SIAM GS Minitutorial

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Special acknowledgements

This material is dedicated to the memory of J.A.Wheeler.

References

- Lake, Enhanced Oil Recovery, 1989

- Smith, Van Ness, Abbott, Chemical Engineering Thermodynamics, 1949 ... 2001.

- Firoozabadi, Thermodynamics of Hydrocarbon Reservoirs,

- Zhang, Geochemical kinetics

  Many papers on multiphase multicomponent flow.

- Falta, Pruess (1985)

- Forsyth, Simpson (1989)

- Michelsen (1993 and may others)

- Class, Helmig (and Bastian) (2002...)

- STOMP manual, TOUGH manual

Components (C) and phases (p)
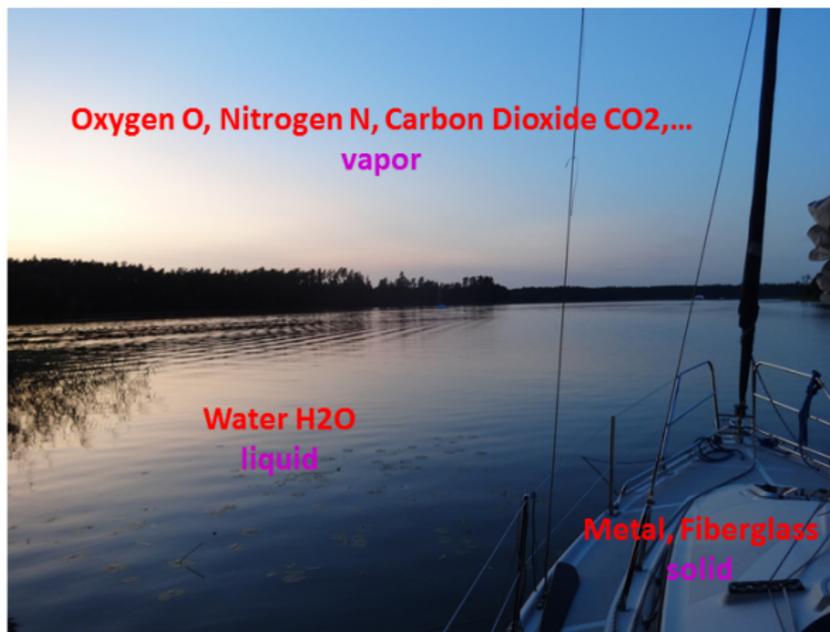
C=Water
in 3 phases p=vapor (gas), liquid, solid (ice)

Temperature T

vapor   *liquid*   *solid*

T=100

T=0
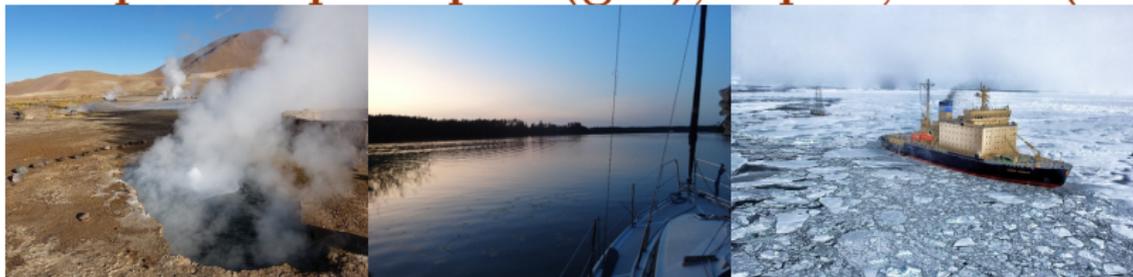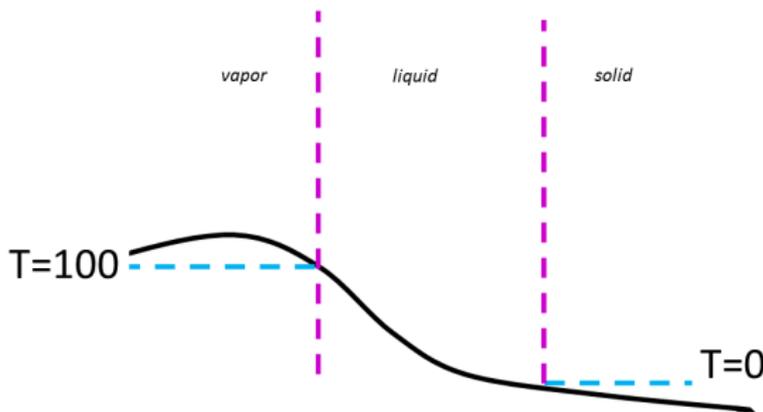
Glossary and U*N*I*T*S 101

1 Mole: amount $\approx 6 \times 10^{23}$ molecules of a substance.

Mixture of C components with total n moles, $n = n_1 + \ldots n_C$.

With multiple phases, eq., liquid and vapor: $n = n_l + n_v$.

Molar mass M [g/mol]. For a mixture, $M = \sum x_i M_i$; here $x_i = \frac{n_i}{n}$ are mole fractions, with $\sum_i x_i = 1$. (Sometimes we also use y_i or z_i.)

Mass fraction $\eta_i = x_i \frac{M_i}{M}$. Mass fraction in phase p is denoted by η_p^i.

