Phase interface in multicomponent mixtures at porescale. What matters at macro (Darcy) scale?

Malgorzata Peszyńska [1]
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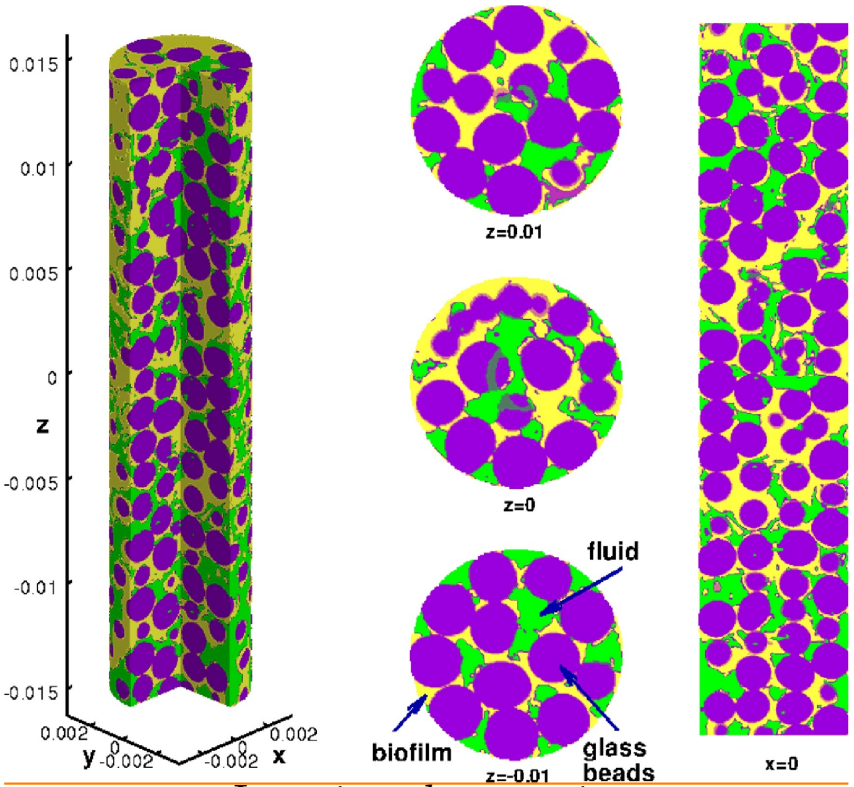
Obstructions at Pore Scale from Imaging

Biofilm growth in glass beads.

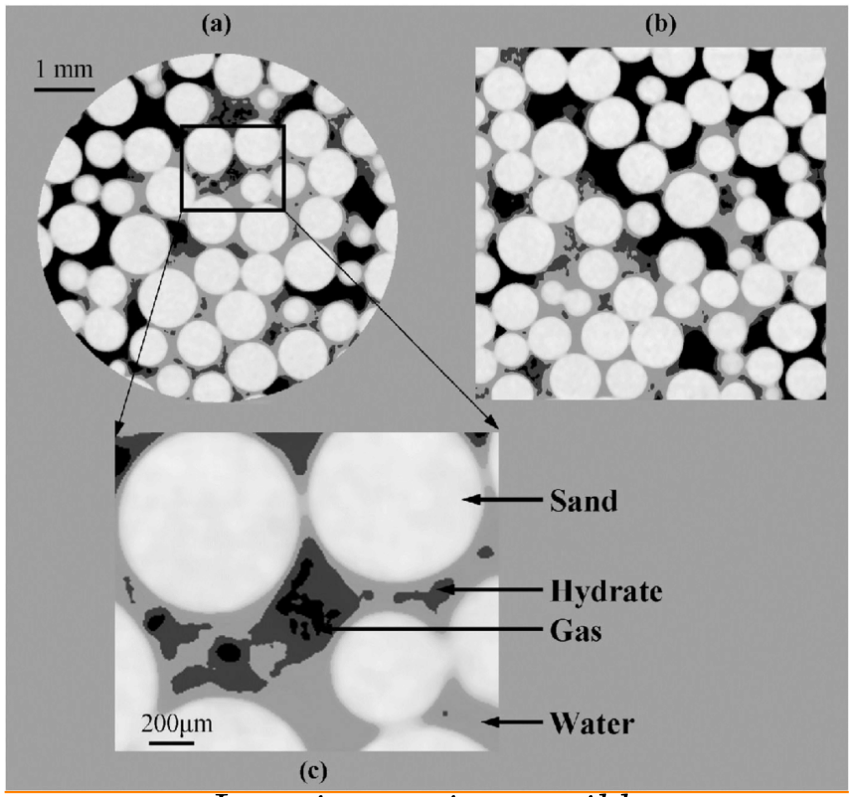
[P-TrykozkoIltisSchlueterWildenschild'2016]



Imaging destructive

Gas hydrate in silica sands.

[ZhangYangLiuSongYong'2015]

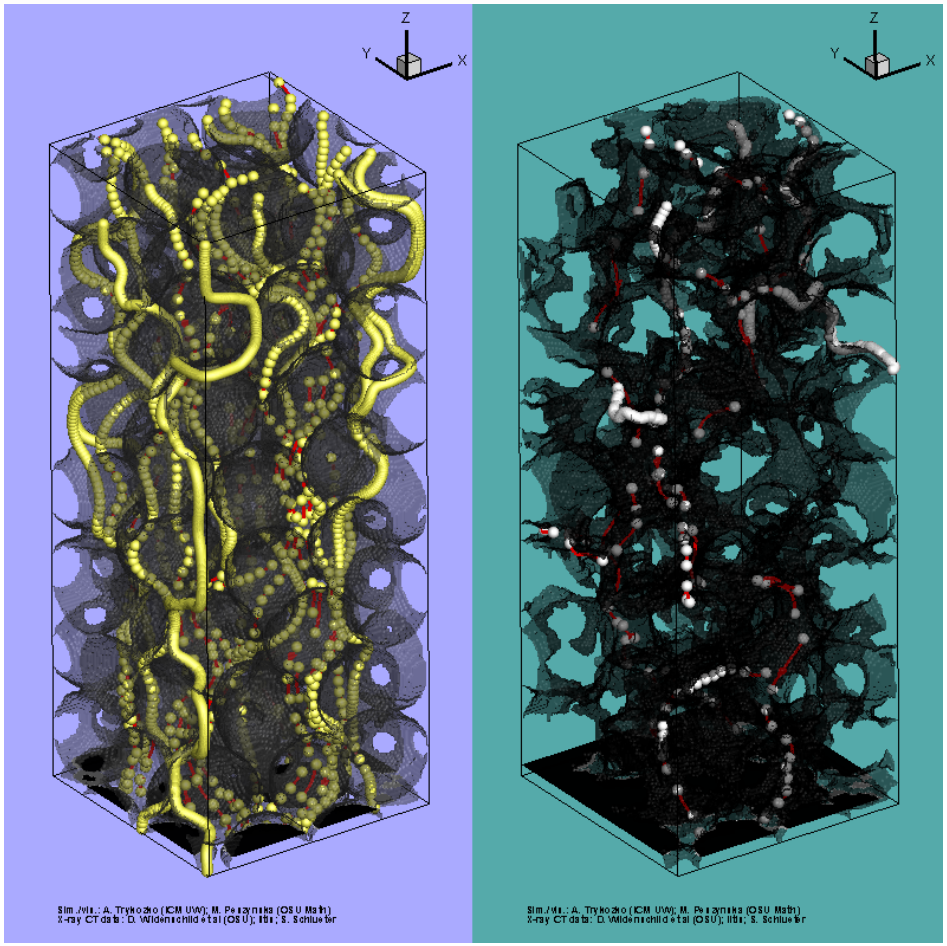


Imaging ≈ impossible

Goal: determine permeability $K = K(B)$ or $K = K(S_h)$

Stokes $\boxed{-\mu\Delta_y u = -\nabla_y p} \Longrightarrow$ Darcy's law $\boxed{-\mu U = -K\nabla_x P}$

Porescale modeling: reality check



[PTrykozkoIltisSchlueterWildenschild'16]

Movie

Micro-CT image and (FV) flow simulation

	# cells
Voxel grid	> 100M
REV voxel grid	$\approx$ 1K-10M
Flow grid on D_f (N-Stokes) in 3D:	O(10M)
Grid for DNS of coupled transport which causes interface evolution: (phase transition or reactions)	$O(10M \times \frac{T}{\Delta t})$

In practice, we are restricted to voxel grids.

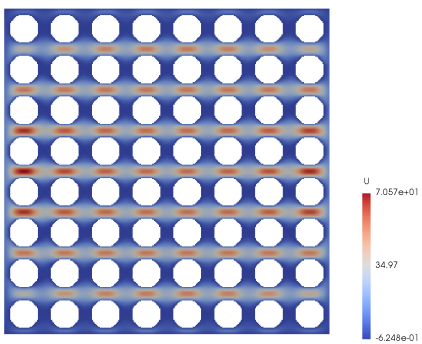
Fluid domain $D_f(t)$; Obstructions $D_o(t)$.

Impact of obstructions D_o in $D_f(x)$ on $K(x)$

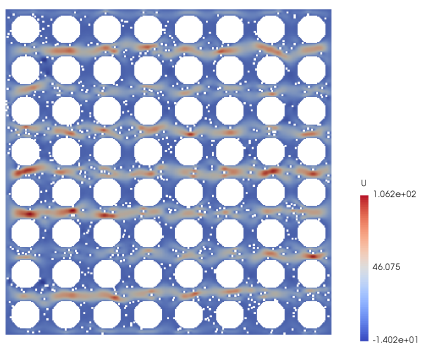
Numerical homogenization of Stokes flow $(u(y), p(y)), y \in D_f(x)$ **gives permeability** $K(\mathbf{x})$**:** $\mu\langle u\rangle = -K\nabla\langle p\rangle$

[Tartar'80-]; [PTrykozko et al'08,'11,'13,'17-]; [CostaKennedyP'18]

How does flow depend on D_o ?



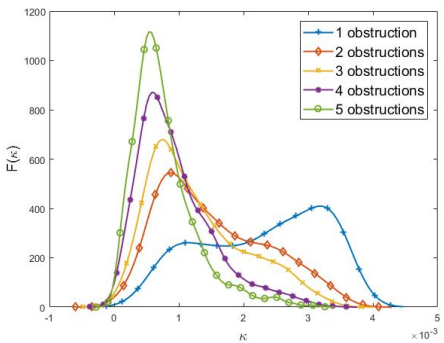
$|D_o| = 0$

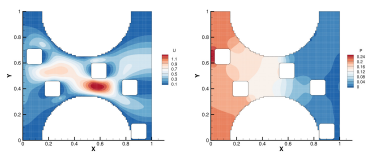


$|D_0| > 0$

Simulation of the interface $\Gamma = \partial D_o \cap \partial D_f$ depends on many unknown quantities: e.g., initial conditions.

How does K depend on D_o ?





Single-pore solution

Idea: reduce the model; use stochastic parametrization

Interface Γ stochastic? $D_f = D_f(\omega; x) \Rightarrow K(x) = K(\omega; x)$, $\omega \in \Omega$.

Stokes solver at (stochastic) porescale with partially permeable obstructions

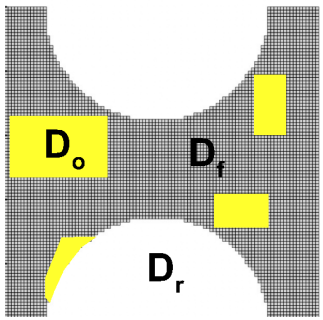
HybGe-Flow3D avoids remeshing of $D_{f,o} = D_f \cup D_o$
[Costa'2016 PhD Thesis; CostaKennedyP'18CompGeo]]

- FV formulation [Patankar'80, EymardGallouetHerbin'00, Versteeg'07]
- (Multi-colored ILU=Power(q) enhanced ILU(p) preconditioner); Paralution.

Stochastic immersed boundary

$$\begin{aligned} -\mu\nabla^2 u_\eta + \frac{1}{\eta} 1_{D_o} u_\eta + \nabla p_\eta &= f, \quad \text{in } D_{f,o}, \\ \nabla \cdot u_\eta &= 0, \quad \text{in } D_{f,o}. \end{aligned}$$

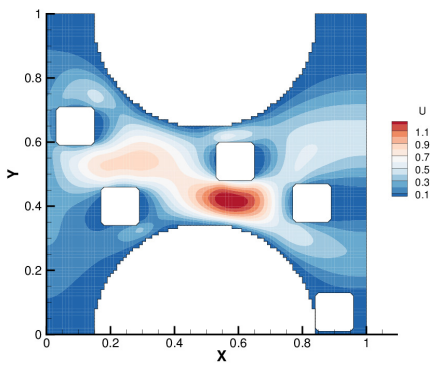
$u_\eta = 0$, on Γ_{wall}, and other b.c.



