Equation-Of-State Based Diffuse Interface Modeling of Multi-Component Two-Phase Flow with Partial Miscibility

Shuyu Sun
King Abdullah University of Science & Technology

In collaboration with:
X. Fan (KAUST), J. Kou (Hubei Eng U), Y. Li (KAUST), Z. Qiao (HK Poly U), T. Zhang (KAUST).

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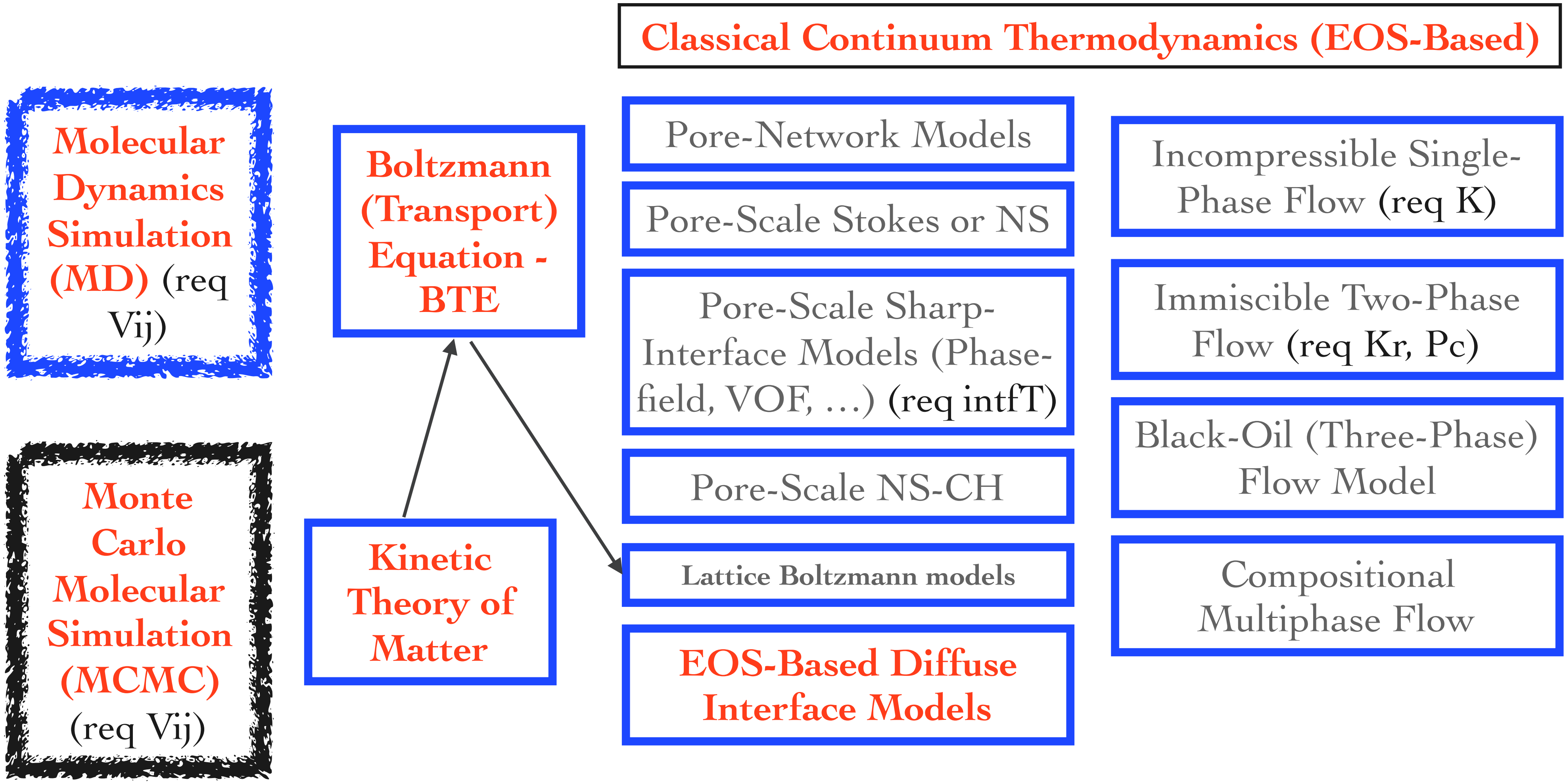
Introduction and Motivation

Modeling Porous Media Flow/Transport at Various Scales



Classical Continuum Thermodynamics (EOS-Based)

Molecular Dynamics Simulation (MD) (req Vij)

Monte Carlo Molecular Simulation (MCMC) (req Vij)

Boltzmann (Transport) Equation - BTE

Kinetic Theory of Matter

Pore-Network Models

Pore-Scale Stokes or NS

Pore-Scale Sharp-Interface Models (Phase-field, VOF, …) (req intfT)

Pore-Scale NS-CH

Lattice Boltzmann models

EOS-Based Diffuse Interface Models

Incompressible Single-Phase Flow (req K)

Immiscible Two-Phase Flow (req Kr, Pc)