Molar volume $V_M = \frac{V}{n} = \frac{M}{\rho}$.

```
Molar mass of CH_4 is ≈ (12 + 4)· 1g/mol = 16.04 g/mol.
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Density $\rho = \frac{M}{V}$. Phase density ρ_p.

Saturation S_p of phase is volume fraction of that phase. (Concept similar to but quantitatively different than $\frac{n_p}{n}$.)

For VLE (two phase vapor-liquid equilibria): x_i liquid phase mole fraction (corresponds to η_l^i), y_i is vapour (gas) phase mole fraction (corresponds to η_g^i), z_i overall mole composition.

Raoult's law $y_i P = x_i P_i^{sat}$ makes assumptions (vapor phase is ideal gas, liquid phase is ideal solution). It is only appropriate in subcritical conditions.

Fugacity f defined as $\lim_{P \to 0} \frac{f}{P} = 1$. Usually we write $f = \phi P$ and define $\phi : \int_0^P \frac{z(p)-1}{p} dp$. This quantity can be measured, and calculated from EOS.

Fugacities are useful in mixture equilibria calculations.

What are phases and components

Phases $p = 1, \ldots N_p$. Components $c = 1, \ldots N_c$.

Generic diagram
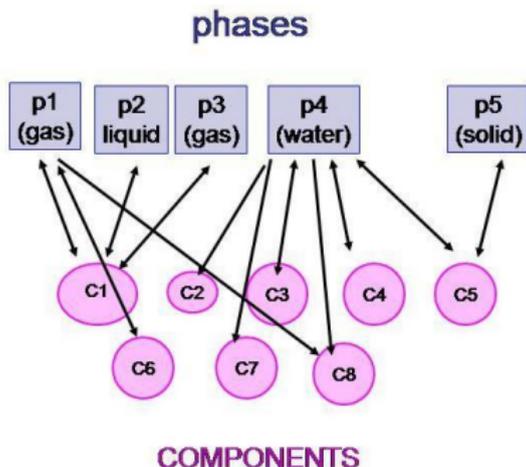
Examples
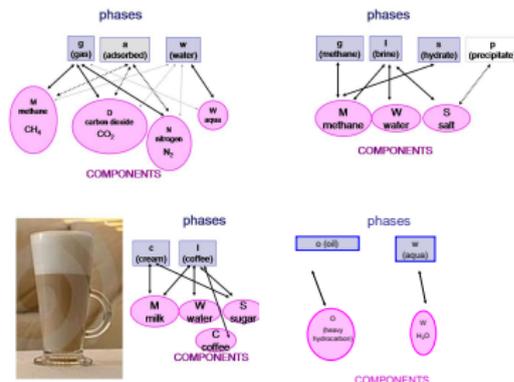
Must know how the composition η_p^c. This depends on (P, T).
Phase transition requires energy change and in turn affects (P, T).

Phases and components.
Flow and transport in porous media

For every component $C = 1, \ldots N_c$

$$\partial_t(\phi \sum_p \rho_p S_p \eta_p^C + (1-\phi)\rho_s \eta_s^C) + \sum_p \nabla \cdot (J_p^C) = q_C. \tag{1}$$

Phase saturations S_p ($\sum_p S_p = 1$), densities ρ_p, pressures P_p (or one pressure P)
Mass (or mole) fractions η_p^C. For every $p = 1, \ldots N_p$, $\sum_C \eta_p^C = 1$.
Need to define fluxes J_p^c (advective, from Darcy's law) plus diffusive.

Closure: Need to specify η_p^C via "phase equilibria".

Alternative (kinetic): for a fixed component C, and two phases $p = l, g$

$$\partial_t(\phi \rho_l S_l \eta_l^C) + \nabla \cdot (J_l^C) = q_c + Q_C^{lg} \tag{2}$$

$$\partial_t(\phi \rho_g S_g \eta_g^C) + \nabla \cdot (J_g^C) = -Q_C^{lg} \tag{3}$$

Must know mass transfer rates Q_C^{lg}.

Additionally to mass conservation ....

Need an energy equation for $T = T(x, t)$.
(Include latent hear of phase transformation).

$$\partial_t(\phi \sum_p \rho_p S_p U_p + (1 - \phi)\rho_s U_s) + \sum_p \nabla \cdot (J_p^T) = q^T \qquad (4)$$

U_p: phase internal energy. E.g., $U_p = H_p$ (enthalpies); with latent heat, e.g.
$L = H_v - H_l$. Also, one can simplify $U_p \approx c_p T$.
Alternative: assume the system is isothermal; fix $T(x)$.

Simple example: count equations and unknowns

Example II.1 ($N_p = 2, N_C = 2$, immiscible case)

Consider (1), with $C = W, N$, and $p = l, n$ (Water and Oil (or Gas) and liquid and nonwetting=nonaqueous) phases. Set $\eta_s^C = 0$.

$$\partial_t \left(\phi(\rho_l S_l \eta_l^W + \rho_g S_g \eta_g^W) \right) + \nabla \cdot (J_l^W + J_g^W) = q_W. \tag{5a}$$

$$\partial_t \left(\phi(\rho_l S_l \eta_l^N + \rho_g S_g \eta_g^N) \right) + \nabla \cdot (J_l^N + J_g^N) = q_N. \tag{5b}$$

Assumptions and closure, total [+11]

$S_l + S_n = 1$ [+1].
$\sum_C \eta_p^C = 1$. [+2]
Mass conservation equations [+2]
Define $J_p^C = \eta_p^C v_p \rho_p$ (ignore Ficks's)
Darcy's law $v_p = v_p(S_p, \nabla p)$ [+2]
Provide $\rho_p = \rho_p(P, T, \{\eta_p^C\})$
Provide or ignore capillary pressure
$P_l - P_n = P_c(S_l)$. [+1]
Assume isothermal conditions T known. [+1]
Assume immiscibility $\eta_l^N = 0$, $\eta_n^W = 0$. [+2]

Variables [+11]

Saturations S_l, S_n [+2]
Mass fractions $\{n_p^C\}$ [+4]

Phase velocities v_p [+2]

Phase pressures P_p [+2]

Temperature T [+1]

In practice, we eliminate many unknowns, and solve (5) for one P_p and one S_p.

Simple example: count equations and unknowns

Example II.1 ($N_p = 2, N_C = 2$, **immiscible case**)

Consider (1), with $C = W, N$, and $p = l, n$ (Water and Oil (or Gas) and liquid and nonwetting=nonaqueous) phases. Set $\eta_s^C = 0$.

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Provide $\rho_p = \rho_p(P, T, \{\eta_p^C\})$

Provide or ignore capillary pressure

$P_l - P_n = P_c(S_l)$. [+1]

Assume isothermal conditions T known. [+1]

Assume immiscibility $\eta_l^N = 0, \eta_n^W = 0$. [+2]

Variables [+11]

Saturations S_l, S_n [+2]   +1

Mass fractions $\{n_p^C\}$ [+4]   +2

Phase velocities v_p [+2]

Phase pressures P_p [+2]   +1

Temperature T [+1]

-2

NUMBER?

In practice, we eliminate many unknowns, and solve (5) for one P_p and one S_p

More complicated example, 2×2

Example II.2 (VLE example, $N_p = 2, N_C = 2$, miscible case)

Consider (1), with $C = W, N$, and $p = l, n$ (Water and Oil (or Gas) and liquid and nonwetting=nonaqueous) phases. Set $\eta_s^C = 0$.

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$$\partial_t \left(\phi(\rho_l S_l \eta_l^N + \rho_g S_g \eta_g^N) \right) + \nabla \cdot (J_l^N + J_g^N) = q_N. \tag{6b}$$

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Darcy's law $v_p = v_p(S_p, \nabla p)$ [+2]
Provide $\rho_p = \rho_p(P, T, \{\eta_p^C\})$
Provide or ignore capillary pressure
$P_l - P_n = P_c(S_l)$. [+1]
Provide energy equation for T.   [+1]
Provide/solve VLE for η_p^C. [+2]

Variables [+11]

Saturations S_l, S_n [+2]
Mass fractions $\{\eta_p^C\}$ [+4]

Phase velocities v_p [+2]

Phase pressures P_p [+2]

Temperature T [+1]