Motivated by [Canuto'07; Peskin'02; Mittal'05].

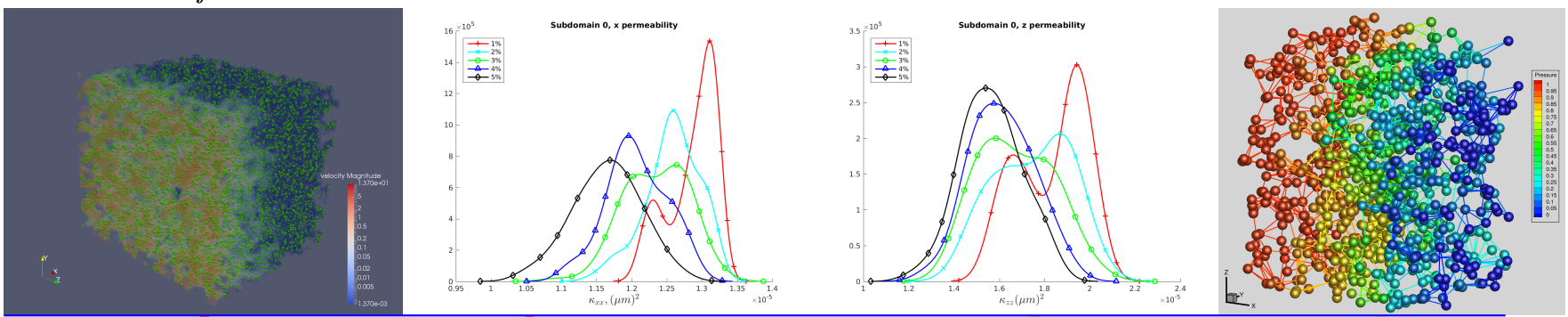
Independently, [Angot'99, AngotBruneauFabrie'99]
This formulation "avoids" the BJS interface condition.

Obtain $\| u_\eta \|_{L^2(D_o)} = O(\sqrt{\frac{\eta}{\mu}})$ **(Today** $\eta \approx 0$**.)**



Work in realistic geometries with $D_f(\omega)$ (pore-network as an intermediate scale)

sandstone $D_f(\omega)$ $K(\omega)$ *sandstone pore-network* $\mathcal{D}(\omega)$



Geometry [Lindquist et al]. Flow and upscaling [CostaKennedyP'18]

Success: can obtain experimental pdf of $K(\omega)$ off-line.

Challenge: calibrate the pdf of $D_f(\omega), \omega \in \Omega$ to restrict sampling to realistic geometries for the process

- Use imaging data? ($!!!), sometimes impossible
- Use DNS of the underlying process? (`computing time` !!!)

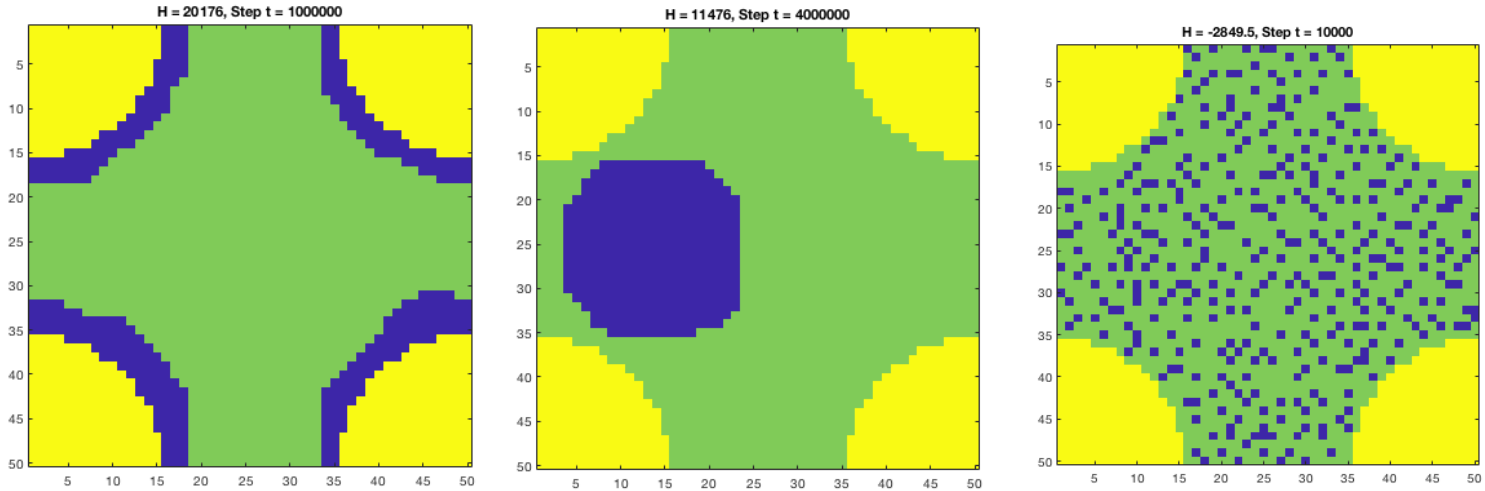
DNS=*Direct Numerical Simulations*

Construct realistic $D_o(\omega), \omega \in \Omega$ with DNS

Idea: construct $\omega \in \Omega$ guided by the images/DNS;

[PUmhoefer, in progress; data science tools]

Which of the geometries below is "correct" for a given process ?



biofilm growth hydrate growth colloids

- In MCMC: a lattice-based Hamiltonian accounts for fluid-wall interactions and fluid-fluid interactions.

  Hamiltonian calibrated with training data (CT images or DNS).

- In DNS: choose PF (phase-field) model and account for fluid-solid interactions, multiple phases & components in fluid

PF for single component phase transition

Liquid (water)- solid (ice) phase transition: Stefan problem

Temperature $T(x,t)$ and order parameter $\phi(x,t)$, $x \in \Omega, t > 0$ satisfy

Energy equation: $\partial_t(T + L\phi) - \nabla^2 T = 0$

Temperature-phase rule: $\frac{\partial \phi}{\partial t} + \partial_\phi \mathcal{F}(\phi) = 0$

Micro-scale (interface) $O(\mathrm{nm})$

$\frac{\partial \phi}{\partial t} + \partial_\phi \mathcal{F}_{\epsilon,a}(\phi) = 0$

Nonconvex $\mathcal{F}_{\epsilon,a}(\phi)$

$\mathcal{F}_{\epsilon,a}(\phi) = \int_\Omega \frac{a\epsilon}{2}|\nabla\phi|^2 + \frac{1}{\epsilon} f(\phi) - LT\phi$

$\phi \in H^1(\Omega)$

f nonconvex

f smooth or non-smooth

Macro-scale $O(\mathrm{m})$

$\frac{\partial \phi}{\partial t} + \partial_\phi \mathcal{F}(\phi) \ni 0$

Convex $\mathcal{F}(\phi)$

$\mathcal{F}(\phi) = I_{[-1,1]}(\phi) - \int_\Omega LT\phi$

$\phi \in L^\infty$

In equilibrium, $\phi \in sign(T)$, non-smooth

Γ-convergence [Visintin'96, Models of Phase Transitions]

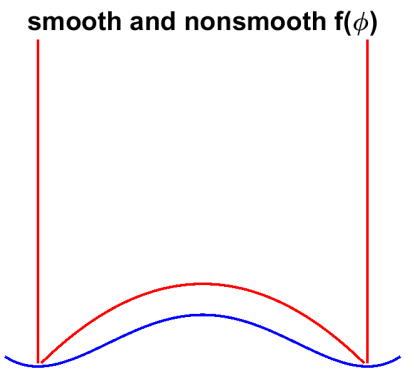
When f smooth, $\mathcal{F}_{\epsilon,a} \underbrace{\to}_{\epsilon \to 0} \mathcal{F}_a \underbrace{\to}_{a \to 0} \mathcal{F}$

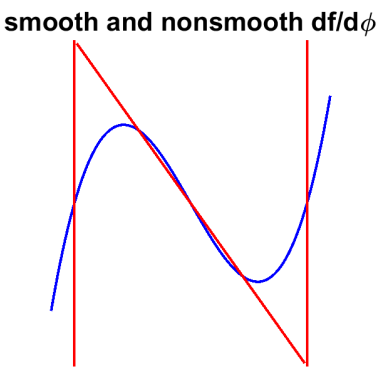
PF for single component phase transition
Regularity at micro-scale: (non-)smooth f

Liquid (water)- solid (ice) phase transition: Stefan model

Energy equation:	$\partial_t(T + L\phi) - \nabla^2 T = 0$
Temperature-phase rule:	$\frac{\partial \phi}{\partial t} + \partial_\phi \mathcal{F}_{\epsilon,a}(\phi) = 0$
Non-convex $\mathcal{F}_{\epsilon,a}(\phi)$	$\mathcal{F}_{\epsilon,a}(\phi) = \int_\Omega \frac{a\epsilon}{2}\lvert\nabla\phi\rvert^2 + \frac{1}{\epsilon} f(\phi) - LT\phi$

f non-convex, smooth	"double-well potential" $f(\phi) = (1-\phi^2)^2$
f non-convex, non-smooth	$f(\phi) = I_{[-1,1]}(\phi) + 1 - \phi^2$





Computations and analysis difficult for smooth f.

Require

$h = O(\epsilon^k), \tau = O(\epsilon^m)$

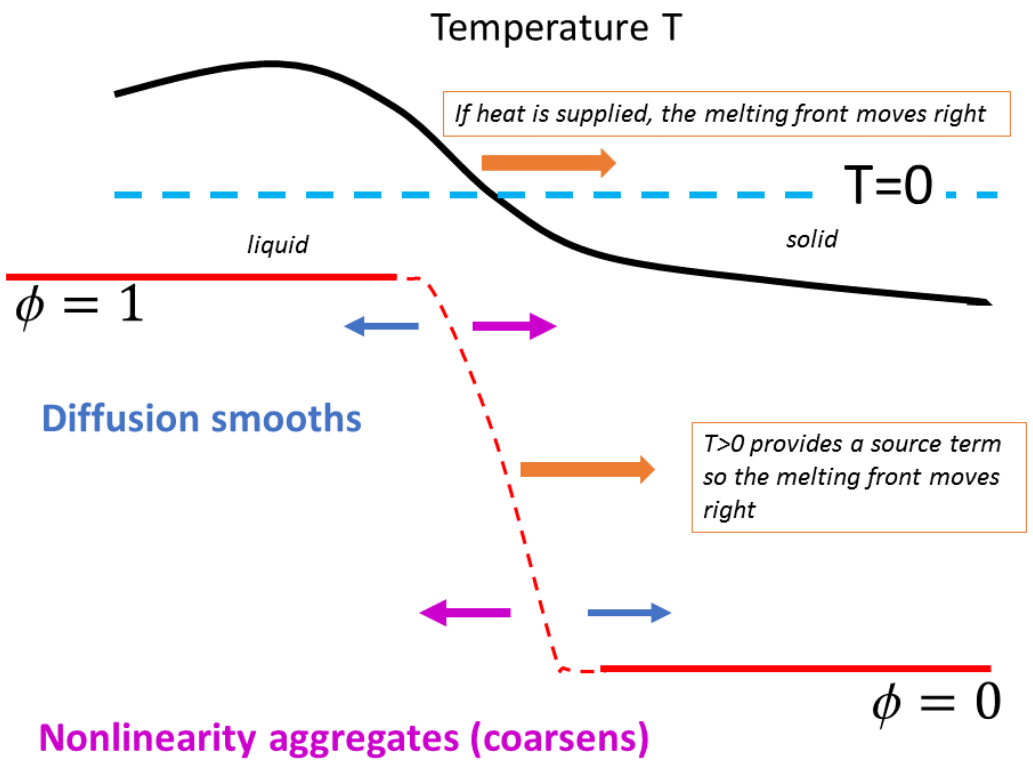
Evolution of ϕ in PFT is a competition

Variables: temperature T, phase/ order parameter ϕ.

$$\partial_t(T + L\phi) - \nabla^2 T = 0$$

$$\partial_t \phi - \epsilon \nabla^2 \phi + \frac{1}{\epsilon} \varpi(\phi) = LT$$

ε is the width of interface; $\varpi = \frac{df(\phi,T)}{d\phi}$; f is the energy density



PFT: Smooth vs non-smooth f: Regularity and numerics

Some known results for $\dot{\phi} + \partial_\phi \mathcal{F} \ni 0$

Allen-Cahn or Ginzburg-Landau models

Smooth f

[ShenYang'2010, Feng et al'*, ZhangDu'10]

$\phi \in H^1(H^m \cap L^4) \cap H^2(H^1) \cap H^3(H^{-1})$

Semi-implicit schemes, stabilization (e.g., Eyre splitting)

FE & spectral methods

$E = O(\exp(\epsilon^{-2}))$, $h = O(\epsilon), \tau = O(\frac{1}{\epsilon^k})$

Non-smooth f: PVI

[Johnson'76, Vuik'90, Baiocchi'89, NochettoVerdi'*]

$\phi \in L^\infty(W^{2,p}) \cap H^1(H^1) \setminus H^2(H^{-1})$

Fully implicit schemes

FE/FD

$E = O(\tau + h)$

Results on biofilm & nutrient & flow model

Channel-scale computations with coupled flow-PFT for biofilm-nutrient model as a 3×3 system [ZhangKlapper'10,'11].