Black-Oil (Three-Phase) Flow Model

Compositional Multiphase Flow

Molecular scale
atomic … coarsening

Mesoscopic scale
… nanopore …

Pore scale
small pores … fractures …

Darcy scale
core/lab scales … field scales

Cahn–Hilliard-Navier-Stokes phase-field model

- CH-NS for incompressible immiscible two-phase flow:

$$\begin{aligned} \phi_t + \nabla\cdot(\mathbf{v}\phi) &= M\Delta\mu, \\ \mu &= \lambda(-\Delta\phi + \mu_b(\phi)), \\ \rho\left(\mathbf{v}_t + (\mathbf{v}\cdot\nabla)\mathbf{v}\right) + \mathbf{J}\cdot\nabla\mathbf{v} &= \nabla\cdot(\eta\mathbf{D}(\mathbf{v})) - \nabla p - \phi\nabla\mu, \\ \nabla\cdot\mathbf{v} &= 0, \end{aligned}$$

$$\begin{aligned} \mathbf{D}(\mathbf{v}) &:= \nabla\mathbf{v} + \nabla\mathbf{v}^T, \\ \mathbf{J} &:= \frac{\rho_2-\rho_1}{2}M\nabla\mu, \\ \rho &:= \frac{\rho_1-\rho_2}{2}\phi + \frac{\rho_1+\rho_2}{2}, \\ \eta &:= \frac{\eta_1-\eta_2}{2}\phi + \frac{\eta_1+\eta_2}{2}. \end{aligned}$$

- Implied conservation property: $\rho_t + \nabla\cdot(\rho\mathbf{v}) + \nabla\cdot\mathbf{J} = 0.$

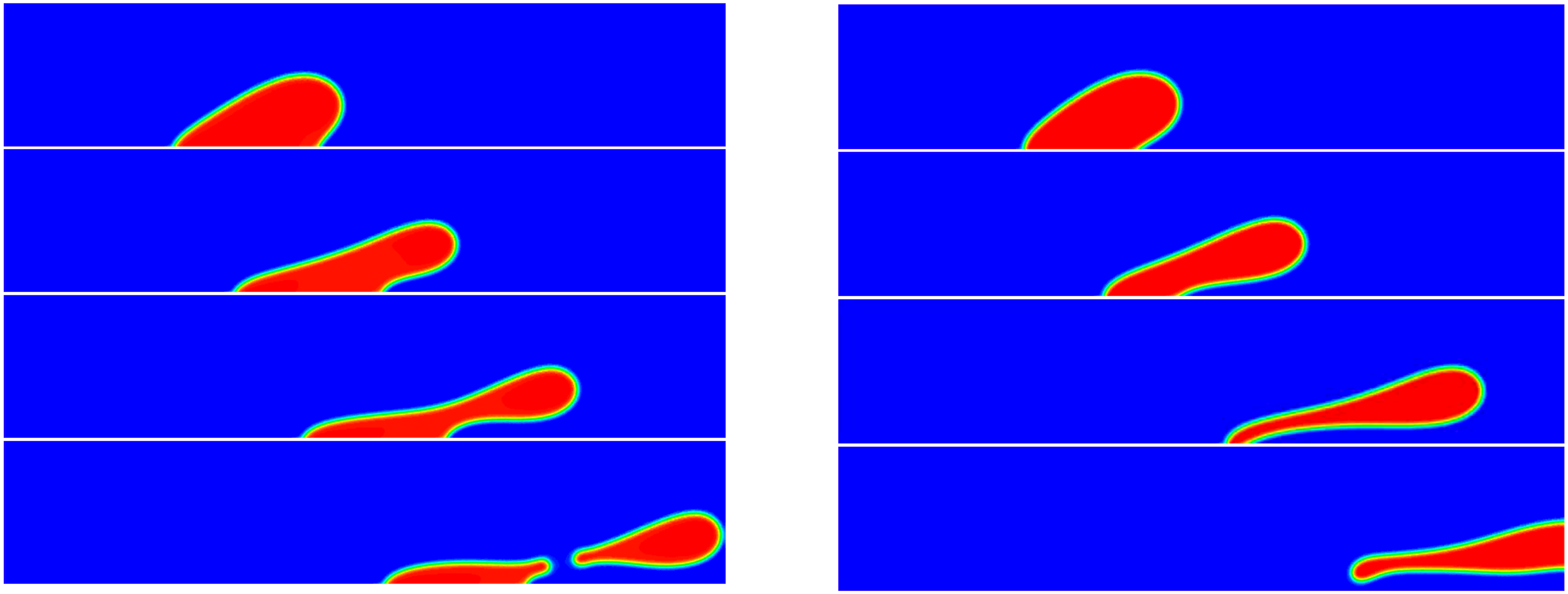
- Ginzburg-Landau double-well potential

$$F[\phi] = \lambda\int_\Omega\left(\frac{1}{2}|\nabla\phi|^2 + f_b(\phi)\right),\quad \mu = \frac{\delta F}{\delta\phi},$$