Here the choice of primary unknowns can be tricky. We solve for T. Then we choose other primary uknowns from {one P_p, one S_p, two η_p^C}. More later.

More complicated example, 2×2

Example II.2 (VLE example, $N_p = 2, N_C = 2$, miscible case)

Consider (1), with $C = W, N$, and $p = l, n$ (Water and Oil (or Gas) and liquid and nonwetting=nonaqueous) phases. Set $\eta_s^C = 0$.

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$P_l - P_n = P_c(S_l).$ [+1]

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Variables [+11]

Saturations S_l, S_n [+2]   +1

Mass fractions $\{\eta_p^C\}$ [+4]   +2

Phase velocities v_p [+2]

Phase pressures P_p [+2]   +1

Temperature T [+1]

-2

NUMBER?

Here the choice of primary unknowns can be tricky. We solve for T. Then we choose other primary uknowns from $\{one\ P_p,\ one\ S_p,\ two\ \eta_p^C\}$. More later.

Deceivingly simple example

Example II.3 ($N_p = 2$ ($p = l, g$), $N_C = 1$ ($C = W$))

Mass conservation

$$\partial_t(\phi \sum_n \rho_p S_p) + \sum_n \nabla \cdot (J_p) = q$$

Simulates water flow in (hypothetical) conditions when both the liquid and gas phases (vapour, steam) phase can be present.

(Realistic models include air component).
Must know J_p=advection (velocity from Darcy's law)+ diffusion (Fick's law).

Phase data

PT diagram for [water] Antoine equation

L, p=l
P > PSAT

T= 100
DeltaP=-0.5565

V, p=g
P < PSAT
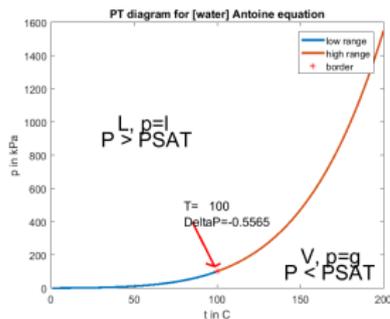
Also, need $\rho_p(P, T)$.

Phase solver

Primary unknown: P.
If $P < P^{sat}(T)$, $p = g$.
If $P > P^{sat}(T)$, $p = l$.
What if $P = P^{sat}(T)$?

Need an an energy equation

... or assume T is known.

Continue Ex. II.3. What else is needed

Need density $\rho_p(P)$ for $p = l, g$. Also, what if $P = P^{sat}(T)$?

"Gas density determined from gas side of saturation line"
"Aqueous density determined from liquid side of saturation line"

- EOS: gives V for a given P, T and thus density; see PV diagram
- Or, use lookup tables
  NIST REFPROP, ASME steam tables, Engineering Toolbox, or ...

If $P = P^{sat}(T)$
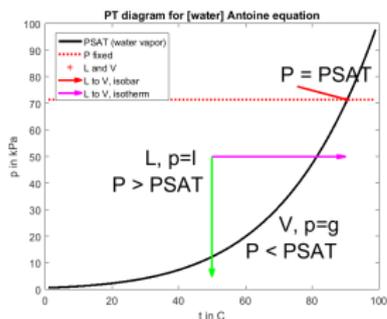
PV diagram
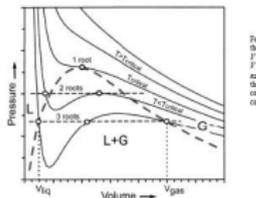
Fig. B1. Illustration of P-V-T relationships calculated with the Redlich-Kwong equation (Eqn. B1) or similar cubic equations of state for a pure fluid (G = gas, L = liquid, and the dashed line denotes the phase boundary). See text.

Can calculate the density
$\rho_l(P, T), \rho_g(P, T)$ from EOS.

EOS=Equation Of State is substance specific. More than 100 EOS!!!

Given P, T, solve for V_M. $\quad P = \frac{RT}{V_M - b} - \frac{\theta(V_M - \eta)}{(V_M - b)(V_M^2 + \delta V_M + \varepsilon)}$

Values of a, b are known for a given component.
Or, rewrite using z-factor $z = \frac{PV_M}{RT}$. Solve
$z^3 - z^2 + z(A - B - B^2) - AB = 0$, where, e.g., $A = \frac{aP}{(RT)^2}$.

- Ideal gas $\quad P = \frac{RT}{V_M}$

- VdW $\quad P = \frac{RT}{V_M - b} - \frac{a}{V_M^2}$

- RKS $\quad P = \frac{RT}{V - b} - \frac{a}{(V_M)(V_M + b)}$

- PR $\quad P = \frac{RT}{V_M - b} - \frac{a}{(V_M^2 + 2bV_M - b^2)}$

`Algebra example:  calculate` B.
`Calculate` ϕ `for a gas obeing VdW:` $\ln\phi = \frac{b}{V_M - b} - \frac{2a}{RTV_M} - \ln(1 - \frac{a(V_M - b)}{RTV_M^2})$

Back to Ex. $N_p = 2$, $N_C = 1$, STOMP

How to use EOS in practice

Look-up tables.

What if capillary pressure is important?

STOMP uses the ASME Steam Table formulations to compute the vapor pressure of water, which is a function of temperature. This vapor pressure is then reduced via the Kelvin equation for capillary pressure. This vapor pressure then serves as the partial pressure of water in the gas phase, which is used to compute the mole and mass fractions of water in the gas phase. The remaining component is air. If the vapor pressure equals the gas pressure, then the gas phase is fully saturated with water vapor. Transitions from single-phase aqueous to two-phase gas-aqueous occurs when the sum of the air and water vapor exceed the aqueous pressure, thus creating capillary pressure and unsaturated conditions.

Forsyth, Simpson '1999

$N_p = 1$, $N_c = 2$ (water and solute)

Mass conservation ($S_l = 1$)

$$\begin{aligned}
\partial_t(\phi \rho_l \eta_l^C) + \nabla \cdot (J^C) &= q_C \\
\partial_t(\phi \rho_l \eta_l^W) + \nabla \cdot (J^W) &= q_W
\end{aligned}$$

Model simulates water flow and the advection-diffusion of solute.
If water assumed incompressible, we retrieve the usual Darcy eqn
solved for the flow, and transport equation solved for concentration
$\rho^C = \rho_l \eta_l^C$.

Primary unknowns: P, and ρ^C.
No phase solver necessary, but we may need $\rho_l(P)$. E.g., assume
slightly compressible liquid.

EOS, multiple components (mixture)

In EOS (such as PR, or RKS)

... replace a, b by $a = \sum_j x_i x_j a_{ij}$, $b = \sum_i x_i b_i$.
Interaction coefficients $a_{ij} = (1 - \delta_{ij})\sqrt{(a_i a_j)}$.

Pure components might not have "ideal behavior".
Density and other calculations get difficult.
When $N_p > 2$, and $N_C > 2$, things get harder.

Back to Ex. II.2 $N_p = 2$ $N_C = 2$, fun example

Motivation: CO2 in a soda bottle

Closed bottle, $P \in [270, 380]kPa$, at room $T = 20C$.
Outside the bottle, $P \approx 100kPa$.

Closed bottle: $P > P^{sat}$. Open bottle: $P < P^{sat}$.
Of course, P^{sat} now is for CO2 dissolved in water.

Variables involved in phase equilibria: P, T, x_1, x_2, y_1, y_2