Pore-scale computations with coupled NS-Flow & biofilm-nutrient PVI model [PTISW'16];

Analysis [GokieliKenmochiNiezgodka'18].

FE analysis of biofilm-nutrient model as a 2×2 system of PVI [AlhammaliP'18]; no flow/advection; $O(\tau + h)$.

Biofilm model at porescale: Navier-Stokes flow & biofilm-nutrient PVI

Biofilm models range from cellular lattice models [Valocchi et al] through phase field [ZhangKlapper 2011-] through degenerate/singular PDE [Eberl'2003-]. The common feature is that they account for the (*) constraint $B(x,t) \le B^{max}$. Our model is based on a simple observation that (*) can be realized by a parabolic variational inequality (PVI). ($\sim$ One-phase Stefan problem).

Model (use $\Lambda = \partial_B I_{[-\infty, B^{max}]}(B)$) [PTISW'16]

$$\partial_t B - \nabla \cdot (D_b(B)\nabla B) + \nu \cdot (vB) + \Lambda = f(B,N),$$
$$\partial_t N - \nabla \cdot (D_n(N)\nabla N) + \nu \cdot (vN) = -k_0 f(B,N)$$

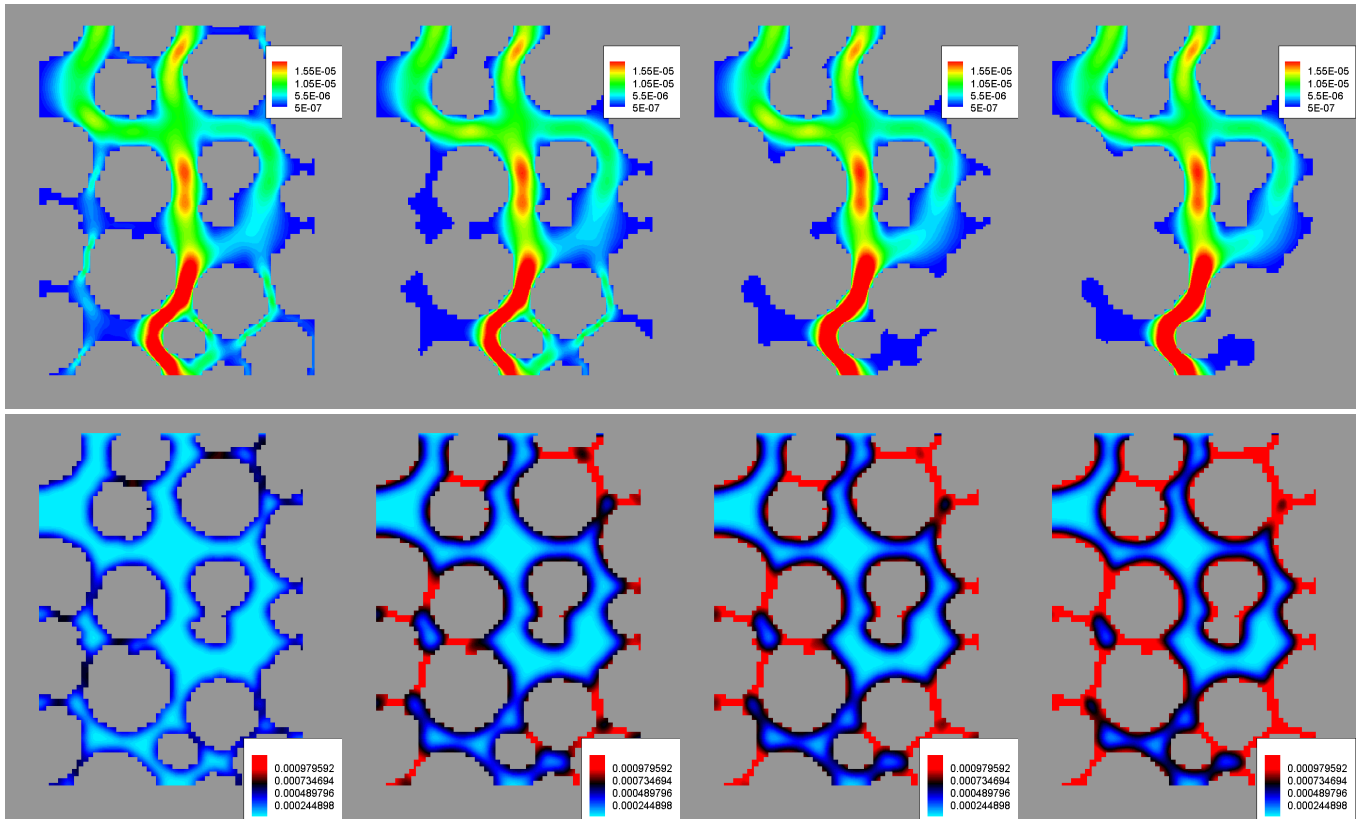
init. cond. b.c.; &v found by Navier Stokes solver

Analysis [GokieliKenmochiNiezgodka'18].

FE analysis of biofilm-nutrient model ($v = 0$) as a 2×2 system of PVI [AlhammaliP'18, manuscript]; $O(\tau + h)$ in $L^2(H^1), L^\infty(L^2)$; confirmed by numerical experiments. Challenge in analysis: $B_{tt} \notin L^2(H^{-1})$.

Proof: extends [Johnson'76,Vuik'90] to nonlinear system.

Biofilm model at porescale: Navier-Stokes flow & biofilm-nutrient PVI



Pore-scale computations with coupled NS-Flow & biofilm-nutrient PVI model [PTISW'16]. Followed by upscaling.

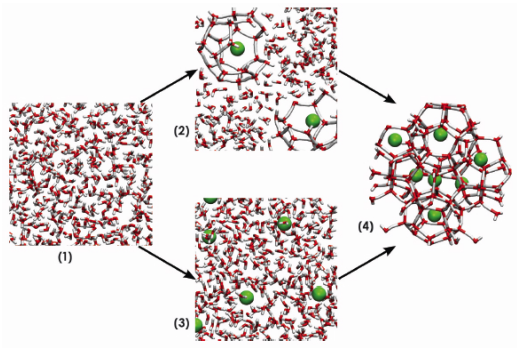
Result: Upscaled $K = K(B)$ strongly depends on initial conditions and geometry.

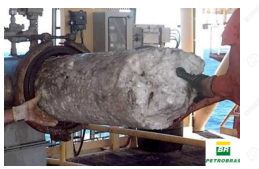
Hydrate formation/dissociation modeling

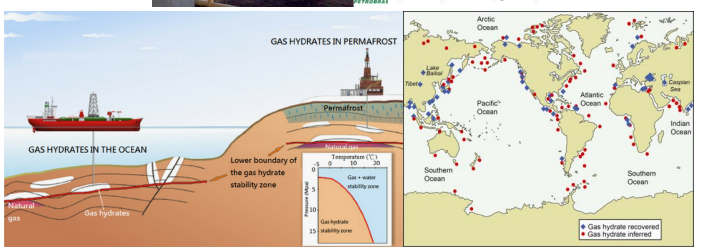
Methane hydrate: crystal made of two components: M and W.

If You Never Heard of Methane Hydrate, That Might Be Good News [P.; SIAM News 2018]

- Liquid- solid phase transition
  MD and DFT models: Colorado School of Mines
- Micro-scale (diffuse interface=PF)
  Known smooth f model (2 components, 2 phases);
  In progress: non-smooth f (PVI), three phases, boundary effects
- Macro-scale (basin/production scale)
  Sharp interface model known; some analysis and numerics







Walsh et al [Science'2009; JCP'2011];

pictures by M.Torres, from USGS

Macro-scale: Multi*-PDE model $\mathcal{M} - \mathcal{S} - \mathcal{P} - \mathcal{T}$

For each component $C = M, S, W$, consider all phases p

$$\partial_t \sum_{p=l,h,g} \phi S_p \rho_p X_{pC} + \nabla \cdot \left(\sum_{p=l,h,g} v_p \rho_p X_{pC} \right) - \nabla \cdot \left(\sum_{p=l,h,g} d_{pC} \rho_p \nabla X_{pC} \right) = 0$$

Energy equation "similar"

`Comprehensive model of Liu, Flemings [JGR'08]; see also Lake [1989]`

Model in [PTorresTrehu'10] comprehensive but delicate, and complex. Results exhibit large gradients and discontinuities. Very sensitive to thermodynamics and phase behavior (equilibrium) solver. Need very accurate "real" data for simulations of case scenarios to proceed.

Simplify model $\mathcal{M}-\mathcal{S}-\mathcal{P}-\mathcal{T}$ to $\mathcal{M}$

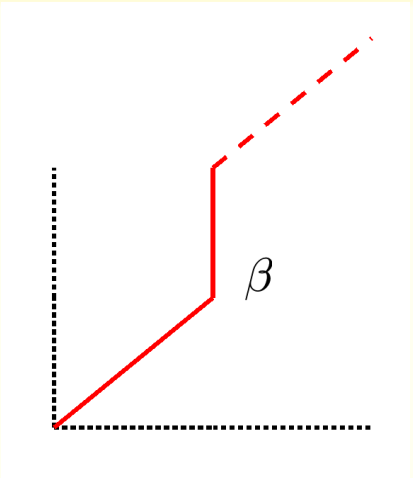
The delicate and complex nature of $\mathcal{M}-\mathcal{S}-\mathcal{P}-\mathcal{T}$ begged for analysis of the model and of numerics, which seemed impossible, while the dynamics in (some) results of [LF'08] required only the simplifed evolution. Thus we considered first just a very simplified $\mathcal{M}$ model.

Model $\mathcal{M}$ for evolution of N, in hydrate zone ($p = h, l$)

- Simplify, solve for $\boxed{X, N}$

$$\boxed{\partial_t N + \mathcal{T}(X) = 0}$$

- $\mathcal{T}$ transport operator
  (diffusion or advection)
- $N = \beta(x; X)$
- $\beta = \beta(x;)$ monotone multivalued
- $\beta(x;)$ not affine-bounded



Mathematical structure: PME (Porous Medium Equation) (& tweak: family of convex integrands, & comparison principle). Space-parametrized Stefan pbm.

Our results on hydrate at macro (Darcy) scale

[GibsonMedinaPShowalter'14] Diffusion only (subgradient case), hydrate zone

E/U; equation holds in $L^2(H^{-1})$, $N \in H^1(H^{-1})$, $X_{lM} \in L^2(H_0^1)$

[PShowalterWebster'15] Diffusion & advection, hydrate zone

E/U; equation holds in $C^0(L^1)$, $N \in C^0(L^1)$, $X_{lM}(\cdot, t) \in W_0^{1,1} a.e.$

Gas zone?