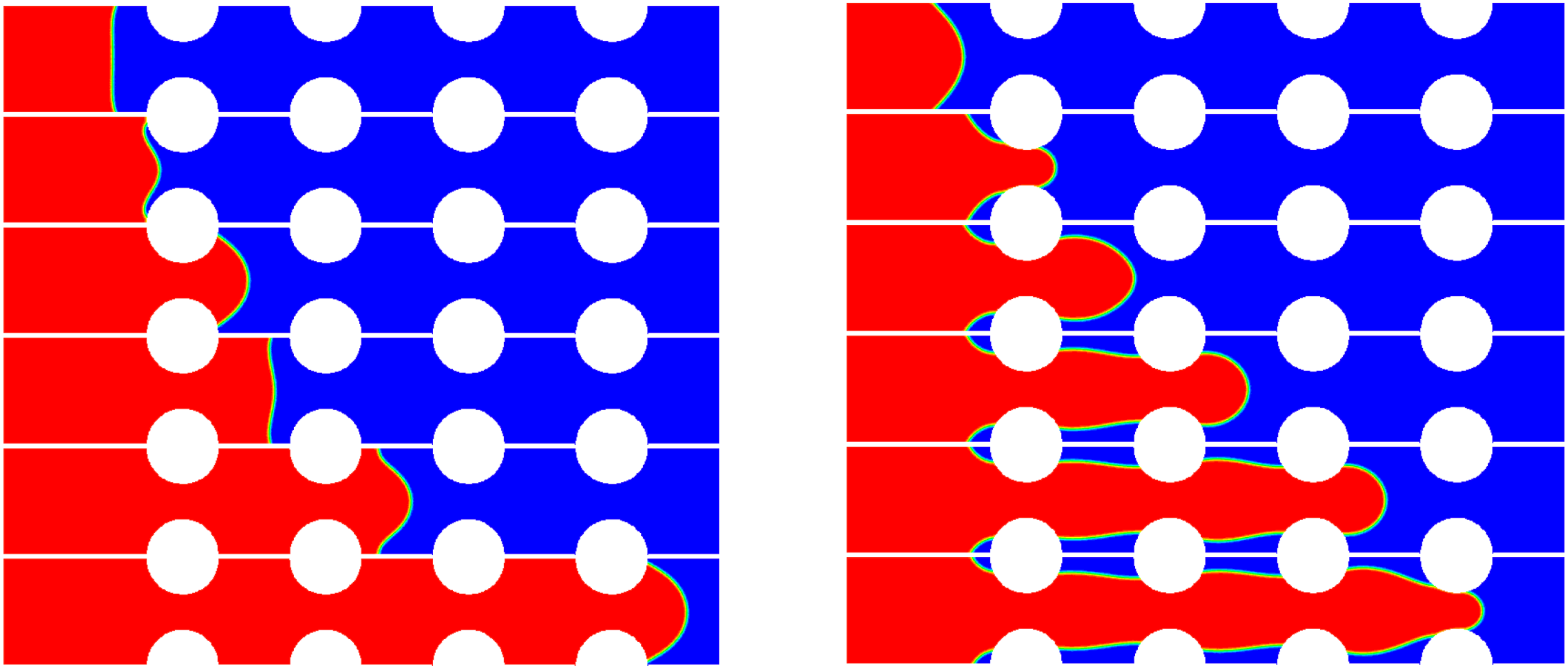
$$f_b(\phi) = \frac{1}{4\zeta^2}(\phi^2-1)^2,\quad \mu_b(\phi) = f_b'(\phi) = \frac{1}{\zeta^2}(\phi^3-\phi).$$

- Together with proper boundary/initial conditions (GNBC)

Application of CH-NS: affect of wettability to two-phase flow



Application of CH-NS: affect of surface roughness to two-phase flow



Significance of partial miscibility

- Partial miscibility as a key phenomenon
  - It is a common phenomenon in petroleum engineering, and it affects many important properties including: density, compressibility, viscosity, surface tension, wettability, relative permeability, and capillary pressure.
- An important example: **CO_2 enhanced oil recovery**
  - Injected as gas or liquid-like carbon dioxide superfluids.
  - CO_2 can be partially or completely miscible within the oil phase.
  - Major mechanisms:
    - Swelling of the oil phase due to dissolved CO_2;
    - Reduction in the viscosity of the oil due to dissolved CO_2;
    - Oil components dissolved in the CO_2 phase, which is easy to flow;
    - Possible reduction in surface tension with the reservoir rock.

DI model for compositional multiphase flow

- Momentum equation (N-S) of the diffuse interface (DI) model:

$$\begin{aligned}\partial_t(\rho\mathbf{v}) + \nabla\cdot(\rho\mathbf{v}\otimes\mathbf{v}) =& \rho\mathbf{g} + \nabla\left((\xi - \frac{2}{3}\eta)\nabla\cdot\mathbf{v} - p\right)\\ &+ \nabla\cdot\left(\eta(\nabla\mathbf{v} + \nabla\mathbf{v}^T)\right) - \nabla\cdot\left(\sum_{k,j}\lambda_{k,j}\nabla\rho_k\otimes\nabla\rho_j\right),\end{aligned}$$

- Mass conservation of the DI model:

$$\partial_t\rho_k + \nabla\cdot(\mathbf{v}\rho_k) + \nabla\cdot\mathbf{J}_k = 0, \quad \mathbf{J}_k = -\sum_j M_{k,j}\nabla\mu_j$$

- Equation of state:

$$\begin{aligned} f &= f_b(\rho_1,\cdots,\rho_N,T) + f_\nabla(\nabla\rho_1,\cdots,\nabla\rho_N),\\ \mu_j &= \mu_j^b(\rho_1,\cdots,\rho_N,T) + \mu_j^\nabla,\\ p &= p_b(\rho_1,\cdots,\rho_N,T) + p_\nabla.\end{aligned}$$

- Together with proper boundary/initial conditions.

