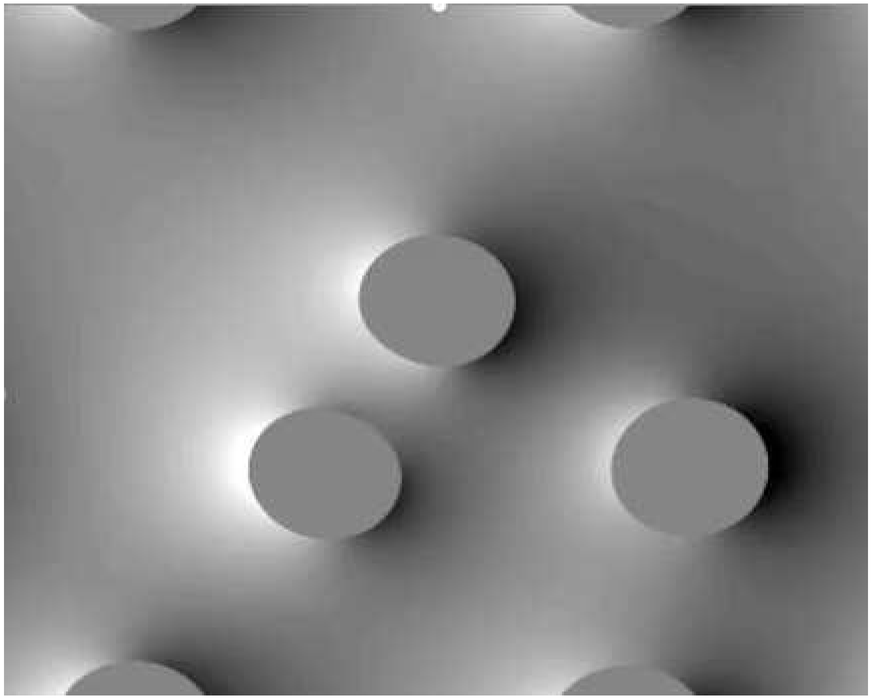
Li, J.-Q., Fan, T.-H., Phase-Field Modeling of Metallic Powder-Substrate Interaction in Laser Melting Process, *Int. J. Heat Mass Transfer* ***133***, 872-884, 2019.

Results:

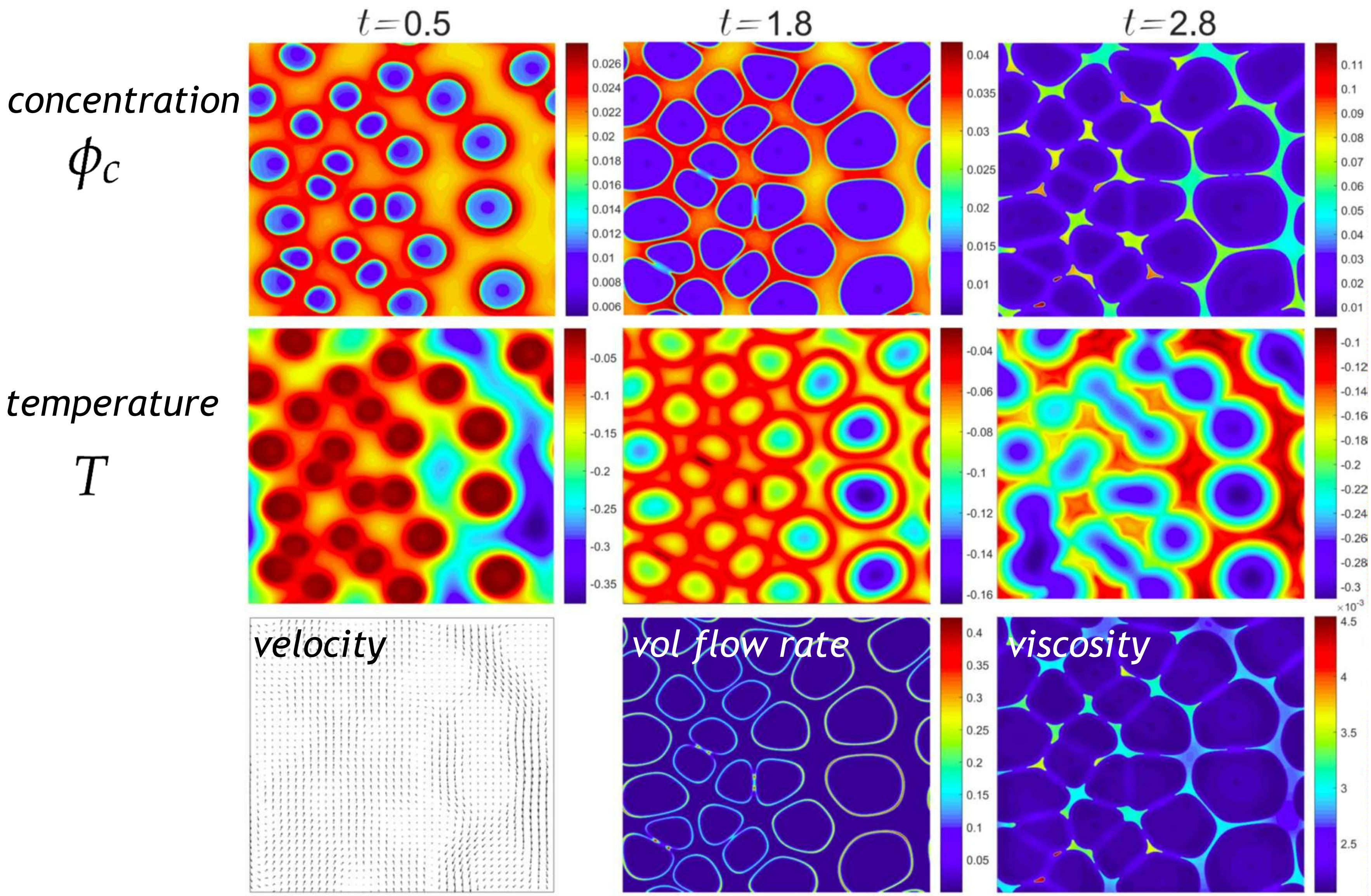
velocity



vorticity



Collective crystal motion, sintering, and freeze concentration



Summary of phase-field model

- Allen-Cahn eq. for solid-liquid interfacial evolution
- Cahn-Hilliard eq. to determine concentration field
- Fully coupled energy eq. for temperature distribution
- Navier-Stokes-Korteweg and continuity eqs. for fluid motion

Computation

Pseudo spectral method, variable coefficients, periodic domain, velocity pressure splitting and projection, 2d uniform mesh 1600x1600, scaled time step 2×10^{-4}, with given nucleation sites, onset of freezing, and uniform cooling rate.

Perspectives

- Phase field method is promising in modeling multiphase, multiphysics pharmaceutical processes.
- Growth dynamics of ice crystals and transient evolution of freeze concentration effect can be better understood, simulated, and possibly better predicted.
- *Potential topics:* multiscale computation to resolve macro- and meso-scale freezing dynamics, protein stability and kinetics near interface, nucleation and uncertainty quantification, prediction of structure-property-process efficiency, **validations** …

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