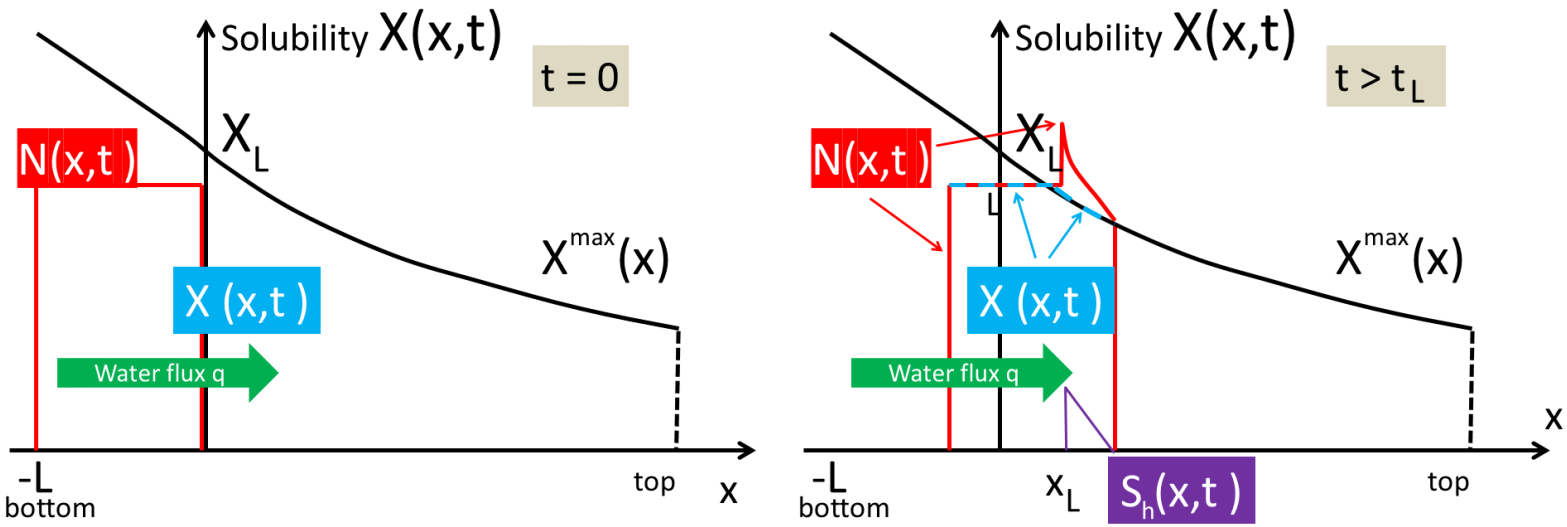
Not yet. Further challenges (viscous and capillary terms).

Implications of analysis for numerical schemes

Low-order stable discretizations are a good choice.
Solver for phase behavior: semi-smooth Newton
Stability & convergence: [PShin, in progress]
Time-stepping schemes for coupled system and comparison with data [PMedina et al, PHong et al'16-'17-'18]

SIAM NEWS'2018 movie

Advection (counter) example [PSW'15]

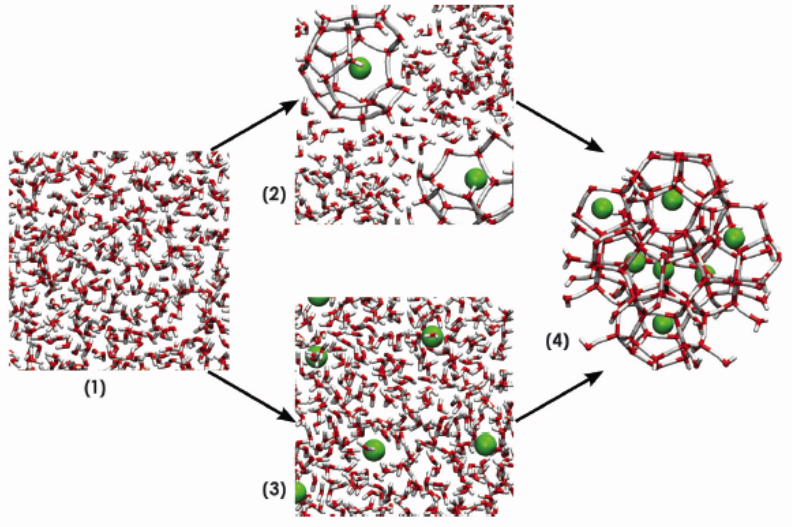


Analytical solution explains the discontinuity of hydrate saturation

Also, [C.Shin, current work on regularization of $\beta^{-1}(x;\cdot)$] and movie.

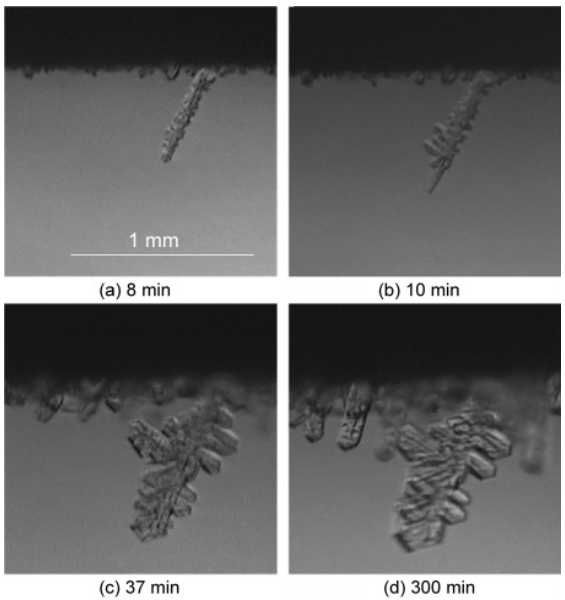
Hydrate across the scales (sub-micro and micro)

Molecular [nm/μs]



Molecular Dynamics (MD),
Density Functional Theory (DFT)

Interface scale [mm/min]



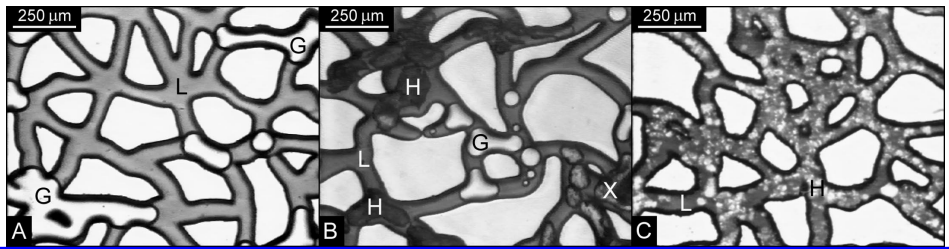
Phase-field Theory (PFT)

European SRF; Walsh et al [Science'2009]; Walsh et al [JCP'2011]; Walsh et al movie 2009, Ohmura, Matsuda, Uchida et al [Crystal GD'2005]

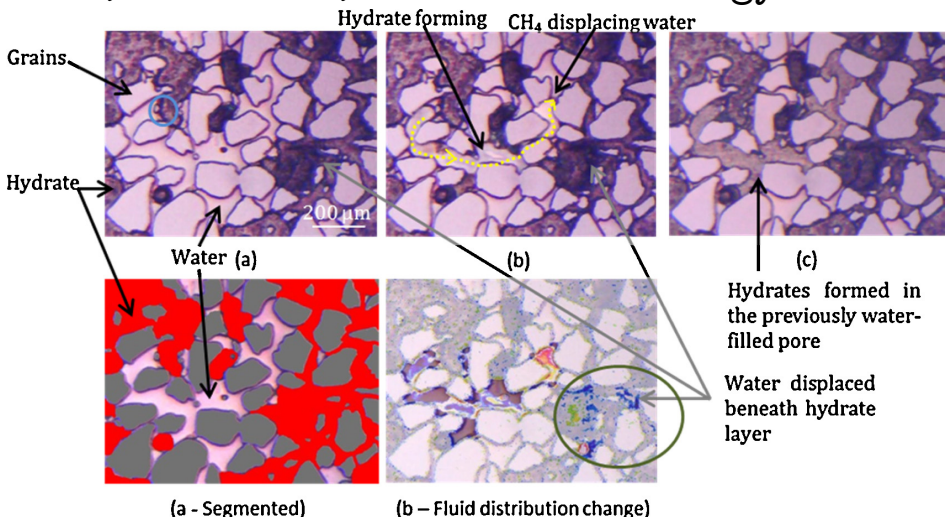
We will use modeling ideas from Tegze et al [JCP'2006]; Granasy, Warren et al; Kvamme et al ['2004-]

Hydrates at porescale and below

Imaging difficult but not impossible



Tohidi, Anderson, Clennell [Geology'2013]



L.P.Hauge, ...A.Kovscek, M.A.Ferno [IJGC'16]

Modeling tricky

Darcy scale models are borderline adequate.
What physics governs phase transitions in confined space?

- Gibbs effect
  (kinetics, premelted film, thermal regelation)
- van-der-Waals
  (intermolecular) forces lower freezing temperature, thermodynamics affected by the pore walls, capillary effects/phase tension may be significant

Rempel,Buffett[JGR'1997]; Jain,Juanes [JGR'2010]

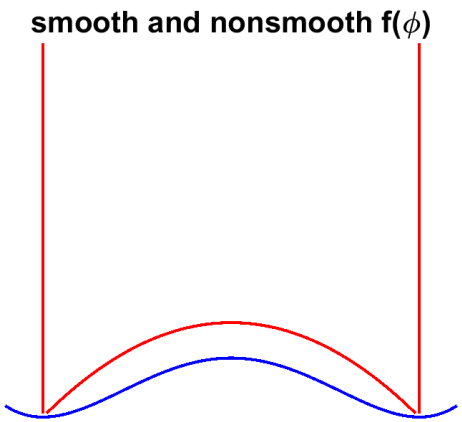
How to describe hydrate/gas at porescale and produce DNS?

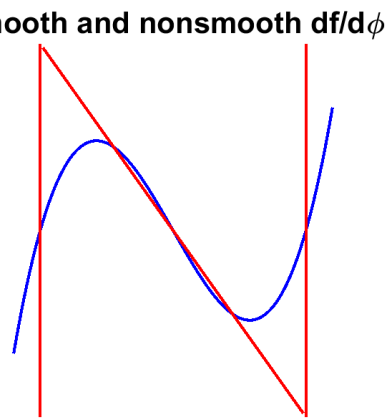
Answer: a reasonable adaptable extendable PF model.

Phase field models for multiple components (mixtures): big picture

Generally, gradient dynamics $\dot{\phi} + \frac{\partial \mathcal{F}}{\partial \phi} \ni 0$

$\mathcal{F}$ is the free energy functional (convex at macroscale, nonconvex at meso/micro scales); $\mathcal{F}(\phi) = \int |\nabla \phi|^2 + \int f(\phi) + \ldots$ is the double well potential, and $f(\phi)$ is the free energy density



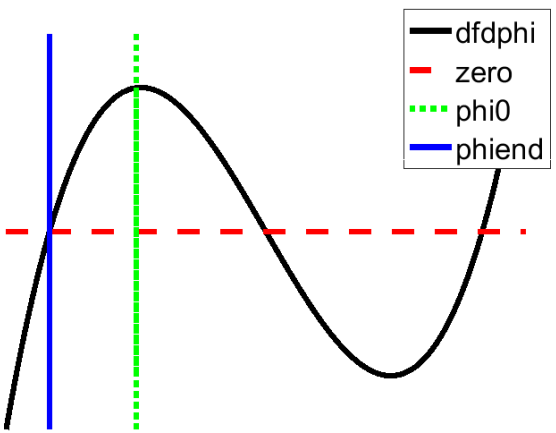


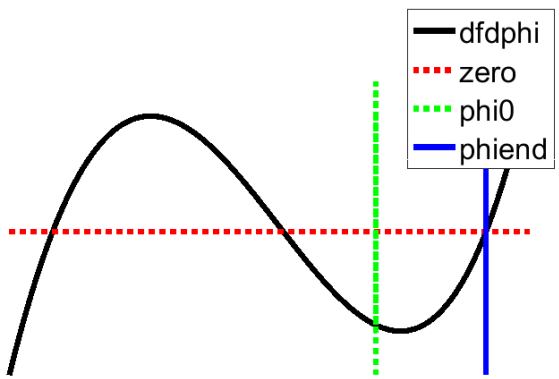
[Warren, Boettinger (1992-), Murray, Kobayashi, A.A. Wheeler, McFadden, Granasy, Kvamme, Tegze, and their collaborators (1998-)] have proposed, tested, and analyzed various formulations for multicomponent systems. Applications very successful in metallurgy. PF-TC as a mean-field theory can be derived from DFT.

Coarsening ODE evolution model two phases, one component, smooth ϖ

Consider $\dot{\phi} + \varpi(\phi) = LT$, with $\phi(0) = \phi_0$.

(Symmetric) $\varpi(\phi)$ promotes phase separation *even* when $T = 0$.