A Few Special Cases of Interest in Petroleum Reservoirs

Cahn-Hilliard-like model for fluid mixture

- If we assume velocity vanish everywhere, the momentum equation reduces to the equation below, which we do not need:

$$0 = \rho \mathbf{g} - \nabla p - \nabla \cdot \left(\sum_{k,j} \lambda_{k,j} \nabla \rho_k \otimes \nabla \rho_j \right).$$

- Mass conservation reduces to:

$$\partial_t \rho_k + \nabla \cdot \mathbf{J}_k = 0, \quad \mathbf{J}_k = -\sum_j M_{k,j} \nabla \mu_j.$$

- Equation of state remains:

$$\begin{aligned} f &= f_b(\rho_1, \cdots, \rho_N, T) + f_\nabla(\nabla\rho_1, \cdots, \nabla\rho_N), \\ \mu_j &= \mu_j^b(\rho_1, \cdots, \rho_N, T) + \mu_j^\nabla, \\ p &= p_b(\rho_1, \cdots, \rho_N, T) + p_\nabla. \end{aligned}$$

- Together with proper boundary/initial conditions.

Allen-Cahn-like model for fluid mixture

- Again, we assume velocity vanish everywhere, we then do not need the momentum equation.

- Furthermore, we approximate the Maxwell–Stefan diffusion by the Allen-Chan equation with enforced global conservation:

$$\partial_t \rho_k = -\sum_j M_{k,j} \left(\mu_j - \mu_j^c \right) .$$

- Equation of state remains:

$$\begin{aligned} f &= f_b(\rho_1, \cdots, \rho_N, T) + f_\nabla(\nabla \rho_1, \cdots, \nabla \rho_N), \\ \mu_j &= \mu_j^b(\rho_1, \cdots, \rho_N, T) + \mu_j^\nabla, \\ p &= p_b(\rho_1, \cdots, \rho_N, T) + p_\nabla. \end{aligned}$$

- Together with proper boundary/initial conditions.

Equilibrium model for fluid mixture

- At equilibrium, the fluid velocity (at the continuum scale) vanishes everywhere; we do not need the momentum equation.

- Furthermore, both the Cahn-Hilliard-like and the Allen-Cahn-like equations reduce to

$$\mu_j = \mu_j^c.$$

- Equation of state remains:

$$\begin{aligned} f &= f_b(\rho_1, \cdots, \rho_N, T) + f_\nabla(\nabla\rho_1, \cdots, \nabla\rho_N), \\ \mu_j &= \mu_j^b(\rho_1, \cdots, \rho_N, T) + \mu_j^\nabla, \\ p &= p_b(\rho_1, \cdots, \rho_N, T) + p_\nabla. \end{aligned}$$

- Together with proper boundary conditions and given total mass of each species in the fixed domain.

NVT Flash Calculation for Bulk Phases Only

Classical NPT flash calculation

- Problem statement
    - Input data:
        - Number of species and ID of each species
        - Temperature
        - Pressure
        - The amount of each species (in moles)
    - Output variables:
        - Number of phases (assumed to be 2 for two-phase flash)
        - The amount of species i in phase j
        - Composition (mole fraction of each species) in each phase
        - Mole fraction of each phase in the mixture
        - Molar density of each phase
        - Total compressibility of the mixture
        - Partial molar volume for each species

Classical NVT flash calculation

- Problem statement
  - Input data:
    - Number of species and ID of each species
    - Temperature
    - Volume (instead of pressure)
    - The amount of each species (in moles)
  - Output variables:
    - Number of phases (assumed to be 2 for two-phase flash)
    - Pressure
    - The amount of species i in phase j; Composition in each phase
    - Mole fraction of each phase in the mixture; Molar density of each phase
    - Total compressibility of the mixture
    - Partial molar volume for each species

NVT flash versus NPT flash

- Conventionally, NVT flash is computed through a nested optimization approach. In an outer loop we iterate for pressure, which is used in the PT-flash in the inner loop to find a pressure for which the volume constraint is satisfied. This method has three drawbacks:
    - Badly computationally expensive as it needs many iterations of PT-flashes before the true pressure is obtained.
    - For specified pressure, temperature, and overall molar fractions, the equilibrium state of the system might not be uniquely determined.
    - In compositional simulation the pressure is not known a-priori and this makes the complication of constructing the pressure evolutional equation. No balance equation describes the evolution of the pressure field.

Mathematical model for liquid-gas phase equilibrium

- We consider the gas-liquid phase equilibria of the mixture of M(M ≥ 1) components with given overall volume, given temperature T and given overall mole numbers. Superscript L and G denote liquid and gas phase, respectively.

- The NVT flash problem can be formulated as

$$\{\mathbf{N}^G, V^G, \mathbf{N}^L, V^L\} = \underset{\widehat{\mathbf{N}}^G, \widehat{\mathbf{N}}^L, \widehat{V}^G, \widehat{V}^L}{\arg\min} \; F(\widehat{\mathbf{N}}^G, \widehat{\mathbf{N}}^L, \widehat{V}^G, \widehat{V}^L),$$

$$\text{subject to : } \widehat{\mathbf{N}}^G + \widehat{\mathbf{N}}^L = \mathbf{N}^t, \quad \widehat{V}^G + \widehat{V}^L = V^t,$$

$$\widehat{N}_i^\alpha \geq 0, \widehat{V}^\alpha \geq 0, \; (i = 1, 2, \cdots, M, \; \alpha = G, L).$$

- Here the total Helmholtz free energy is the sum of the contribution from each phase:

$$F(\mathbf{N}^G, V^G, \mathbf{N}^L, V^L) = f_b(\mathbf{n}^G)V^G + f_b(\mathbf{n}^L)V^L, \;\; \mathbf{n}^G = \frac{\mathbf{N}^G}{V^G}, \;\; \mathbf{n}^L = \frac{\mathbf{N}^L}{V^L}.$$

- The Helmholtz free energy density function can be modeled via EOS.