Now $x_1 = \eta_l^W$, $x_2 = \eta_l^{CO2}$, $y_1 = \eta_g^W$, $y_2 = \eta_g^{CO2}$.
How to calculate these after the bottle is opened?
What is the proportion of the moles n_l in $p = l$ and n_g in $p = v$
phases? (Sometimes denoted by $\mathcal{L}$ and $\mathcal{V}$).

How to solve for equilibria

Must identify primary variables. Must have data on η_p^C.

Typically $\quad \eta_p^C = \eta_p^C \left(P, T; \left\{ \eta_p^C \right\}_{p=1,\dots N_p, C=1,\dots C} \right)$

$P \quad T \qquad\qquad N_C$

$$\left(\eta_p^C \right)_{p,C}, \; (S_p)_p$$

Phase behavior solver determines the composition, primary & secondary unknowns

VLE solver for Ex. II.2 $N_p = 2, N_C = 2$

Binary mixture ($N_C = 2$), which can be in a liquid or vapour phase, or a mixture of these. VLE=Vapour-Liquid-Equilibrium.

Example II.4 (VLE calculations)

(A) For a given P, T, produce a phase diagram.
Instead of one $P^{sat}(T)$ curve separating L and V regions, we have a lot more.
(B) At a given P, T, and for overall composition z_i, what are the proportion of the phases?
This is called "flash" solver.

Assume ideal properties (Raoult's law $y_i P = x_i P_i^{sat}$.).
Assume Antoine eqn holds (T[C], P[kPa]), $\ln P_j^{sat}(T) = A_j - \frac{B_j}{T+C_j}$. (Invert for $T_j^{sat}(P)$ if needed.) Recall $P = \sum_i P_i$ thus at bubblepoint

$$PBUB[P \text{ at bubblepoint }] = \sum_i x_i P_i^{sat} \qquad (7)$$

$$PDEW[P \text{ at dewpoint }] = \frac{1}{\sum_i \frac{y_i}{P_i^{sat}}} \qquad (8)$$

$$[\text{FRACTIONS }] \sum_i x_i = 1 = \sum_i y_i. \qquad (9)$$

Example for VLE

Component 1, (acetonitrile) $A_1 = 14.2724; B_1 = 2945.47; C_1 = 224.00$;
Component 2, (nitromethane) $A_2 = 14.2043; B_2 = 2972.64; C_2 = 209.00$;

Example II.5 (Given $T = 75C$, produce P-x_1 and P-y_1 plots)

Soln: write
$P = P(T; x_1) = P_1^{sat}(T)x_1 + (1 - x_1)P_2^{sat}(T)$.
The plot $(x_1, P(T; x_1))$ is the bubblepoint plot.

Write $y_1 = x_1 \frac{P_1^{sat}(T)}{P(T; x_1)}$. The plot $(y_1, P(T; x_1))$ is the dewpoint plot.
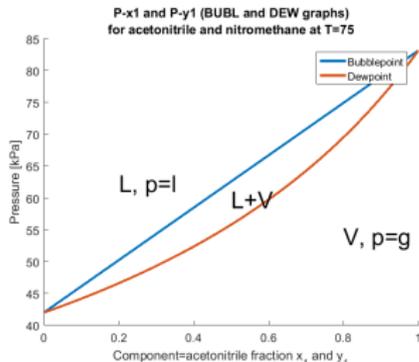
Example II.6 (Produce PT diagram for a binary mixture)

Soln: assume $z_1 = 1$. Continue as on the left. Move on to $z_1 = 0.5$ etc.
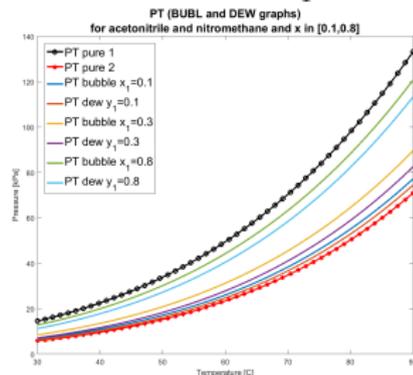
Note: close to the critical regime the bubble and dew curves curve and coalesce.

Data from [Smith, Van Ness, Abbott'2001]. My MATLAB code at
http://math.oregonstate.edu/~mpesz/GS19/

K values, and how to use them

Define $K_i = \frac{y_i}{x_i}$, from Raoult's law $K_i = \frac{P_i^{sat}}{P}$, thus $K_i = K_i(P, T)$. K values are published in tables.

Example II.7 (Compute K values for the Ex. II.9)
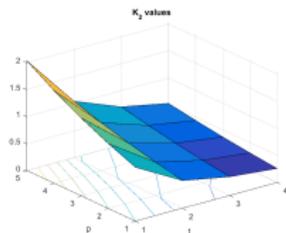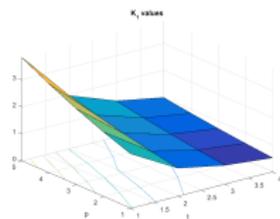
Example II.8 (Given overall composition z_1, z_2, z_3 with $N_C = 3$, and K tables for each, find PBUB amd PDEW pressures at a given $T = T_0$.)

Solution: use $y_j = z_j$ and look-up table; determine $P = P_0$ for dewpoint by trial and error for which $\sum_i y_i / K_i = 1$. Bubblepoint: similar, set $x_j = z_j$.

VLE solver, demystified

Example II.9 (Problem (B) (Flash): given T, P, and K tables, find the composition.)

Soln: Assume and total amount of mixture
$\sum z_i = 1$. We seek number $\mathcal{V}$ of moles in vapour.
Calculate or look-up K_1, K_2 values at the given
T, P.
Use $\mathcal{L} + \mathcal{V} = 1$,
and $z_i = x_i \mathcal{L} + y_i \mathcal{V}$.
Rewrite as below and solve for $\mathcal{V}$.

$$\sum_i \frac{z_i K_i}{1 + \mathcal{V}(K_i - 1)} - 1 = 0. \qquad (10)$$

Found VLE fractions: liquid= 0.35 vapour= 0.65
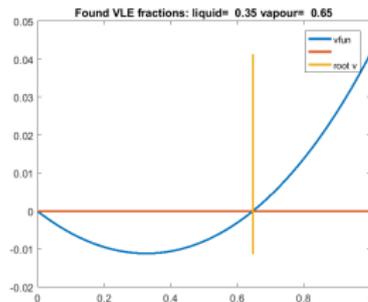
Example II.10 (Given $T = T_0$ and $P = P_0$, (PT) diagram and $z_1 = 0.6$, find the composition.)

Soln: We seek again $\mathcal{V}, \mathcal{L}$. Calculate $P_1^{sat}(T_0), P_2^{sat}(T_0)$ from (PT) diagram.
Set $x_1 = z_1$, and calculate $PBUB = P_1^{sat} x_1 + (1 - x_1) P_2^{sat}$.
Set $y_1 = z_1$, and calculate $PDEW = \frac{1}{y_1/P_1^{sat} + y_2/P_2^{sat}}$.
If $P_0 \geq PBUB, \mathcal{V} = 0$. If $P_0 \leq PDEW, \mathcal{V} = 1$.

If $PBUB < P_0 < PDEW$, do flash calculation. Calculate $K_j = \frac{P_j^{sat}}{P_0}$. Follow as in Ex. II.9 to
find $\mathcal{V}$.

Liquid-solid phase transitions

Liquid-solid phase transitions are important in materials science (steel casting), food industry (preservation of freshness with ice), and biomedical applications (cryo-surgery).

Water-ice phase transitions are crucial in the models of sea-ice and studies of the polar regions.
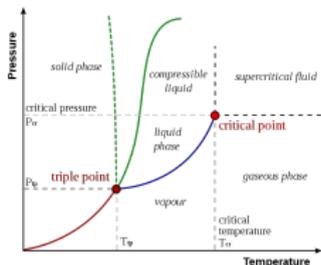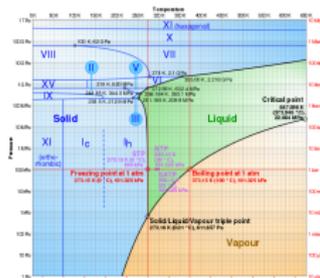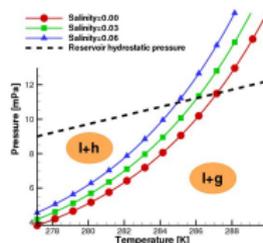
general   water   hydrate

There is no general equation predicting $P_{melting}(T)$ or $T_{melting}(P)$.

Water is anomalous: volume expands for solid.

Modeling liquid-solid, $N_c = 1$, $N_p = 2$ ($p = l, p = s$)

Mass conservation (solid phase does not move)

$$\partial_t(\phi \sum_{p=l,s} \rho_p S_p) + \nabla \cdot (J_l) = q \qquad (11)$$

Simulates flow of ice/water mixture.
Realistic model must include energy equation, $U_p = c_p T$

$$\partial_t(\phi \sum_{p=l,s} \rho_p U_p) - \nabla \cdot (K(T)\nabla T) + \nabla \cdot (v_l T) = q_T \qquad (12)$$

More commonly we solve (after simplifying the above)

$$\partial_t(T + \tfrac{L}{2}\Phi) - \nabla \cdot (K(T)\nabla T) + \nabla \cdot (v_l T) = q_T \qquad (13)$$