$\phi_0 < 0.5$; $\phi(t) \to \phi_{end} = 0$ $\phi_0 > 0.5$; $\phi(t) \to \phi_{end} = 1$

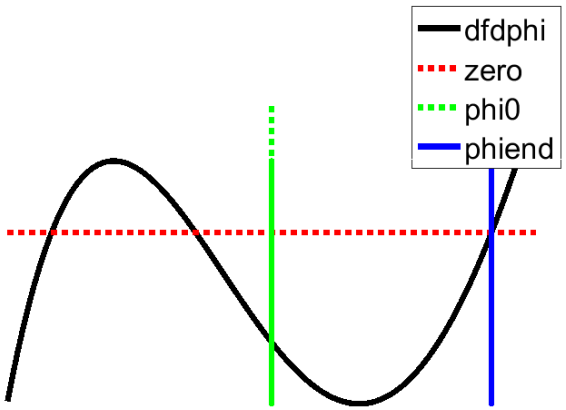
Usually $\varpi(\phi) = \frac{df}{d\phi}$, where $f(\phi, T)$ is a "double-well" potential.

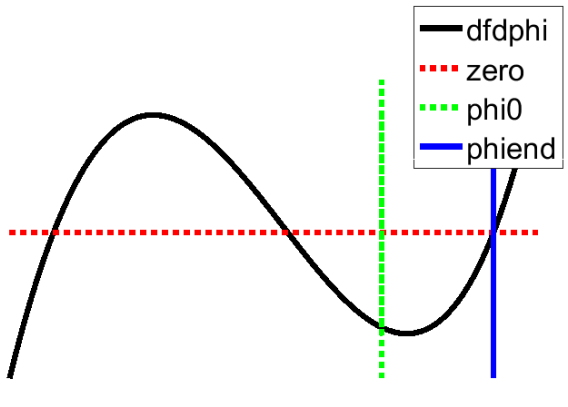
Coarsening ODE evolution
two phases, two components; smooth ϖ

Consider $\dot{\phi} + \varpi(c;\phi) = 0$ with nonsymmetric $\varpi(c;\phi) = \frac{df}{d\phi}(c,\phi)$

small c promotes $\phi = 1$ (liquid)	large c promotes $\phi = 0$ (solid)

Root ϕ_* of $\varpi(c,\phi)$ shifted left **shifted right of center**





Picking initial $\phi_0 > \phi_*$ leads to ...

... $\phi_{end} = 1$ (liquid)

Extend PFT to PFTH for hydrate growth

Multicomponent PFT, binary mixture $W + M$

Evolve ϕ, T, and $c{=}\xi_{lM}$ molar concentration of M

Undercooling (T) $\rightarrow$ Supersaturation (c)

This talk: evolve ϕ, c; keep T fixed

Gradient flow dynamics involves mobilities

$$\begin{aligned} \partial_t \phi &= -M_\phi \left(\nabla^2 \phi - \frac{\partial \mathcal{F}(\phi, c; T)}{\partial \phi} \right) \\ \partial_t c &= \nabla \cdot \left(M_c \frac{\partial \mathcal{F}(\phi, c; T)}{\partial c} \right) \end{aligned}$$

$$\mathcal{F}(\phi, c; T) = \int_\Omega \frac{T}{2} (\nabla \phi)^2 + \frac{T}{2} (\nabla c)^2 + f(\phi, c; T).$$

Orientation (anisotropy) effects $\partial_t \Theta$, with $\mathcal{F} = \mathcal{F}(\cdot; \Theta)$ ignored

Options to construct $f(\phi, c; T)$

1. [Warren/Boettinger] Given $f_A(\phi; T)$, $f_B(\phi; T)$, mix them up:

$$f(\phi, c; T) = c f_B(\phi; T) + (1 - c) f_A(\phi; T) + c \ln(c) + (1 - c) \ln(1 - c)$$

2. [Granasy/Tegze] Given $f_s(c; T)$ and $f_l(c; T)$, mix them up:

$$f(\phi, c; T) = p(\phi) f_l(c) + (1 - p(\phi)) f_s(c) + T w(c) g(\phi)$$

   - $p(\phi)$ interpolates between $\phi = 0$ (solid) and $\phi = 1$ (liquid)
   - energy scale $w(c)$ interpolates between $c = 0, 1$

We adopt and modify formulation 2 which has been tested for fluids and CO2 hydrate formation

... and make a lot of modifications and simplifications based on qualitative analysis ...

Additional references include [Kvamme et al [IJGGC'2007]], [A.A. Wheeler/Warren/Boettinger [PhysRev A'1992]], [Granasy et al [JPhCoMa'2004]], [Tegze et al [JChP'2006]]

Continue

making simplifications,
linearizing nearly linear relationships,
analyzing the qualitative structure,
checking on convexity and concavity of the functionals
cross-checking computational model,
testing the sensitivity . . .

PFH model (ϕ, c), summary

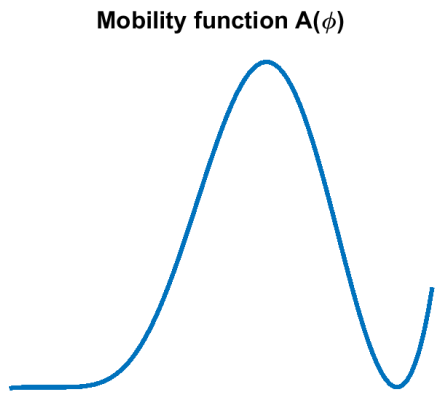
Make parameters invisible so that the structure is visible

- Phase evolution

$$\partial_t \phi - \nabla^2 \phi + \varpi(\phi, c) = 0$$

- Evolution of concentration

$$\partial_t c - \nabla \cdot \left(c \underbrace{A(\phi) \nabla \phi}_{v(\phi)} \right) - d \nabla^2 c = 0$$



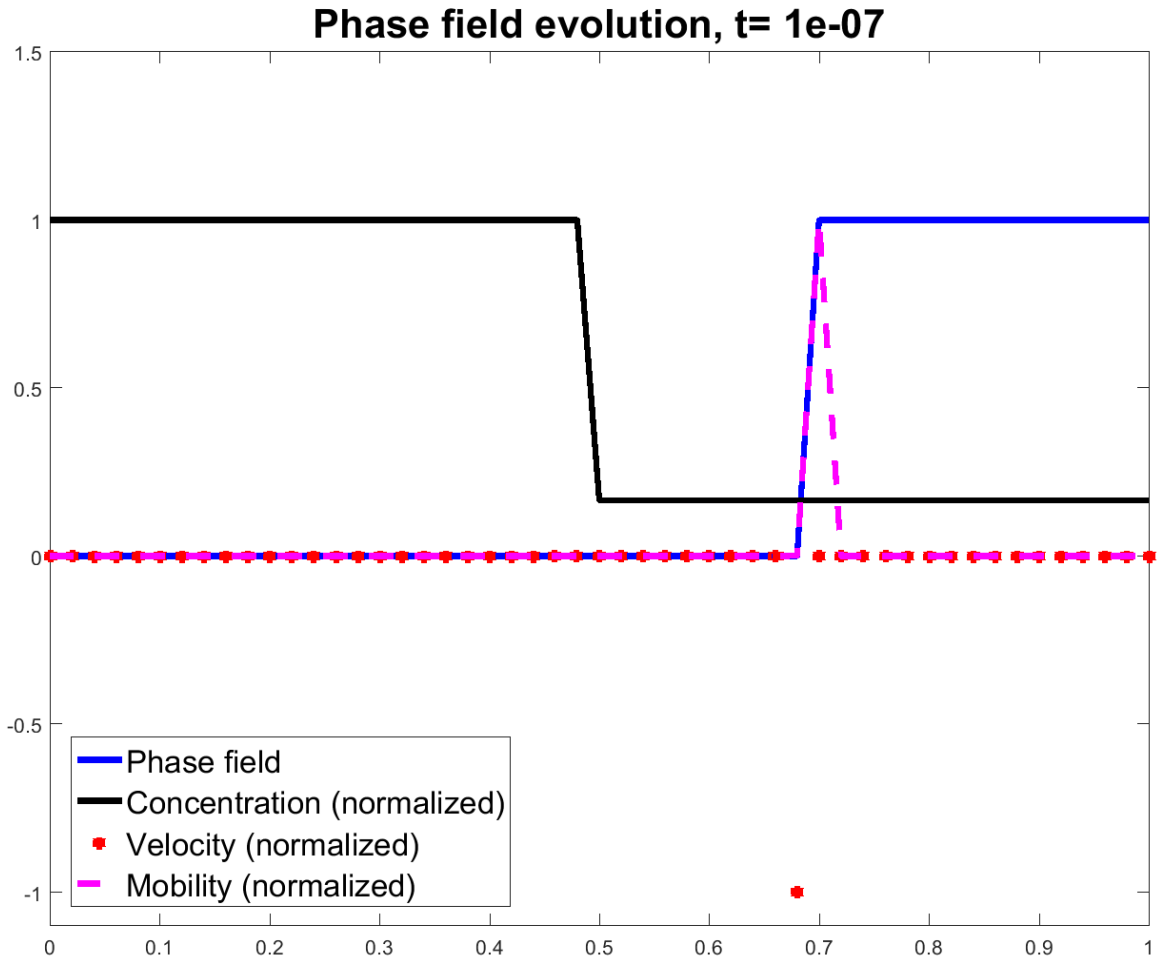
Details: $\varpi(c;\phi) = w(c)g'(\phi) + p'(\phi)\left(f_L(c) - f_S(c)\right)$. *Approximate* $f_s(c)$ *and* $f_l(c)$ *by linear functions [Tegze et al], with slopes* A_s, A_l. *Note* $A_l - A_s > 0$.

Rewrite transport evolution

$\partial_t c = \nabla \cdot \left\{ c(1-c) D(\phi) \nabla \left[(w_B - w_A) T g(\phi) + p(\phi)(f_l' - f_s') \right] \right\}$, *where*

$D(\phi) = D_s + (D_l - D_s)p(\phi)$. *Approximate* $c(1-c) \approx c$, *since* $c \leq 0.16$ *[Tegze et al]. Define* $A(\phi) = D(\phi)\left[(w_B - w_A) T g'(\phi) + p'(\phi)(A_l - A_s)\right]$.

PFH (c, ϕ) illustration: simple example



Start from an incompatible initial condition to evolve towards steady state where $x : \phi(x) = 0$ *matches* $x : \bar{c}(x) = 1$. *Observe evolution of mobility* $A(\phi)$ *and of advection velocity* $v(\phi) = -A(\phi)\nabla\phi$ *always towards the solid phase* $\phi = 0$. *Movie.*

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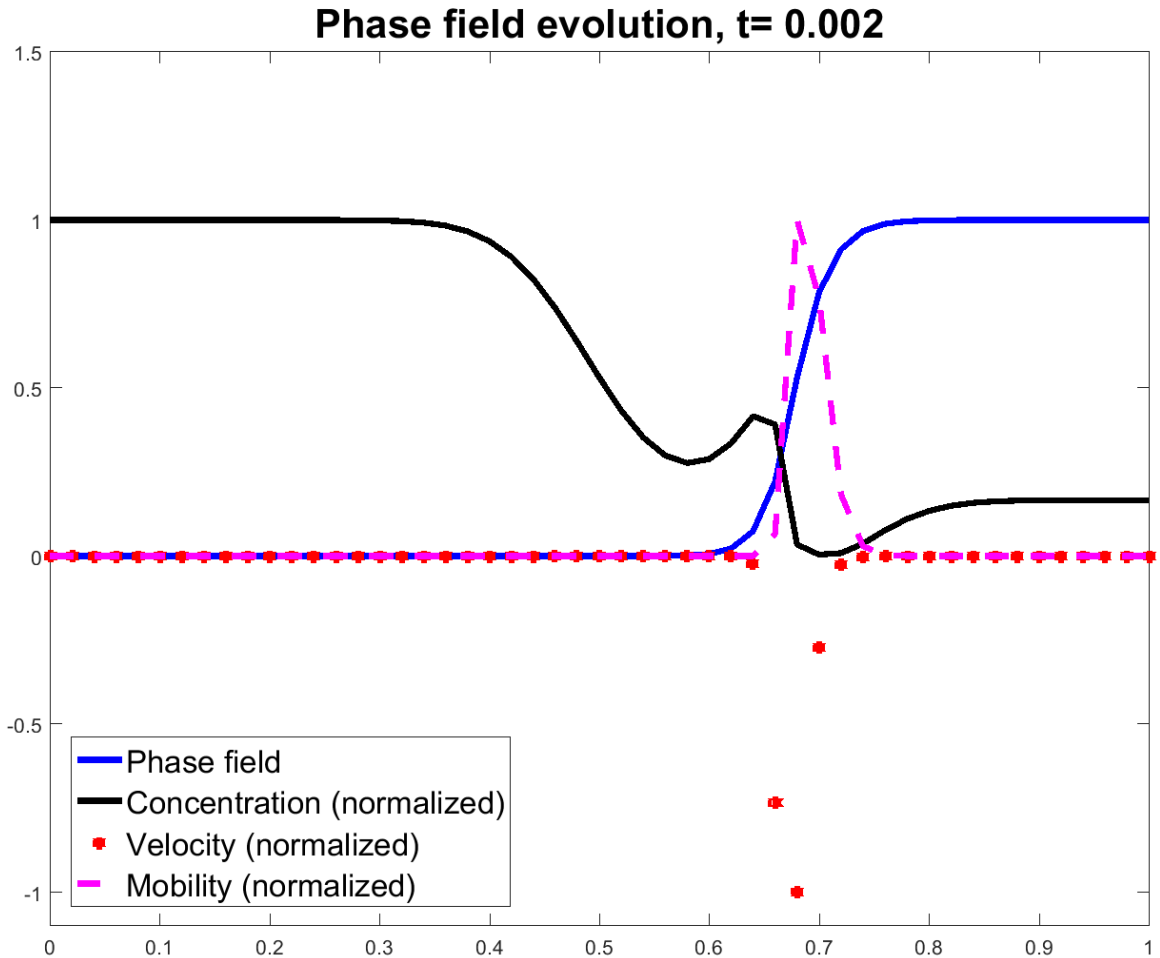