Helmholtz free energy density modeled via EoS

- In Van der Waals' equation of state, the Helmholtz free energy density of a homogeneous fluid is given by

$$f_b\left(\mathbf{n}\right) = f_b^{\text{ideal}}\left(\mathbf{n}\right) + f_b^{\text{excess}}\left(\mathbf{n}\right),$$

$$f_b^{\text{ideal}}\left(\mathbf{n}\right) = RT\sum_{i=1}^{M} n_i\left(\ln n_i - 1\right),$$

$$f_b^{\text{excess}}(\mathbf{n}) = f_b^b + f_b^a = -nRT\ln\left(1 - bn\right) - an^2.$$

- In the Peng-Robinson equation of state, the Helmholtz free energy density of a homogeneous fluid is given by

$$f_b\left(\mathbf{n}\right) = f_b^{\text{ideal}}\left(\mathbf{n}\right) + f_b^{\text{excess}}\left(\mathbf{n}\right),$$

$$f_b^{\text{ideal}}\left(\mathbf{n}\right) = RT\sum_{i=1}^{M} n_i\left(\ln n_i - 1\right),$$

$$f_b^{\text{excess}}(\mathbf{n}) = -nRT\ln(1 - bn) + \frac{a(T)n}{2\sqrt{2}b}\ln\left(\frac{1 + (1 - \sqrt{2})bn}{1 + (1 + \sqrt{2})bn}\right).$$

Solving NVT Flash by using Allen-Cahn-like equation

- Instead of solve the optimization problem, one can convert it to a differential equation system.
- One way to define iteration is to convert the time-independent differential equation to a transient problem first, followed by a robust time marching scheme.
  - Allen-Cahn-like modeling equation approach is one of the simplest methods to convert the time-independent differential equation to a transient problem.
- If we have an unconditionally stable time march scheme for Allen-Cahn-like equation with P-R EOS, then we can have a robust iterative scheme for NVT flash calculation.

For detail, see: J. Kou, S. Sun and X. Wang, "An energy stable evolutional method for simulating two-phase equilibria of multi-component fluids at constant moles, volume and temperature", Computational Geosciences, Volume 20, Issue 1, pp. 283-295, February 2016.

NVT Flash Calculation for Bulk Phases and ***INTERFACES***

Various methods to model the interface between phases

- Three common methods for modeling the phase interface:
  - Molecular dynamics or molecular Monte Carlo simulation, with a certain intermolecular potential function (e.g., Lennard-Jones potential) being assumed.
  - Sharp interface modeling uses a zero thickness two dimensional entity to model the interface, where the molar density experiences a jump across the interface, i.e., level-set method, the volume-of-fluid method, and /or the front tracking method. They commonly encounter difficulty handling topological changes, such as riches, splits and merging.
  - Diffuse interface theory (or gradient theory, or phase field theory) described the interface as a continuum three-dimensional entity separating the two bulk single-phase fluid regions. Molar or mass density changes continuously within the interface.

The gradient theory for multi-component mixtures

- For a mixture composed of M components, the Helmholtz energy of an inhomogeneous fluid can be modeled by:

$$F(\mathbf{n}) = \int_\Omega \left(f_b(\mathbf{n}) + \frac{1}{2} \sum_{i,j} c_{ij} \nabla n_i \cdot \nabla n_j \right) d\mathbf{x}.$$

- The above model contains the density gradient contribution of the Helmholtz energy.
    - It was first proposed by Van der Waals.
    - It is commonly used in phase-field and diffuse-interface models.
    - In chemical literature (especially in papers discussing the prediction of interfacial tension, it is also known as the gradient theory.

Existing methods

- The gradient theory of fluid interfaces has been successfully utilized in chemical and reservoir engineering applications, but usually without the rigorous mathematical fundamental.
- Only the standard finite difference method is applied.
- We will give some mathematical analysis for the gradient theory to calculate the surface tension.
- The adaptive finite element method will be developed and analyzed in theory.

Minimum energy principal

- Suppose that Ω is open, bounded and connected, and has a sufficiently smooth boundary. Let $V = \left(H^1(\Omega)\right)^N$, associate with the norm

$$\|\mathbf{v}\|_V^{\mathbf{2}} = \|\mathbf{v}\|_{(L^2(\Omega))^N}^{\mathbf{2}} + \sum_{i=1}^{M} \|\nabla \mathbf{v_i}\|_{(L^2(\Omega))^d}^{\mathbf{2}}.$$

- Minimize Helmholtz energy to find a minimizer $\mathbf{n} \in V$ satisfying

$$F(\mathbf{n}) = \min_{\tilde{\mathbf{n}} \in V} F(\tilde{\mathbf{n}}),$$

- subject to

$$\int_\Omega \mathbf{n}\, d\mathbf{x} = \mathbf{n}^t,$$

- where $\mathbf{n}^t = (\mathbf{n}_1^t, \ldots, \mathbf{n}_N^t)$ is the fixed amount of given substance.