Here $\Phi = \text{sgn}(T)$ is the order parameter, $\Phi = -1$ in ice, $\Phi = 1$ in water.
Or, $\Phi = \Phi(x,t)$ can have its own dynamics (see IV: Phase Field
models).

Hydrate example; liquid-solid

Phase EQ in practice

By Mark White, PNNL.

Hydrate across the scales (Darcy)

Core/Darcy [m/days]

Basin [km/ka]
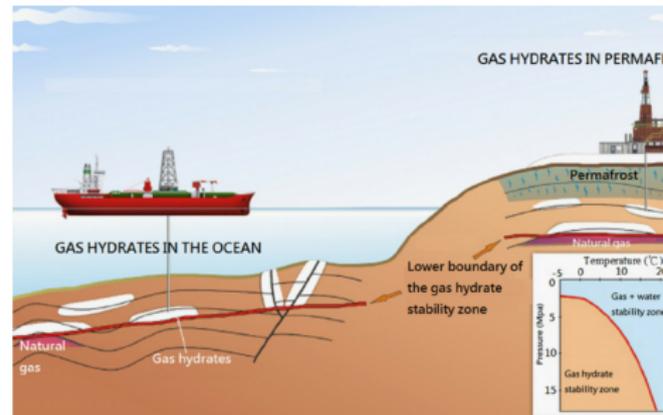
Multi-* PDEs

Mines.edu; Lu et al [Renewable and Sustainable Energy Reviews'2015]

Most of our work is based on X. Liu, P. Flemings [JGR'07], and their other work.

We were also inspired by H. Daigle et al [G3'2011] and K. Berndt [Science'2014]

Methane hydrate models

We present an idealized model of methane hydrate evolution.
It is applicable to time and spatial scale of basin modeling.
It is not directly applicable but can be adapted to production time scales.
It is the only model for MH with well-posedness analysis (+some numerical)

- M. Peszynska, Never Heard of Methane Hydrate? That Might be Good News, SIAM News, January 2018.

- Wei-Li Hong, M. Peszynska, Numerical modeling of gas hydrate dynamics in nature marine sediments: Case studies from Hydrate Ridge, Cascadia Margin and Ulleung Basin, in Gas Hydrates: from Characterization and Modeling to Applications; Chapter 11, edited by Daniel Broseta, Livio Ruffine, Arnaud Desmedt, April 2018, Wiley.

- M. Peszynska, W.-L. Hong, M. Torres, J.-H. Kim, "Methane hydrate formation in Ulleung Basin under conditions of variable salinity. Reduced model and experiments", Transport in Porous Media, 114 (1), 2016, pages 1-27

- M. Peszynska, F.P. Medina, W.-L. Hong, M. Torres, "Reduced numerical model for methane hydrate formation under conditions of variable salinity. Time-stepping variants and sensitivity". Computation (Special Issue on Advances in Flow and Transport in Porous Media), Volume 4, Issue 1, pp 1-19, 2016.

- M. Peszynska, R. Showalter, J. Webster, Advection of Methane in the Hydrate Zone: Model, Analysis, and Examples, Mathematical Methods in Applied Sciences, Volume 38, pp 4613-4629, 2015.

- N. Gibson, P. Medina, M. Peszynska, R. Showalter, Evolution of phase transitions in methane hydrate, J. Math. Anal. Appl. Volume 409, Issue 2 (2014), pp 816-833

Multi*-PDE model

Our work is based on the model [X.Liu, P.Flemings [JGR'2008]]

- Multiphase & Multicomponent $\mathcal{M} - \mathcal{S} - \mathcal{P} - \mathcal{T}$
- Thermodynamics
  - Equilibrium phase behavior (appropriate for basin scale)
  - References to data
  - 1d and 2d examples
  - 'TOUGH-2" or STOMP-HYD flavor [FaltaPruess'2002]

Our $\mathcal{M} - \mathcal{S} - \mathcal{P} - \mathcal{T}$ [PTorresTrehu[ICCS'10]]; comprehensive but delicate

Other approaches: Kinetic phase behavior (appropriate for production scale)

- [S.Gupta, R. Helmig, B. Wohlmuth [Comp.Geo'2016-]]
- STOMP-HYDT-KE

Phase behavior: what is the issue ?

phases

hydrate   liquid   gas

h   l   g

Components

S   W   M

NaCl   H2O   CH4
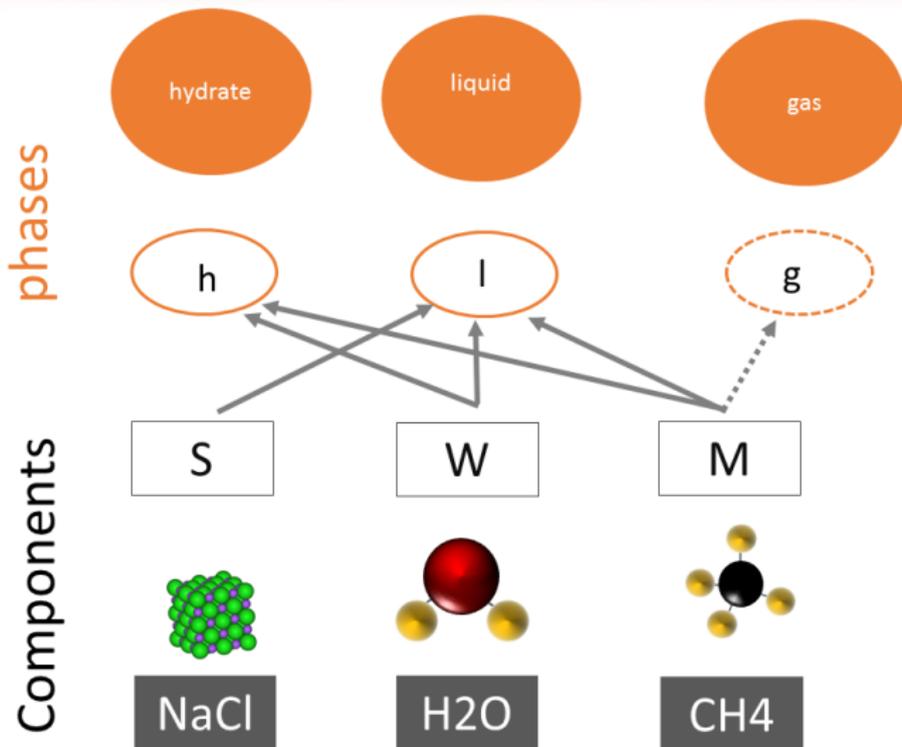
The distribution of components/phases η_{pC} depends on P, T

Hydrate in marine sediments: PT diagram
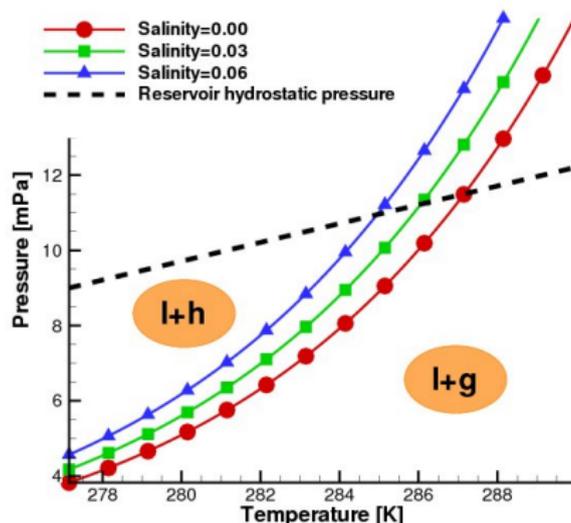
The black line shows typical relationship between $P(x)$ and $T(x)$, i.e., (PT) diagram.

$P(x)$ is hydrostatic (increases with depth)

$T(x)$ follows geothermal gradient (increases with depth).

More: hydrate **stability** in marine sediments
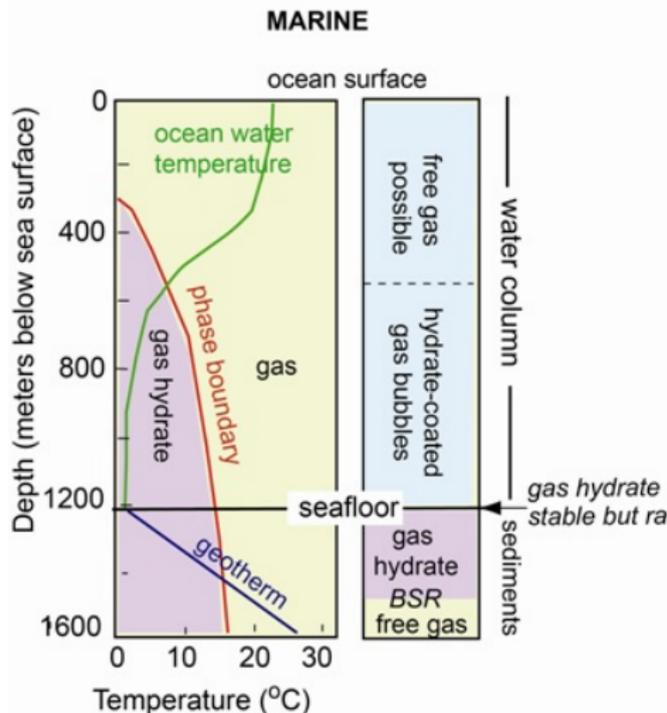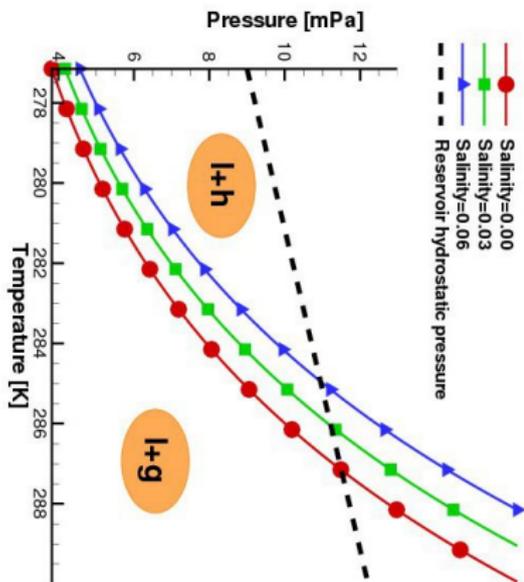
Right image from USGS; Ruppel et al'2007

*Image in the left and image on the right say the same thing*

Phase data: stability and solubility

Solubility$=\chi_{lM}$.
Maximum solubility χ_{lM}^{max} depends on (P, T, χ_{lS})
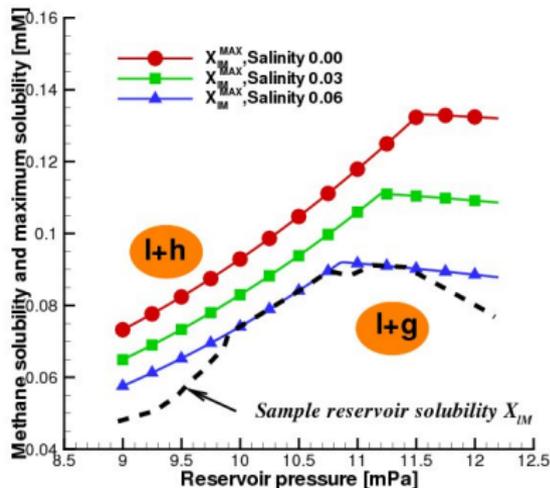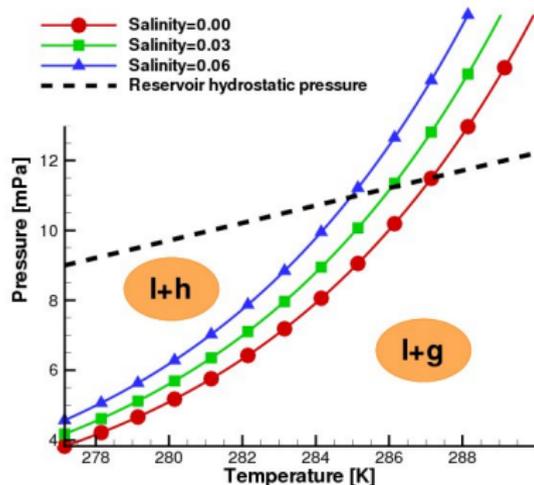
In our reduced models we fix P, T, and consider one of solubility curves $\chi^{max}(x)$.

What does "maximum solubility" mean?

If the amount of methane N_M exceeds χ_{lm}^{max},

......another phase (g or h) forms beside l.

P T small N_M
↓   ↓   ↓

↓

$\chi_{lM} < \chi_{lM}^{max}, S_l = 1$

P T large N_M
↓   ↓   ↓

↓

$\chi_{lM} = \chi_{lM}^{max}, S_l < 1$

in hydrate zone, $S_h > 0$

in gas zone, $S_g > 0$

Simple example
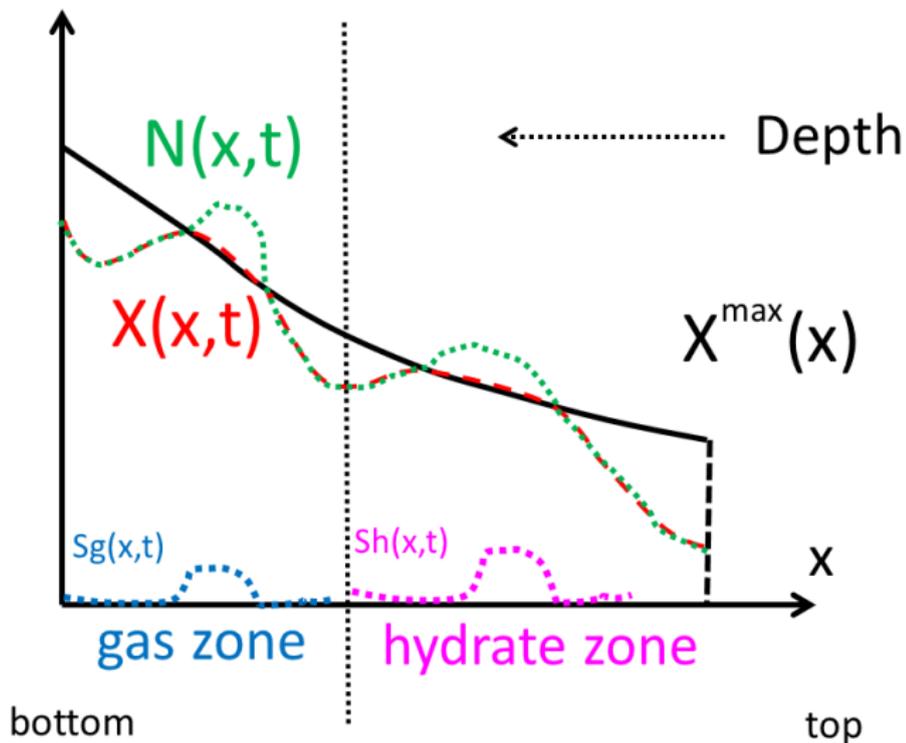
Multi*-PDE model $\mathcal{M} - \mathcal{S} - \mathcal{P} - \mathcal{T}$

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

$$\partial_t \sum_{p=l,h,g} \phi S_p \rho_p \chi_{pC}$$

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

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.

Simplification story $\mathcal{M} - \mathcal{S} - \mathcal{P} - \mathcal{T}$ to $\mathcal{M}$

The delicate and complex nature of $\mathcal{M} - \mathcal{S} - \mathcal{P} - \mathcal{T}$ begged for the analysis of the model and of numerics, which seemed impossible. However, we noticed that (some) results of [LF'08] seemed to require only the simplified evolution.

- *Thus we considered first just a very simplified $\mathcal{M}$ model, in the hydrate zone*

    - *In the end, the word "just" turned out to be inaccurate.*

- *Next we considered a less simplified $\mathcal{M} - \mathcal{P}$ model, with real thermodynamics*

- *Next we considered an even less simplified $\mathcal{M} - \mathcal{S} - \mathcal{P}$ model.*

- *Currently, we are looking at the $\mathcal{M}$ model, in the hydrate + gas zone*

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