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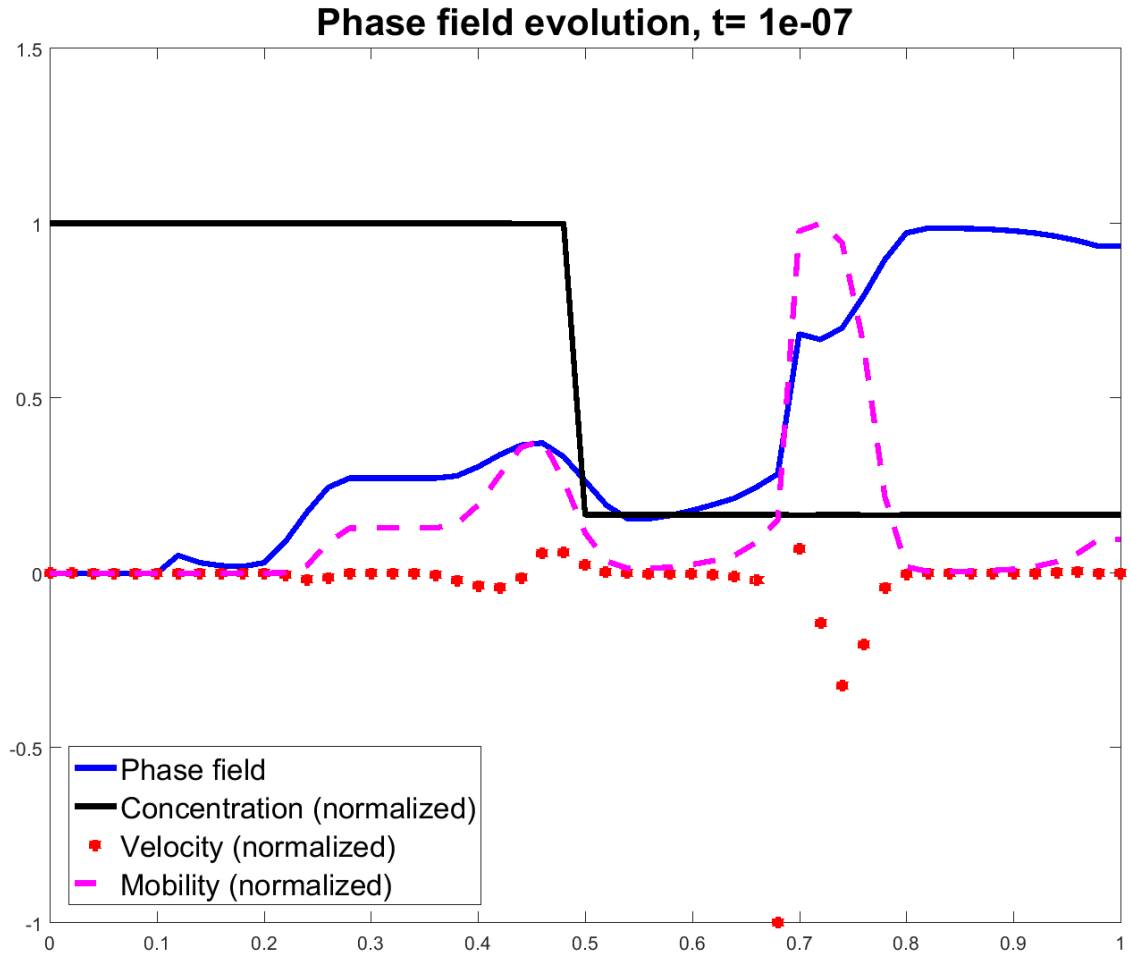
PFH (c, ϕ) coarsening example



Start from an randomized initial condition to evolve towards steady state where $x : \phi(x) = 0$ *matches* $x : \bar{c}(x) = 1$. *Observe evolution of mobility* $A(\phi)$ *and of advection velocity* $v(\phi) = -A(\phi)\nabla\phi$ *always towards the solid phase* $\phi = 0$. *Movie.*

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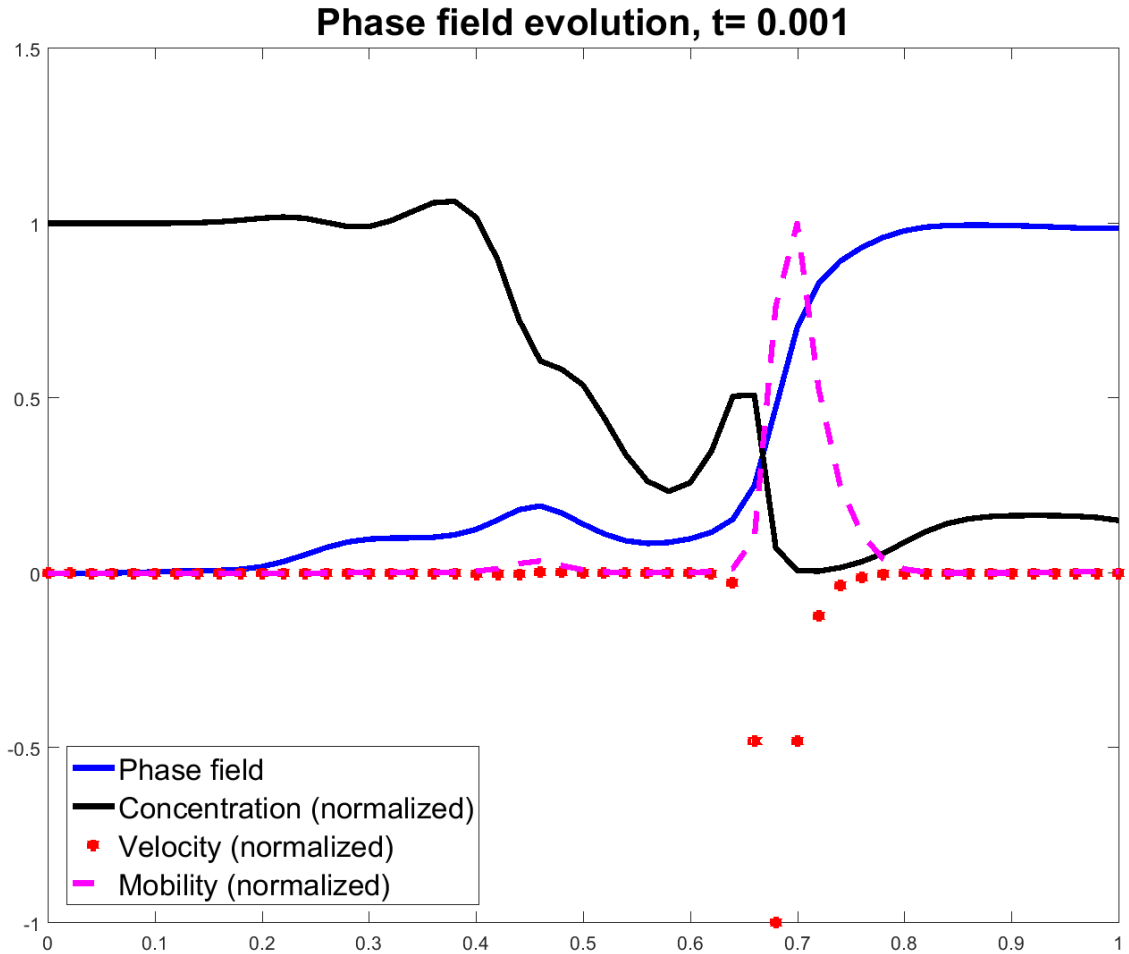

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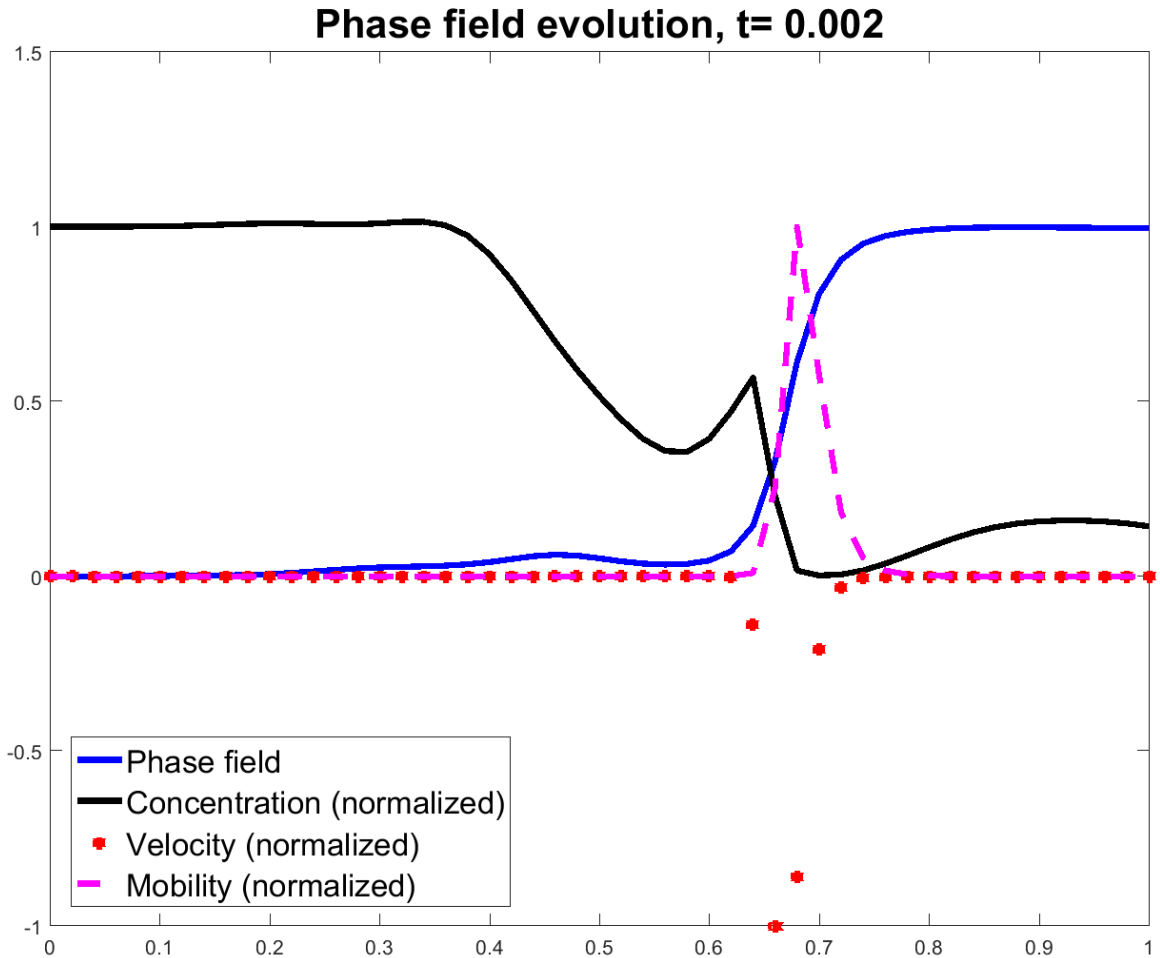