Calculation of surface tension

- The surface tension σ is defined by

$$\sigma = \min_{\tilde{\mathbf{n}} \in V} (F(\tilde{\mathbf{n}}) - F_B(\mathbf{n}_B)),$$

- Let $\mathbf{n}$ be the minimizer of $F(\mathbf{n})$. With the definitions of F and F_B , we find

$$\begin{aligned}
\sigma &= \int_\Omega \left(f_0(\mathbf{n}) - f_0(\mathbf{n}_B) + \sum_{i,j=1}^{M} \frac{\mathbf{1}}{\mathbf{2}} c_{ij} \nabla n_i \cdot \nabla n_j \right) d\mathbf{x} \\
&= \int_\Omega \left(f_0(\mathbf{n}) + P - \sum_{i=1}^{M} \mu_\mathbf{i} \mathbf{n}_\mathbf{i} + \sum_{i,j=1}^{M} \frac{\mathbf{1}}{\mathbf{2}} c_{ij} \nabla n_i \cdot \nabla n_j \right) d\mathbf{x} \\
&= \int_\Omega \left(\Phi(\mathbf{n}) + P + \sum_{i,j=1}^{M} \frac{\mathbf{1}}{\mathbf{2}} c_{ij} \nabla n_i \cdot \nabla n_j \right) d\mathbf{x}
\end{aligned}$$

- where $\Phi(\mathbf{n}) = f_\mathbf{0}(\mathbf{n}) - \sum_{i=1}^{M} \mu_\mathbf{i} \mathbf{n}_\mathbf{i}$.

A finite element method for surface tension prediction

- The Euler–Lagrange equation is:

$$\sum_{j=1}^{M} c_{ij} \triangle n_j = \mu_i^b - \mu_i^c, \quad \text{in } \Omega, \quad i = 1, \cdots, M,$$

$$\mathbf{n} = \mathbf{n}_B, \quad \text{on} \quad \partial\Omega.$$

- We propose the following finite element method.

The scheme is : to find a $\mathbf{n}_h \in V_h$ satisfying

$$\sum_{j=1}^{M} (c_{ij} \nabla n_{h,j}, \nabla \varphi) = \left(\mu_i^c - \mu_i^b, \varphi\right), \qquad \varphi \in W_h, \qquad i = 1, \cdots, M.$$

- The discrete surface tension is computed by

$$\sigma_h = \int_\Omega \left(f_b(\mathbf{n}_h) - f_b(\mathbf{n}_B) + \sum_{i,j=1}^{M} \frac{\mathbf{1}}{\mathbf{2}} c_{ij} \nabla n_{h,i} \cdot \nabla n_{h,j} \right) dx$$

Error estimates on the finite element method

- Error estimate on the calculated molar densities:

$$\|\mathbf{n}-\mathbf{n}_h\|_{(H^1(\Omega))^N} \leq Ch^{\gamma}\|\mathbf{n}\|_{(H^{s+1}(\Omega))^N}$$

- where $\gamma = \min(r, s)$.

- Error estimate on the calculated interfacial tension:

$$0 \leq \sigma_h - \sigma \leq Ch^{\gamma},$$

- A posteriori error estimation for mesh adaption with the goal in reducing the error of our calculated interfacial tension.

- Details see:
  - J. Kou and S. Sun, "An adaptive finite element method for simulating surface tension with the gradient theory of fluid interfaces," *Journal of Computational and Applied Mathematics*, 255: 593–604, 2014.
  - J. Kou, S. Sun, and X. Wang, "Efficient numerical methods for simulating surface tension of multi-component mixtures with the gradient theory of fluid interfaces," *Computer Methods in Applied Mechanics and Engineering*, Volume 292, Pages 92–106, 2015.

Adaptive strategy

- Adaptive finite element methods have been widely used in scientific and engineering applications.
- For surface tension computation, the adaptive technique is capable of effectively capturing the location of interface between two phases.
- We develop a physical-based error estimator that is a computable quantity and depends on the discrete solutions only.

Newton's method

- The discrete equations arising from finite element approximation is a nonlinear system because of μ_i^0 being nonlinear function with respect to .

- Newton's method is used to solve the discrete equations, and however, the convergence of Newton's method strongly depends on the choice of initial approximations.

- We project $\mathbf{n}_H$ onto the refined mesh ε_h as the initial approximation of $\mathbf{n}_h$. This choice can ensure the convergence of Newton's iterations since

$$\sigma_H - \sigma_h \leq Ch^\gamma$$

Numerical example: Binary mixtures

- The tested mixture is methane/decane (CH4/nC10) at the temperature 311K.

- The surface tension is decreasing as the pressure is increasing as expected.