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

- Simplify: $\phi = 1$, $\rho_l = const.$ Rewrite $\boxed{N = \rho_l^{-1}(S_l \rho_l \chi_{lM} + S_h \rho_h \chi_{hM})}$.

- Denote $\boxed{\chi = \chi_{lM}}$ amount transported

- Understand the phase behavior.

  Hydrate forms when (P, T) are favorable and when its solubility (mass fraction) χ_{lM} is at its maximum. This maximum $\chi^{max} = \chi^{max}(P, T, \chi_{lS})$. If there is more $N > \chi^{max}$, then $S_h > 0$.

  This can be written as a Nonlinear Complementarity Condition
  $\chi \leq \chi^{max}(P, T, \chi_{lS}), \ S_h \geq 0, \ (\chi - \chi^{max}(P, T, \chi_{lS}))S_h = 0$.

- If at basin scale, approximate $\chi^{max} = \chi^{max}(x)$ ("freeze (P, T)")

  - $P = P(x)$ is known (hydrostatic)
  - $T = T(x)$ is known (follows geothermal gradient)
  - $\chi_{lS} \approx const.$, or incorporate this in the approximation [PHTK'16]

- If not at basin scale, time-lag the evolution of P, T, χ_{lS}, and recompute χ^{max} after each step.

  This works well for a numerical model but it also means that our well-posedness analysis applies only locally in time.

Structure of model $\mathcal{M}$

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

- Back to NCC

  $\chi \leq \chi^{max}(P, T, \chi_{lS})$

  $S_h \geq 0$

  $(\chi - \chi^{max}(P, T, \chi_{lS}))S_h = 0$.

  Draw a diagram of χ and S_h equivalent to this NCC.
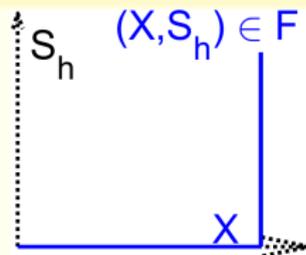
- Now notice that N and χ related by $\chi = \alpha(N)$
  - α <u>monotone,</u> but $\beta = \alpha^{-1}$ *multivalued*

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

  Mathematical structure: PME (Porous Medium Equation)
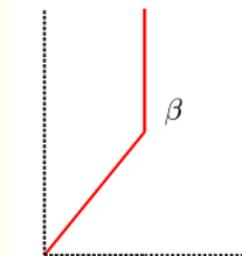
Does the theory of PME apply to $\mathcal{M}$? Almost.

Take a closer look where β is from.

Recall $N = (1 - S_h)\chi_{lM} + RS_h$, $R = const$

Reservoir solubility constraint

(S_h, X_{lM}) in **F**

F^ε

X_{lM}^{MAX}

Hydrate saturation S_h

Solubility X_{lM} [mM]
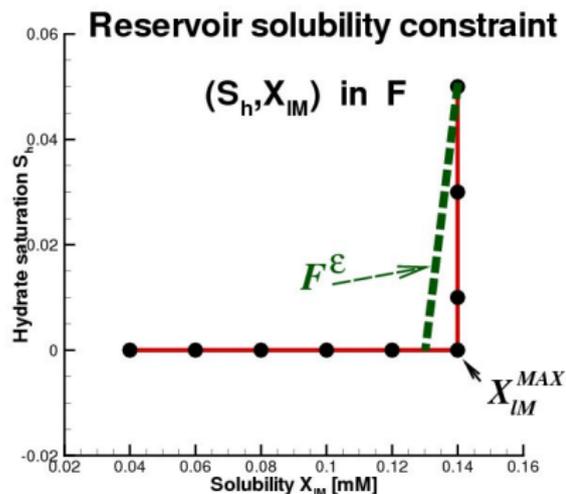
$$\begin{cases} \chi \leq \chi^{max}(x); & S_h = 0 \\ \chi = \chi^{max}(x); & S_h \geq 0 \\ (\chi^{max}(x) - \chi)S_h & = 0 \end{cases}$$

Challenge I: β and α are parametrized by depth (x). The theory of PME requires a tweak (*family of normal convex integrands*).

Summary: we approximate

$$\chi^{max}(x; P, T, \chi_{lS}) \approx \chi^{max}(x)$$

This approximation is reasonable for basin scale models. It may also work for sequential evaluation of phase behavior (e.g., production scenarios), TBA.
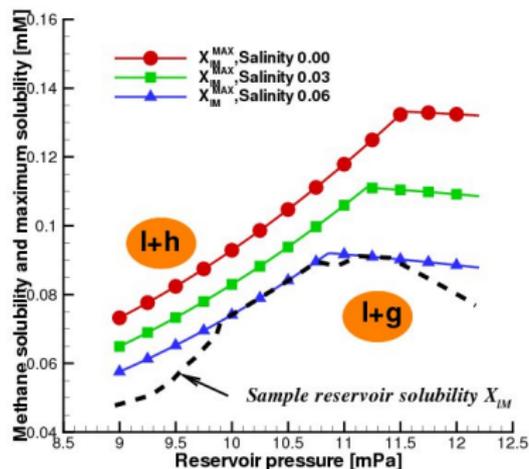

Model $\mathcal{M} - \mathcal{S} =$ two evolution PDEs.
We use $\chi^{max} = \chi^{max}(x, \chi_{lS}(x))$.

Does the theory of PME apply to $\mathcal{M}$ now ?

<u>Challenge II</u>: Theory requires that the graph β is bounded globally by affine functions.
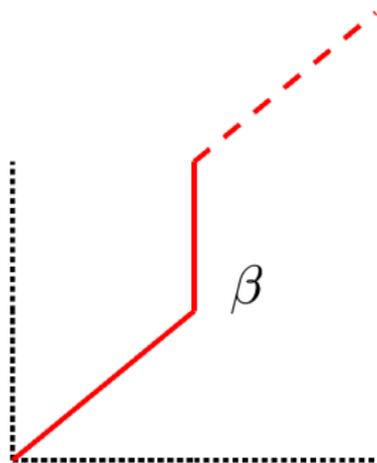
Technique to "extend"

- Extend the original β to $\bar{\beta}$ globally defined

- Prove that v never goes outside

- Conclude that the formal extension does not change our problem

<u>Challenge II overcome</u>: $\beta(x; \cdot)$ requires a comparison principle (sufficient conditions on data must be established)

What does Mathematics know about Hydrates ?

Analysis helps to assess the winner in the competition of

| Advection | × | Diffusion | × | Nonlinearity | × | Heterogeneity |

- [GMPS'14]: well-posedness (diffusion only)
- [PSW'15]: well-posedness (diffusion & advection) & examples

[[∞]] **PME & Stefan free boundary problem**

$$\partial_t N - \nabla^2 \chi = f \ \& \ N \ \boxed{\in} \ \beta(\chi)$$

[[GMPS'14]] **Well-posedness of the $\mathcal{M}$ model**

$$\partial_t N - \nabla^2 \chi = f \ \& \ N \in \beta(\boxed{\mathbf{x}}; \chi)$$

[[PSW'15]] **Analysis & examples for $\mathcal{M} - \mathcal{P}$ model**

$$\partial_t N - \nabla^2 \chi + \boxed{q \cdot \nabla \chi} = f \ \& \ N \in \beta(x, \boxed{t}; \chi)$$

Pressure equation for q; P; Dependence $\beta(\boxed{\mathbf{x,t}}; \chi)$

Some concrete mathematics

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

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

[PSW'15] Diffusion & advection, hydrate zone

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

$$S_h \text{ as bad as } N$$

Gas zone?

Further challenges (viscous and capillary terms). (Numerical)
Analysis in progress.

Implications of analysis for numerical schemes

Low-order stable discretizations are a good choice.

# What about "real reservoir data"?

- Ulleung basin case [PHTK'16, PMHT'16]
- "My" Hydrate Ridge example; inspired by [DaigleDugan]
- Case of episodic gas venting off-coast of Svalbard

The thermodynamics package in these examples is adapted from tabulated results from CSMGem by WeiLi Hong, within the framework we described in [PHTK'16]

Ex. UGBH2-7, Expedition in Korea [PHTK'16]

$Pe < 1$ $Pe >> 1$
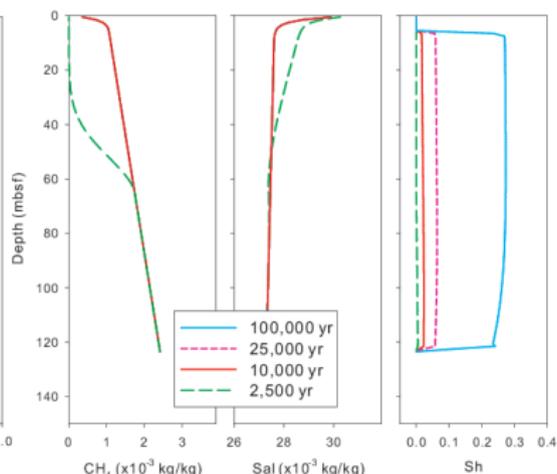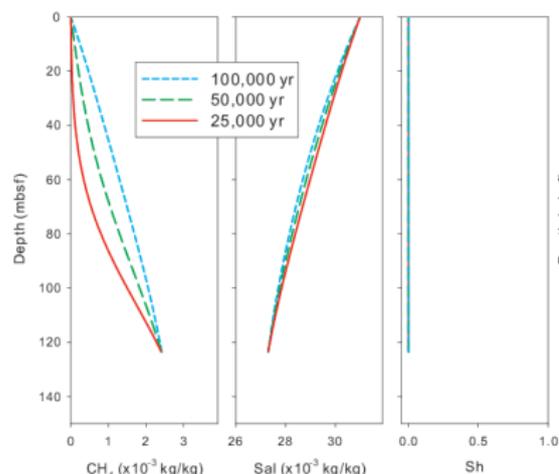
- Diffusive transport produces small hydrate presence
- Advective transport produces substantial hydrate presence
- Very large advection leads to model crash (as predicted by [PSW'15])

Ex. UGBH2-7, Expedition in Korea [PHTK'16]

Goal: explain salinity spikes (markers for hydrate), compare with [LF'06]
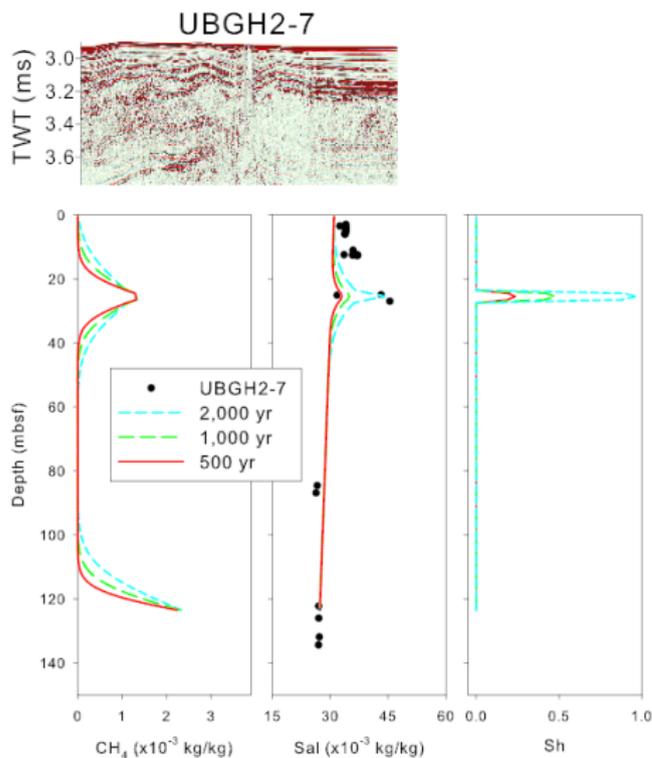
- Thermodynamics model with salinity dependence has large uncertainty