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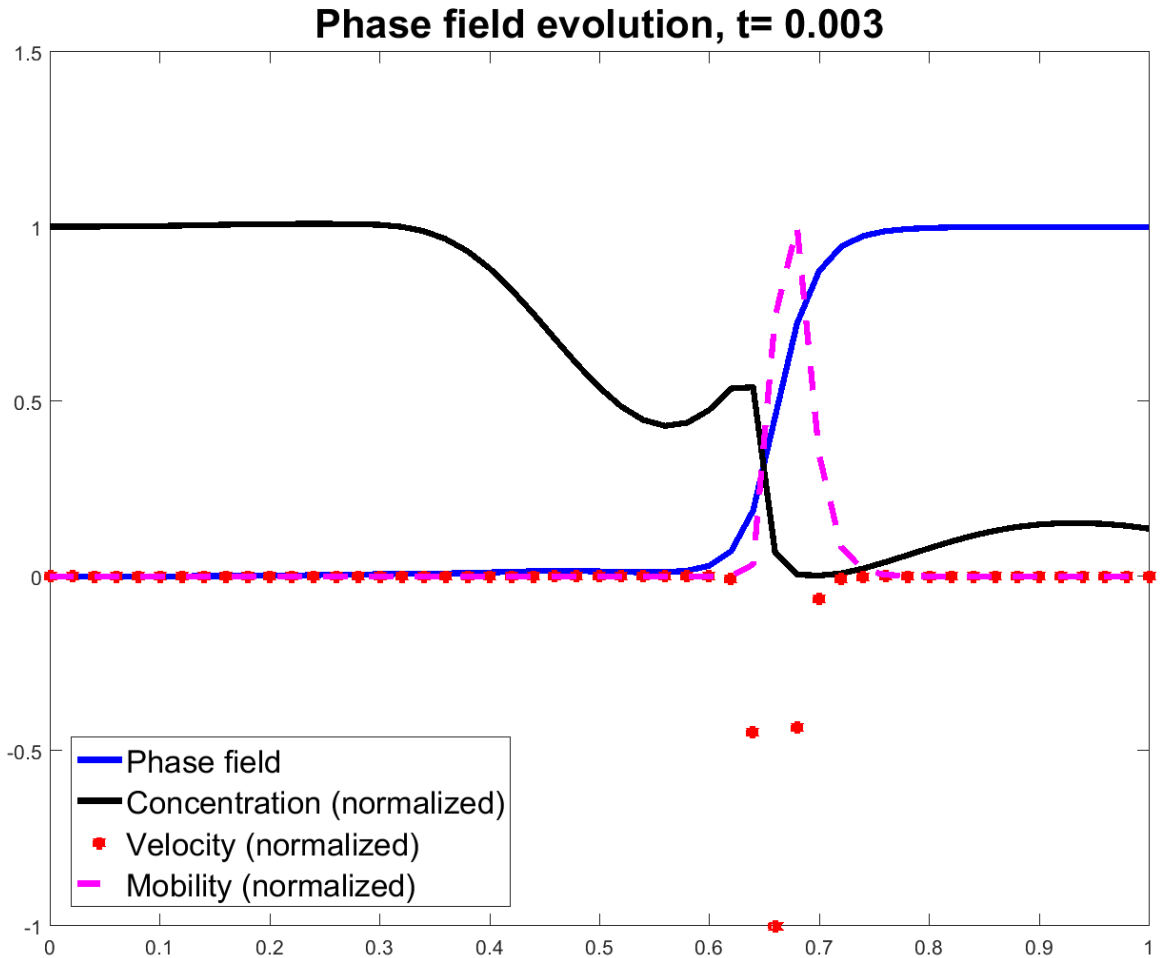

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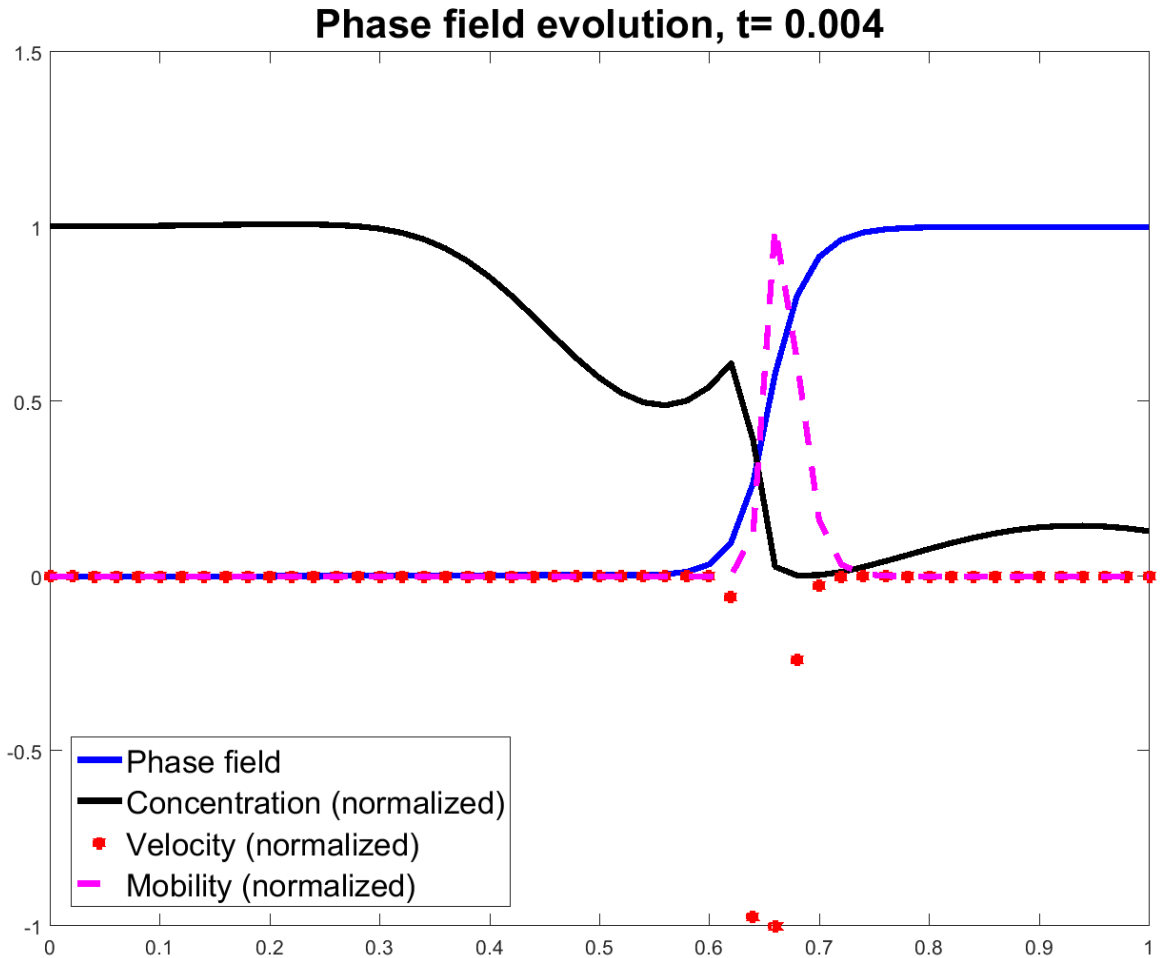

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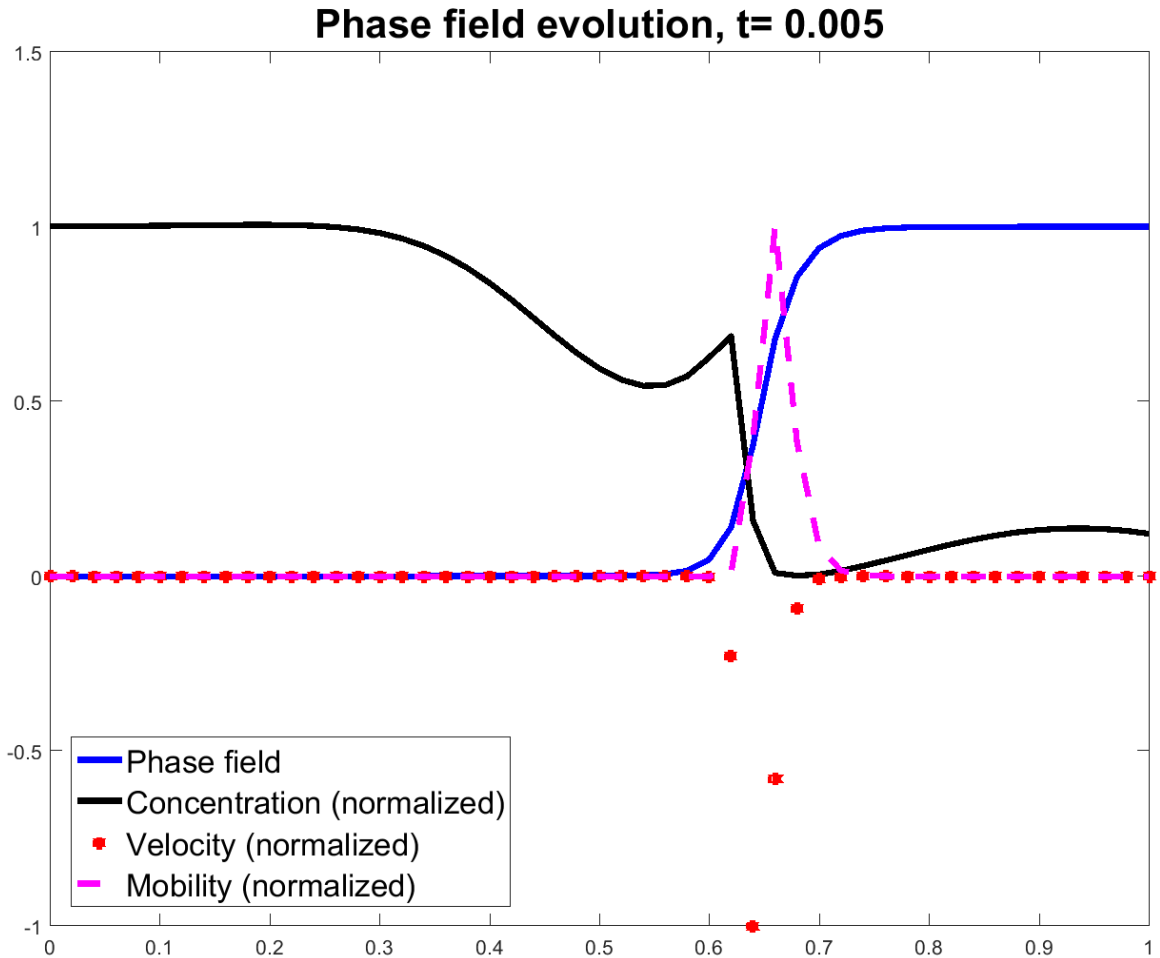

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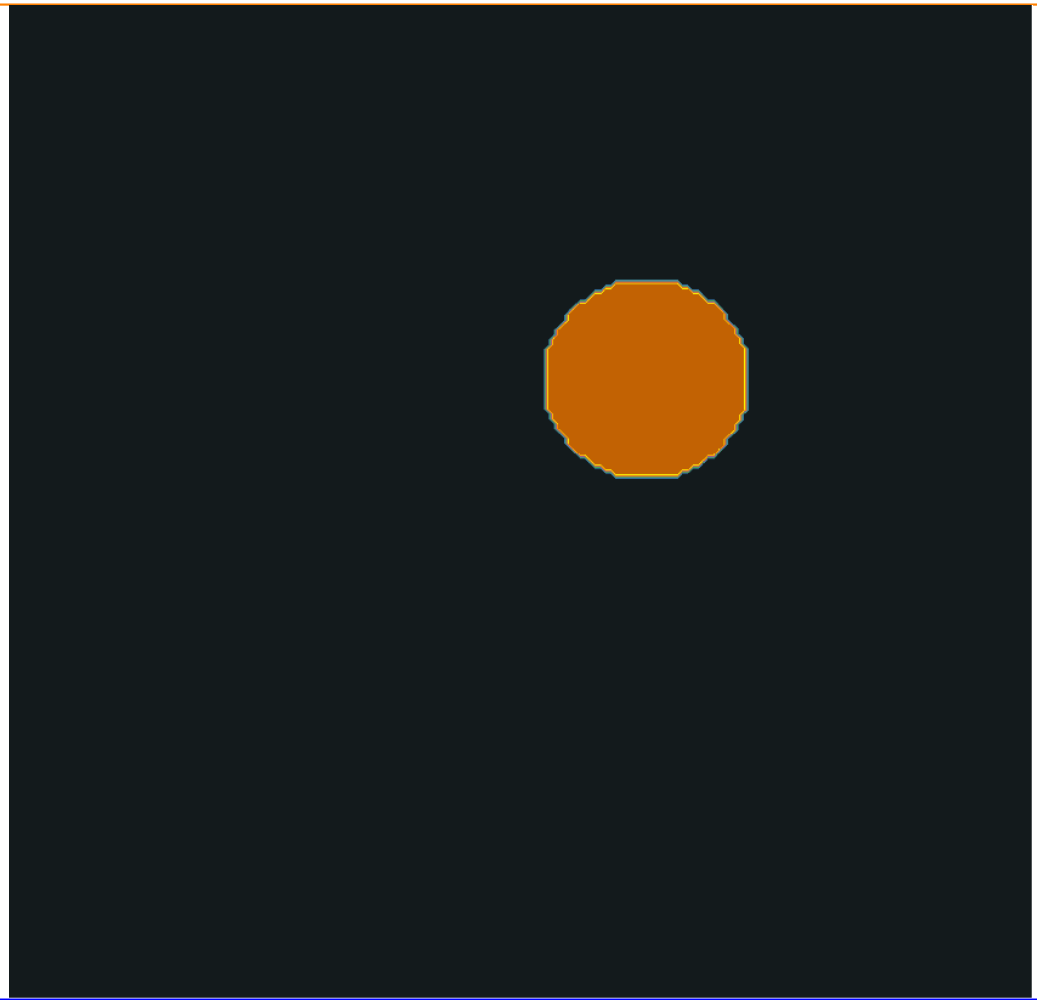
PFT: can we grow crystals? Yes we can.