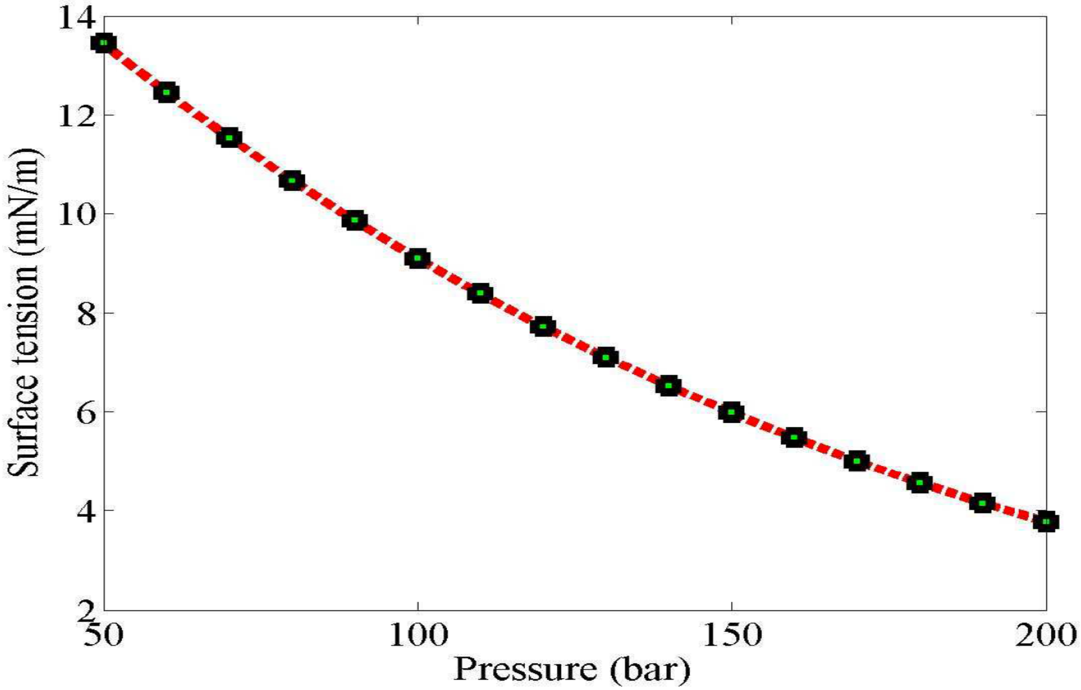


Figure: Surface tension of CH4 and nC10 mixture at 320K

Numerical solution of molar density profiles

- The following figures illustrate the mixture molar density profiles.
- We note that the profile for the light component is not monotone.

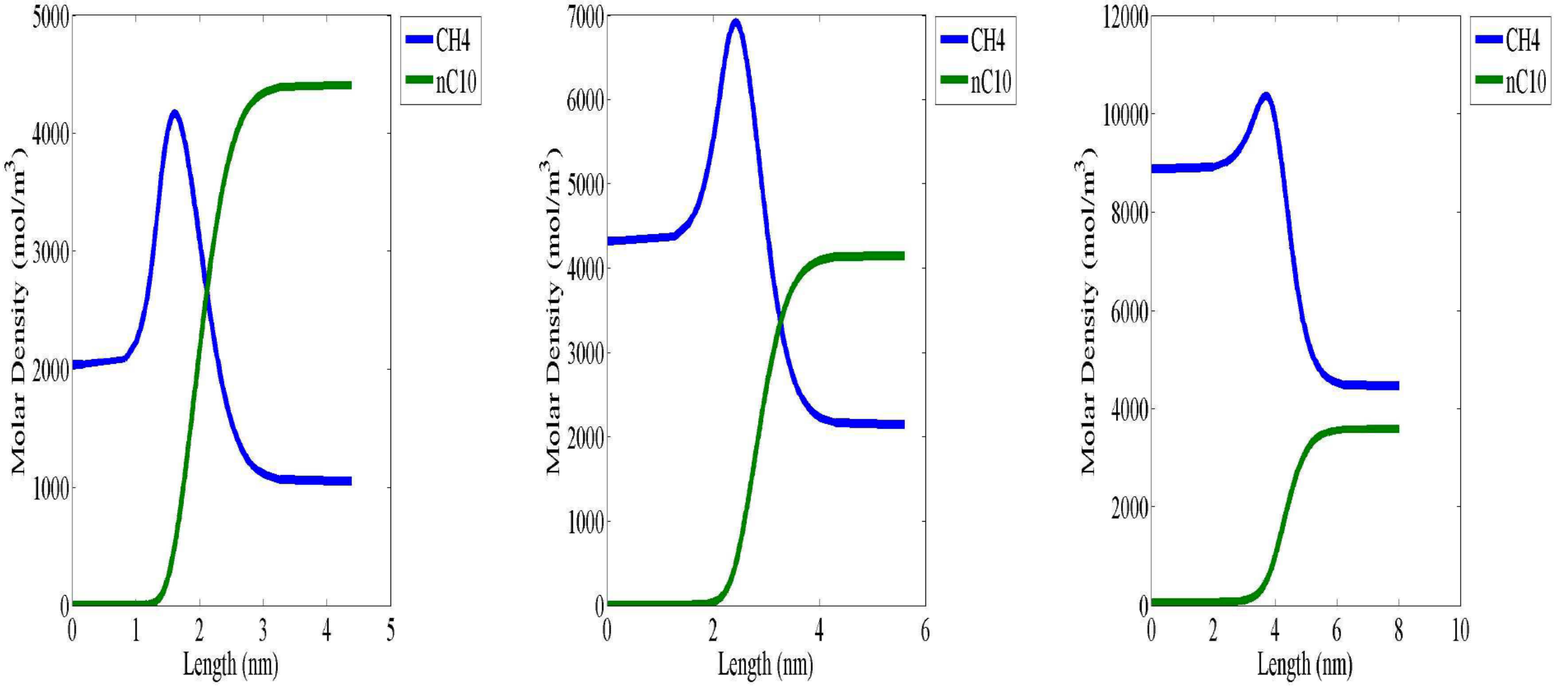


Figure: CH4 and nC10 molar density profiles at 320K and different pressures: 50bar (left), 100bar (center), 200bar (right)

Convex Splitting Semi-Implicit Treatment of PR-EOS

Helmholtz free energy of single-component PR fluid

- For generalized NVT flash in two or three spatial dimensions, an energy-stable (energy-decaying) algorithm is essential.
- Energy-stable algorithms can be also useful for 0D and 1D NVT flash.
- The Helmholtz free energy density is the sum of its ideal gas contribution and the excess Helmholtz free energy density.
- The excess Helmholtz free energy density has two contributions: one from the repulsion or volume exclusion effect, and the other from the molecular pairwise attraction.
- Shortly, we will see that we need treat the ideal gas contribution and the repulsion or volume exclusion effect implicitly; and we need treat the molecular pairwise attraction explicitly.