- Advective fluxes alone do not explain the salinity spikes

- Methanogenic source explains the spikes, but must be stronger than estimated

- Hypothesis [Torres'14] suggests free gas chimneys in hydrate zone. Need $\mathcal{M} - \mathcal{P} - \mathcal{S}$ model without assuming water abundance & fractures.

48 / 73

Ex.: Filling MyHydrateRidge

Challenge:

Thermodynamics depends on type of porous medium (coarse/fine)

"MyHydrateRidge"

- layered $1 - 2 - 1$ porous medium $[100 \times 100]m^2$;
- original rock type $r(x) = 1, 2$ (sand and silt)
- solubility X_{lM}^{MAX} depends on $r(x)$
- upflux [fast, not-so-slow, slow]
- when $K(S_h) \downarrow$, then $P \uparrow$, and fractures form $r(x) = 3$
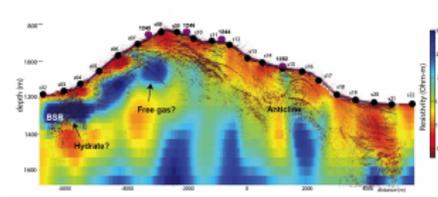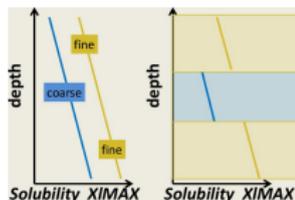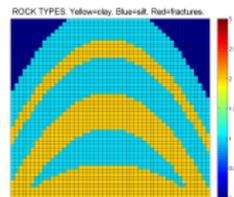
This 2D example is inspired by 1d simulations in [DaigleDugan]

Filling MyHydrateRidge
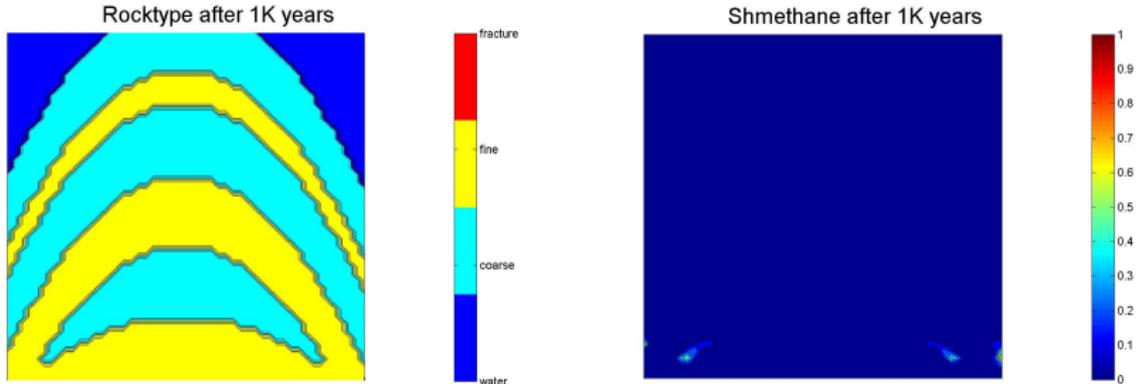
This example is available as My Hydrate Ridge Movie

*Rock type* and *Hydrate saturation*

Filling MyHydrateRidge
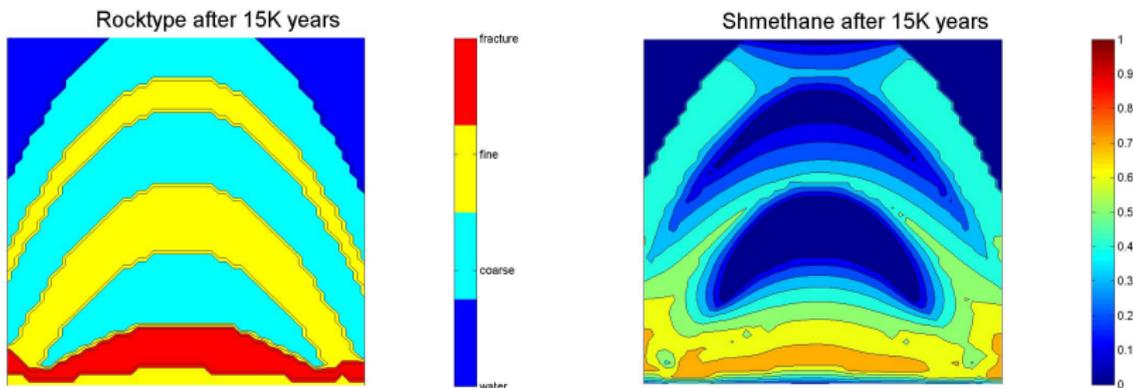
This example is available as My Hydrate Ridge Movie

Rock type and *Hydrate saturation*

# Filling MyHydrateRidge: How was it done?
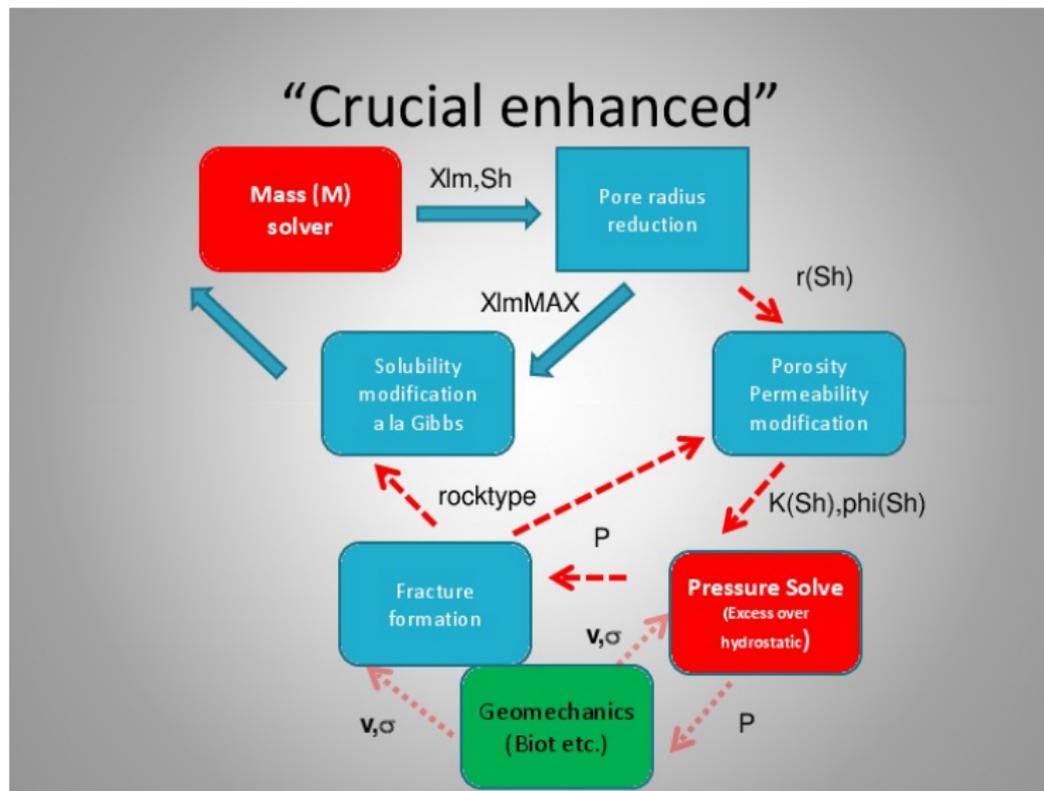
Phase field modeling

References: too many to list just one.
Materials science. Mathematics. Computational physics.
[Visintin, Phase transitions]

Phase field models: big picture

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

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

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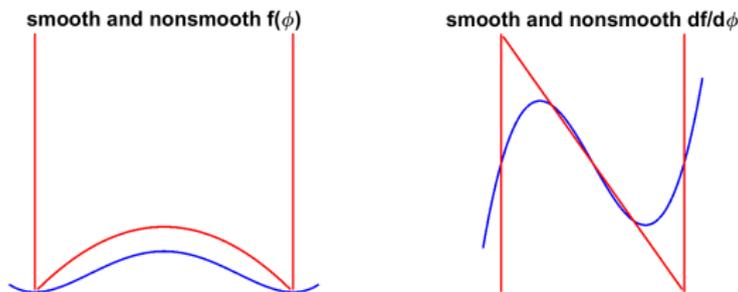
Authors: [Warren, Boettinger (1992-), Murray, Kobayashi, A.A. Wheeler, McFadden, Granasy, Kvamme, Tegze, and their collaborators (1998-)] have proposed, tested, and analyzed various formulations for multicomponent systems. Applications very successful in metallurgy. PF-TC as a mean-field theory can be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

Phase field theory (PFT)

Phase field (PF) theory="diffuse interface", with width $\approx \varepsilon$.

Mathematical perspective: instead of modeling a sharp interface, PF allows a region over which the order parameter ϕ changes.

Applications perspective: PF is an average of DFT[2] which itself is an average of MD[3] or other atomistic level calculations.

Computational science perspective: In reality, the interface region is nanometer wide. In computational models, we use $h >> \varepsilon$. However, PF helps to relax the need for sharp interface.

[2]Density Functional Theory
[3]Molecular Dynamics

Ice-water phase transition model

Stefan problem (ice–water phase transitions)

<u>Variables:</u> temperature T.
<u>Data:</u> latent heat L (*conductivities & heat capacity ignored today*).
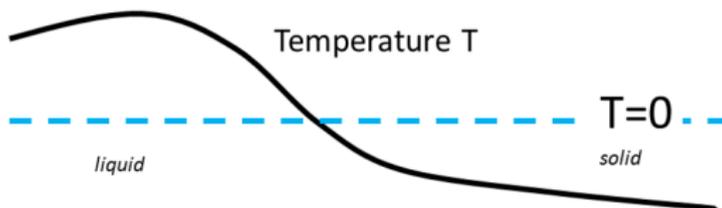
Stefan problem in the strong form

$$\partial_t(T) - \nabla^2 T = 0, \text{ on } \Omega_+ \cup \Omega_-, \& \, [\nabla T \cdot n]|_{T=0} = L n_t$$

Stefan problem in the weak form

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

Model(s) are supplemented by appropriate boundary and initial conditions

Phase transitions with order parameter

<u>Variables:</u> temperature T, phase/ order parameter ϕ, enthalpy U.
Weak-form of Stefan pbm in the phase-temperature-enthalpy form

$$\partial_t \overbrace{(T + L\phi)}^{enthalpy\ U} - \nabla^2 T = 0, \quad \phi \in H(T)$$

Temperature T

T=0

liquid   *solid*

Order parameter ϕ

$\phi = 1$

$\phi = 0$
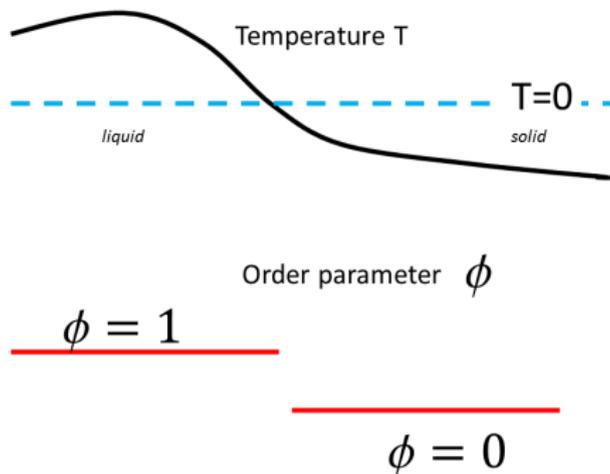
Phase field model (PFT) allows ϕ to evolve

<u>Variables:</u> temperature T, phase/ order parameter ϕ.

$$\partial_t(T + L\phi) - \nabla^2 T = 0 \qquad (14)$$

$$\partial_t\phi - \epsilon\nabla^2\phi + \frac{1}{\epsilon}\varpi(\phi) = LT \qquad (15)$$

Temperature T

T=0

liquid   *solid*

Order parameter ϕ

$\phi = 1$

$\phi = 0$
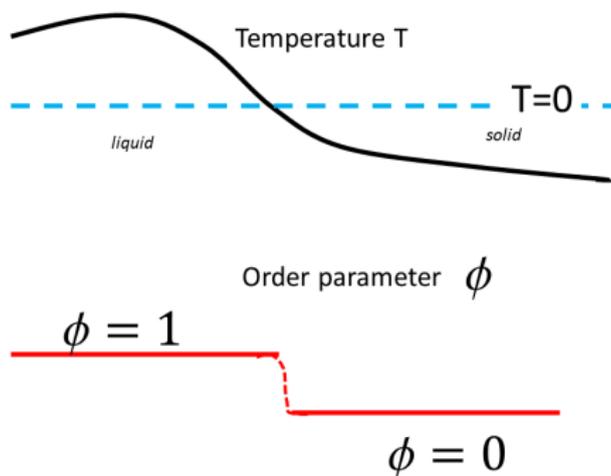
Evolution of ϕ in PFT is a competition

<u>Variables:</u> temperature T, phase/ order parameter ϕ.

$$\partial_t(T + \tfrac{L}{2}\phi) - \nabla^2 T = 0 \qquad (16)$$

$$\partial_t\phi - \epsilon\nabla^2\phi + \frac{1}{\epsilon}\varpi(\phi) = LT \qquad (17)$$

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

Temperature T

If heat is supplied, the melting front moves right

T=0

liquid   solid

$\phi = 1$

Diffusion smooths

T>0 provides a source term so the melting front moves right

$\phi = 0$

Nonlinearity aggregates (coarsens)
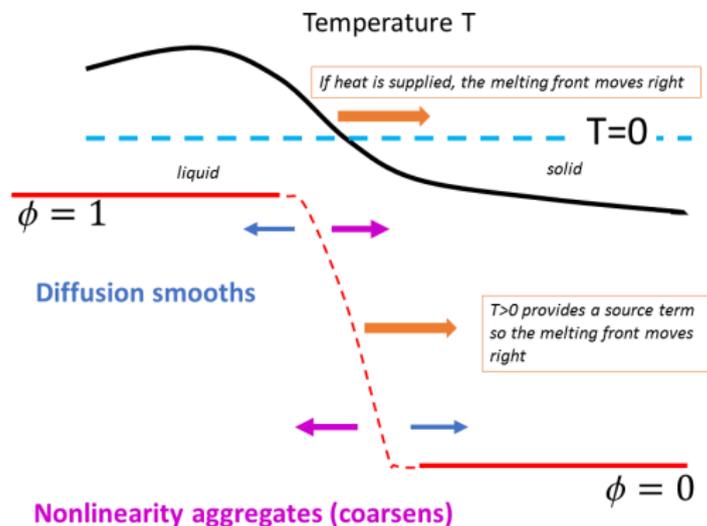
Order parameter notation

Admittedly, one of the biggest challenges when reading literature on PF is the lack of standard notation on order parameter.

Possibilities that I have seen

- $\phi = 1$ in liquid, $\phi = -1$ in solid
- $\phi = 1$ in liquid, $\phi = 0$ in solid
- $\phi = 0$ in liquid, $\phi = 1$ in solid
- $0 \leq \phi_j \leq 1$, $\sum_j \phi_j = 1$

Below we use $\phi = 1$ for liquid and $\phi = -1$ for solid.

Thus Stefan problem changes to

$$\partial_t(T + \tfrac{L}{2}\phi) - \nabla^2 T = 0, \quad \phi \in \mathrm{sgn}(T)$$

ODE evolution model of ϕ driven by T

Write $\phi \in \text{sgn}(T)$ equivalently as $\text{sgn}^{-1}(\phi) \ni T$.

Now give ϕ its own dynamics (i.e., this is kinetics instead of EQ)

$$\partial_t \phi + \quad \text{sgn}^{-1}(\phi) \ni T, \ t > 0$$