Classical crystal growth algorithms allow for undercooling, and promote dendritic growth by adding stochastic fluctuations to the dynamics. The growth starts from an initial "blob"



Or see crystal novoid movie

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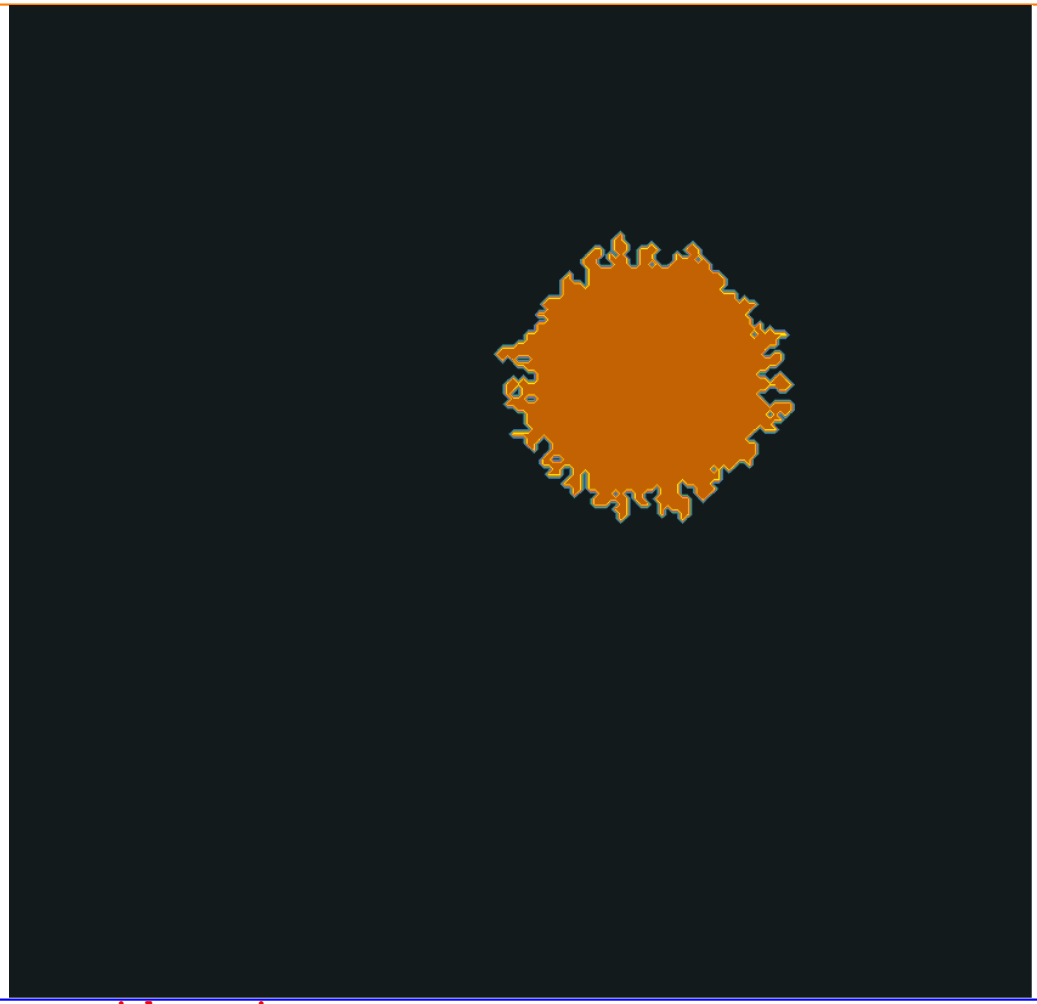

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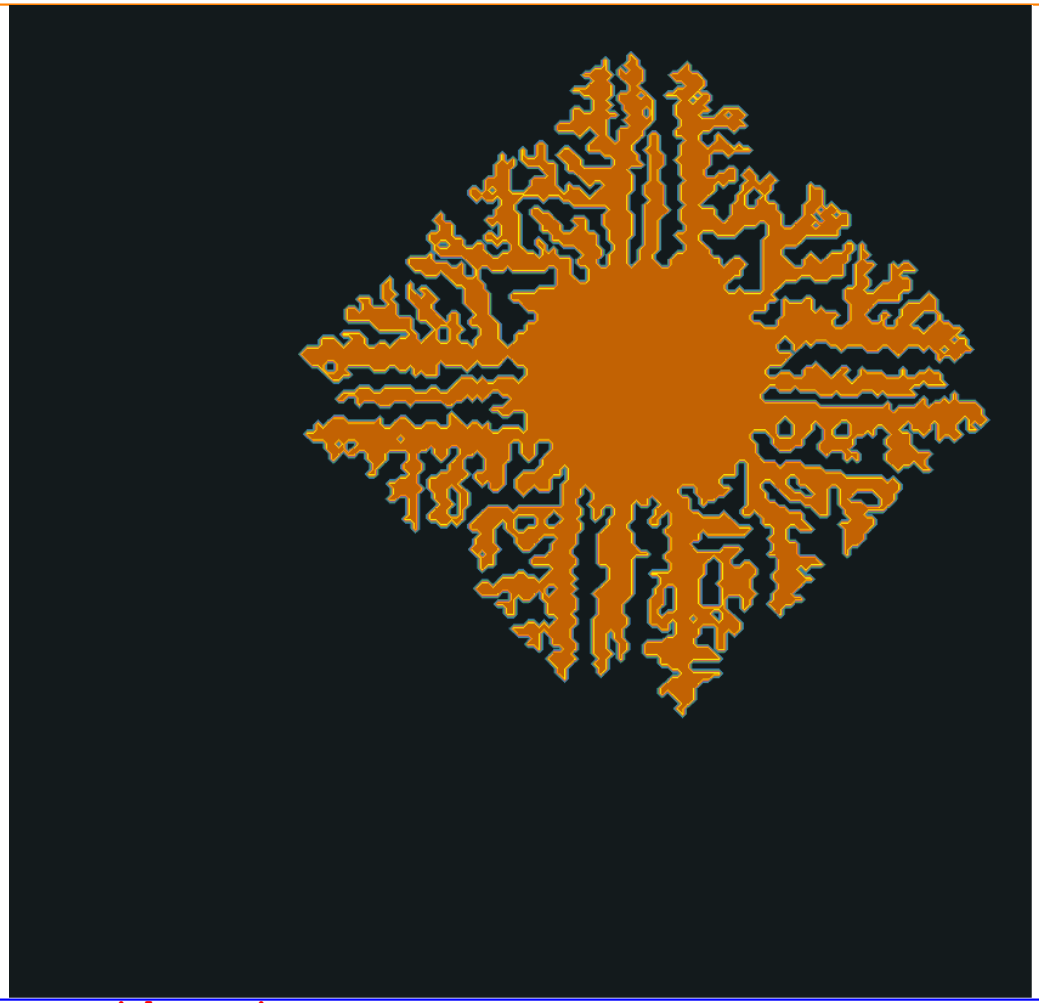
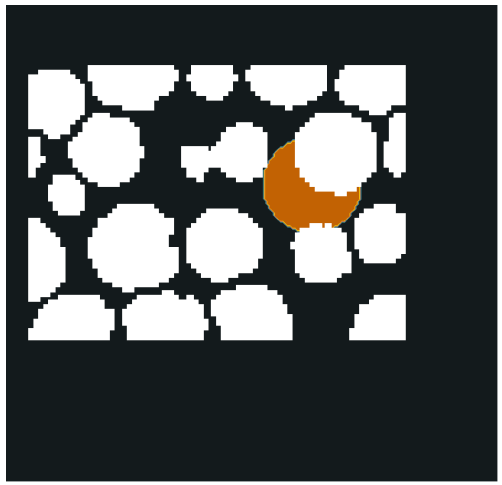


Or see crystal novoid movie

PFT: apply in realistic porescale geometries?

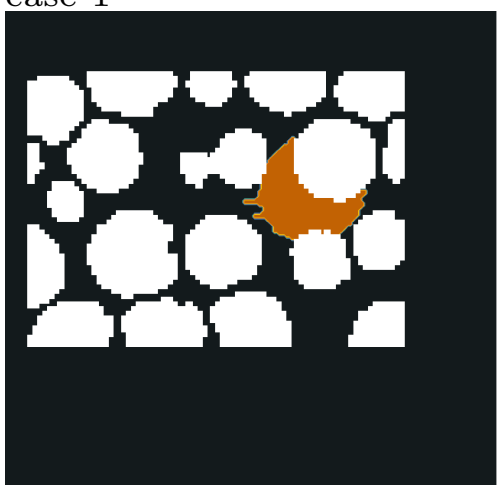
Configuration at $t = 0$ ...



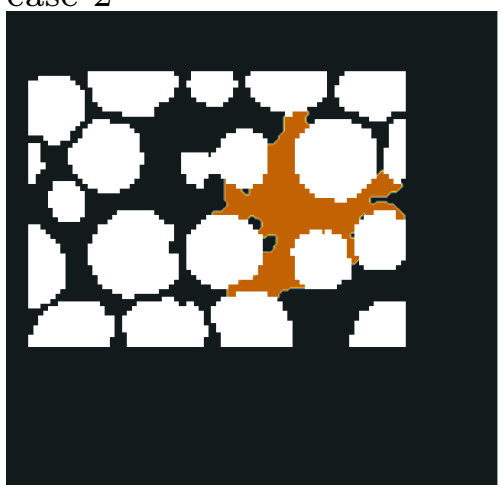
Run simulations which differ by the choice of: capillary length, undercooling, randomness

... simulation results at $t >> 0$ ...

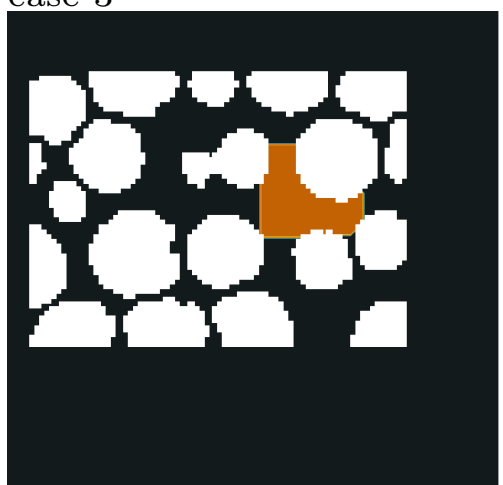
case 1



case 2



case 3



Results are, unfortunately, unpredictable, and seem to be sensitive to the small variations in the physical and simulation parameters

Analysis and a robust numerical solver will help.

Next challenge in modeling

We have shown some progress on DNS of hydrate crystal growth at pore-scale

- Two components: M + W
- Two phases: liquid + solid (hydrate)
- Isothermal

Current work:

- Two components: M + W
- Three phases: liquid + solid (hydrate) + gas
- Non-isothermal

Summary

- Phase transitions and interfaces important
  - Models at macroscale $\neq$ models at interface scale
  - Phase-field models: competition of stabilizing and de-stabilizing terms (diffusive and coarsening)
- Computations delicate: nonlinearity, sharp fronts
  How much accuracy do we really need?
- Modeling is complex; Analysis of PFH largely open
- Must connect micro- to macro- robustly (Γ-limits for Stefan problem)
- What computations are feasible/needed when upscaling?