- Solution $\phi(t) \in Dom(\text{sgn}^{-1})$, $\forall t$, i.e. $-1 \le \phi(t) \le 1$
- In fact, must also have $\phi(0) \in Dom(\text{sgn}^{-1})$
- If $T = 0$, then nothing happens
- If $T > 0$, ϕ increases only up to $\phi = 1$
- If $T < 0$, ϕ decreases only down to $\phi = -1$

Introduce the notion of constraint graph

$c(\phi) = \text{sgn}^{-1}(\phi) = \partial I_{[-1,1]}$. Here I_K is the indicator function of a set (equal 0 on the set, and ∞ outside K.)

Smooth PF model

People uncomfortable with (multivalued) graphs $c(\phi) = \text{sgn}^{-1}(\phi)$ can use instead the regularized, smooth version e.g. $\varpi(\phi) = \frac{1}{\varepsilon}\phi^3$, or the Yosida approximation $c_\lambda(\phi)$.

Now ϕ with "smoother" dynamics

$$\partial_t \phi + (\phi)^3 = T, \, t > 0$$

- But, solution $\phi(t)$ is not guaranteed to stay in $[-1, 1]$.
- Even worse, if $T = 0$, $\phi(t)$ converges to the trivial equilibrium (half-water, half-ice.)

To achieve and control proper dynamics, with stable equilibria at $-1, 1$...., use $\varpi(\phi) = \phi^3 - \phi$

$$\partial_t \phi + \frac{1}{\varepsilon}(\phi^3 - \phi) = T, \, t > 0$$

ODE evolution model, $T = 0$

Consider $\partial_t \phi + \varpi(\phi) = 0$, with $\phi(0) = \phi_0$.

Choose $\varpi(\phi)$ to promote phase separation.
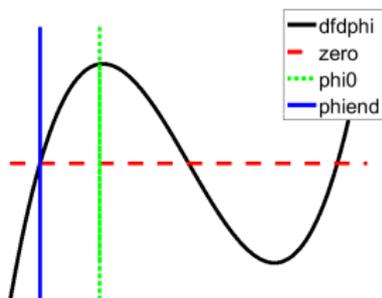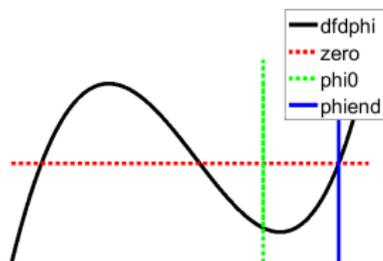
$\phi_0 < 0.5$; $\phi(t) \to \phi_{end} = 0$ $\phi_0 > 0.5$; $\phi(t) \to \phi_{end} = 1$

Compare smooth and nonsmooth $\varpi(\phi)$
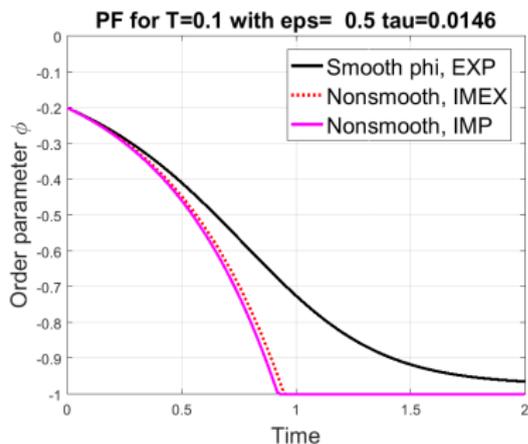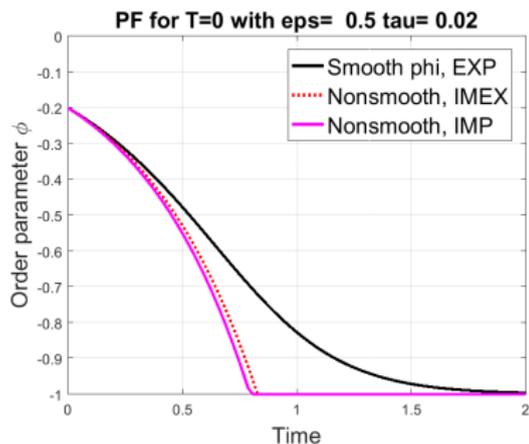
When $T > 0$, smooth model has an equilibrium $\phi_\infty \neq -1$.

*It almost does not matter for the non-smooth model whether we treat the destabilizing term explicitly or implicitly.*

PF replaces equilibrium model $\boxed{\phi \in \text{sgn}^{-1}(T)}$ by

...

PF-T models derived from (postulated) Ginzburg-Landau (Cahn-Allen) energy
functionals, or from thermodynamics focus on entropy (Penrose-Fife).
Conserved? (order, concentration, energy ...) involves ∇^4.

- Phase field (smooth version)

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

  - $\varpi(\phi) = \frac{\partial f}{\partial \phi}$ where $f(\phi)$ is the "double-well" potential
  - $-\varepsilon \nabla^2 \phi$ and $\varepsilon^{-1} \varpi(\phi)$ compete with each other diffuse &
    sharpen the interface, and keep $0 \le \phi \le 1$

- Parabolic Variational Inequality (non-smooth version)

  $$\boxed{\partial_t \phi - \varepsilon \nabla^2 \phi + \varepsilon^{-1}(1 - 2\phi + \lambda) = LT}$$

  - λ is the Lagrange multiplier (penalty term) which keeps
    $0 \le \phi \le 1$; [A. Alhammali, MP on PVI]

# Illustration how coarsening works in PF models

Non-conserved PFT (Cahn-Allen)	Conserved PFT (Cahn-Hilliard)

Cahn-Allen movie   Cahn-Hilliard movie

The simulation shows coarsening behavior starting from white noise
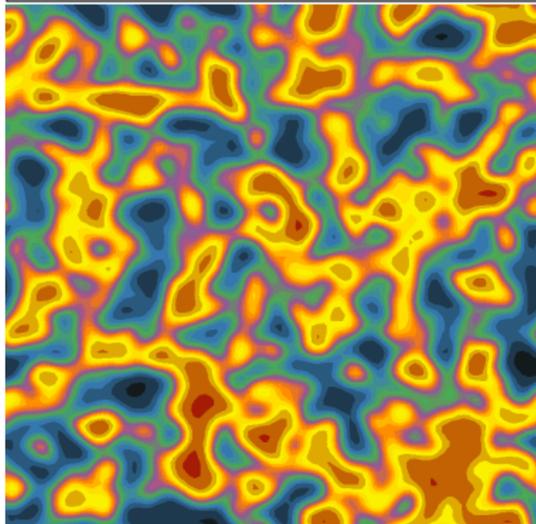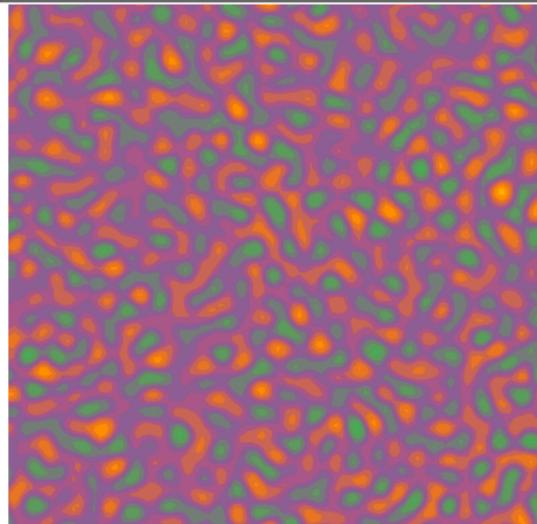
Illustration of PF models

The simulation shows coarsening behavior starting from white noise

Illustration of PF models

| Non-conserved PFT (Cahn-Allen) | Conserved PFT (Cahn-Hilliard) |
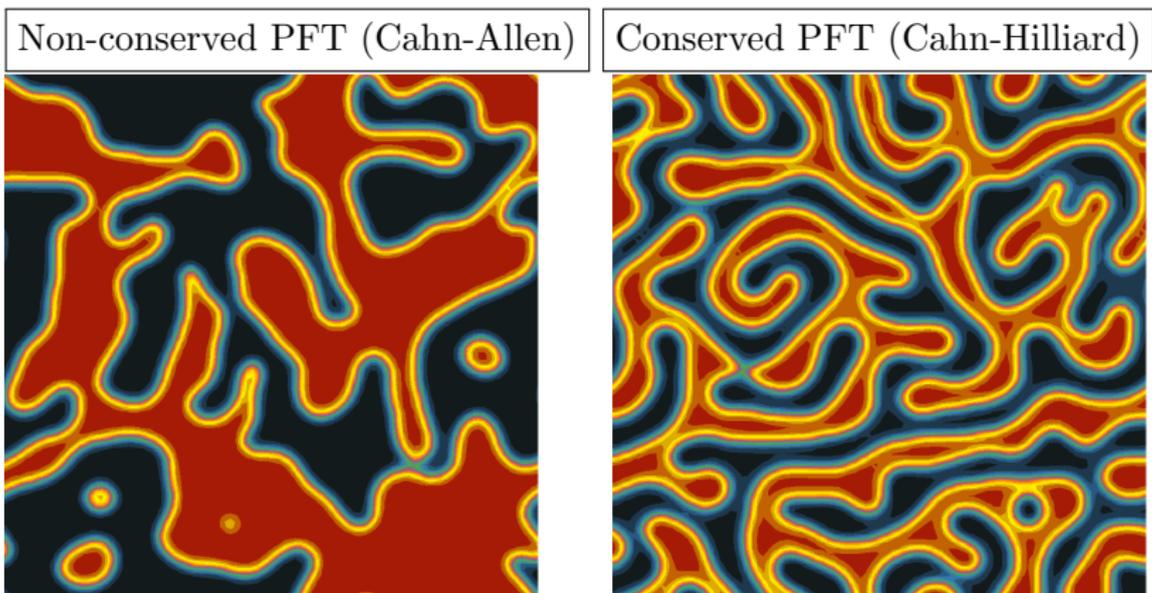
The simulation shows coarsening behavior starting from white noise

Illustration of PF models

Non-conserved PFT (Cahn-Allen)
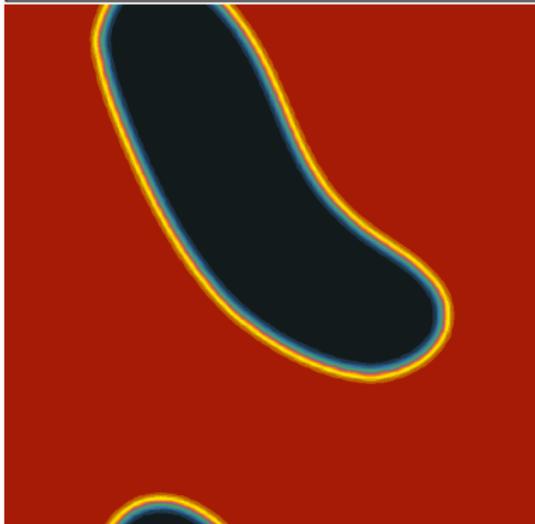
Conserved PFT (Cahn-Hilliard)
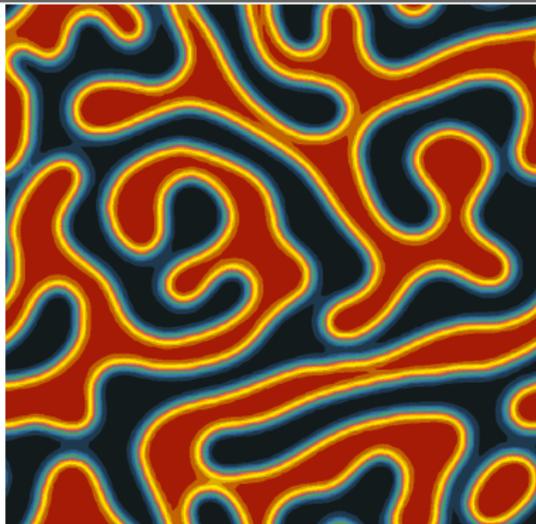
The simulation shows coarsening behavior starting from white noise

Computations with PF models

- Challenge (i): multitude of parameters: some physical, some phenomenological;
- Challenge (ii): want to resolve interface width? But it is $O(nm)$!
  - adaptive gridding of course? Hmmm.
  - resolving fine interfaces rarely feasible for realistic 3d media
- Challenge (iv): time scales and time-stepping delicate
  - convexity splitting may be helpful [with L. Bigler]
- Challenge (iv): boundary conditions largely ignored; wetting angle condition difficult to enforce

Computational physics/chemistry/material science approach: Just Do It!

- use explicit models, with/or ingenuous structure-preserving semigroup solvers [OonoPuri'88], [LiuGoldenfeld'90]; DLA

- add stochastic noise to promote dendrites

Summary: PF (T, ϕ). Outlook towards (T, ϕ, c)

<u>Variables:</u> temperature T, phase/ order parameter ϕ.

$$\partial_t(T + L\phi) - \nabla^2 T = 0 \qquad (18)$$

$$\partial_t \phi - \epsilon\nabla^2 \phi + \frac{1}{\epsilon}g(\phi) = LT \qquad (19)$$

ε *is the width of interface;* $\varpi = \frac{dW(\phi,T)}{d\phi}$; W *is the energy functional*

- Stefan pbm is well studied; low regularity of solutions (U, T)
- PF model (T, ϕ) is very well studied, in various variants (Cahn-Allen, Cahn-Hilliard,...)
- Numerical simulation challenging: nonconvex nonlinearities; time stepping; fine grid needed for small ϵ
- PFT accounts for one component, two phases (one immobile)
- Modeling challenges: PFT for multiple components, two mobile phases (or more).
- Crystals in mixtures? Require PF (T, ϕ, C) and $W(T, \phi, c)$

PF for miscible case

See talk in minisymposium by B. Riviere & M. Prodanovic.

The End

Some materials (e.g., code capsules) are/will be/ posted on my
website.
http://math.oregonstate.edu/~mpesz/GS19
If you are interested, please let me know.