Convex splitting treatment of single-component PR fluid

- **Property 1 (Ideal gas contribution):** Helmholtz free energy density of homogeneous ideal gas is a convex function of molar density.

- **Property 2 (Repulsion contribution):** The repulsion contribution of excess Helmholtz free energy density of homogeneous Peng-Robinson fluid is a convex function of molar density.

- **Property 3 (Attraction contribution):** The attraction contribution of excess Helmholtz free energy density of homogeneous Peng-Robinson fluid is a concave function of molar density.

For detail, see: Z. Qiao and S. Sun, "Two-phase fluid simulation using a diffuse interface model with Peng-Robinson equation of state", *SIAM Journal on Scientific Computing*, 36(4), B708–B728 (21 pages), 2014.

Numerical example without gravity

- A single-component system with the species of isobutane (nC4);
- At the temperature of 350 K; No gravity;
- The volume is specified by a two-dimensional domain =(0, L)x(0, L), where L = 2 × 10^(−8)meters.
- Initial condition: 16 percent of the total volume is saturated liquid in the region of (0.3L, 0.7L)x(0.3L, 0.7L), while the rest (84%) is saturated gas.
- Boundary condition: complete gas wetting condition on the entire boundary of the domain.
- Spatial discretization: the uniform 200 × 200 rectangular mesh.

2D flash without gravity

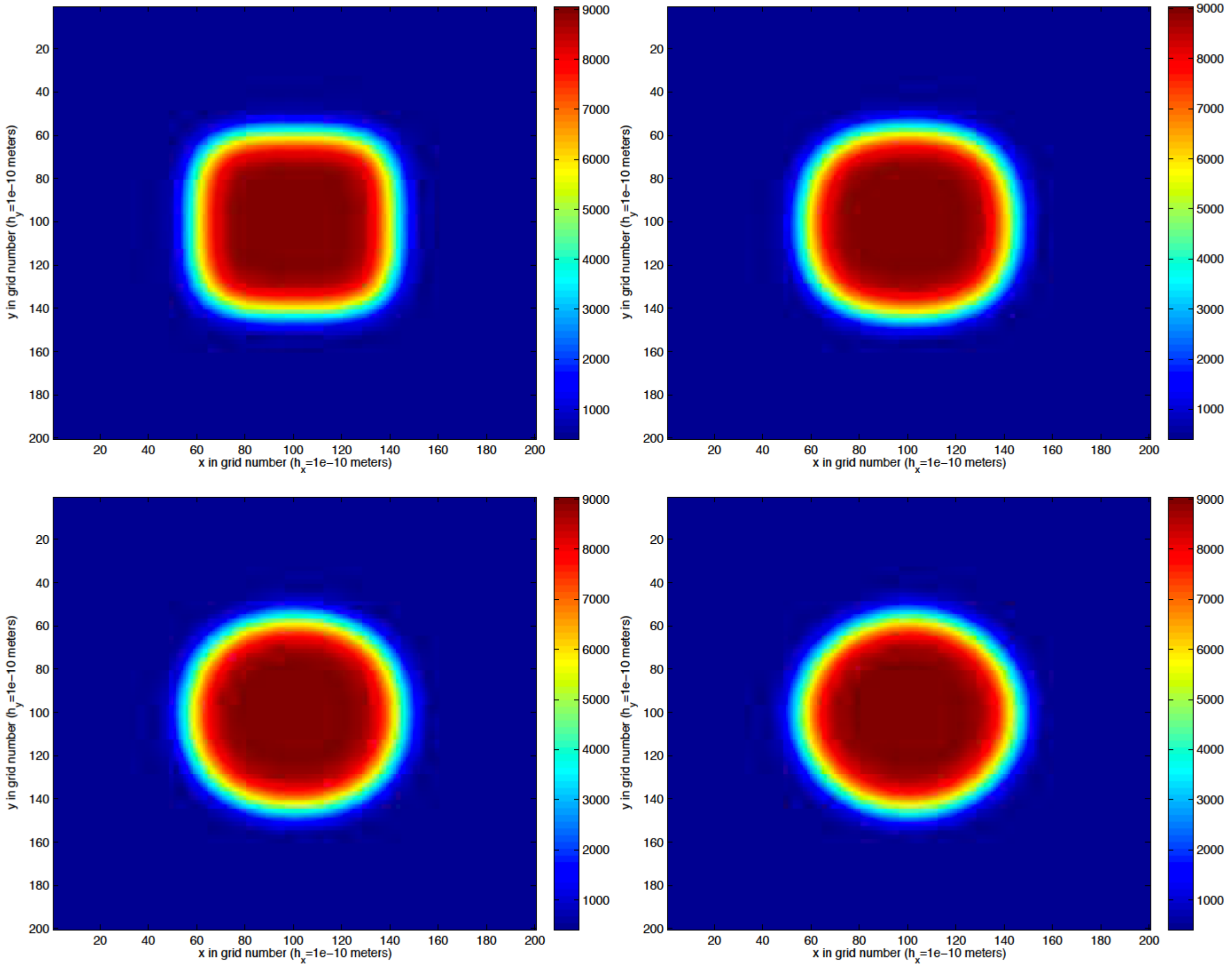


Figure: Molar density profiles after 10, 20, 30, 77 iterations.

2D flash without gravity

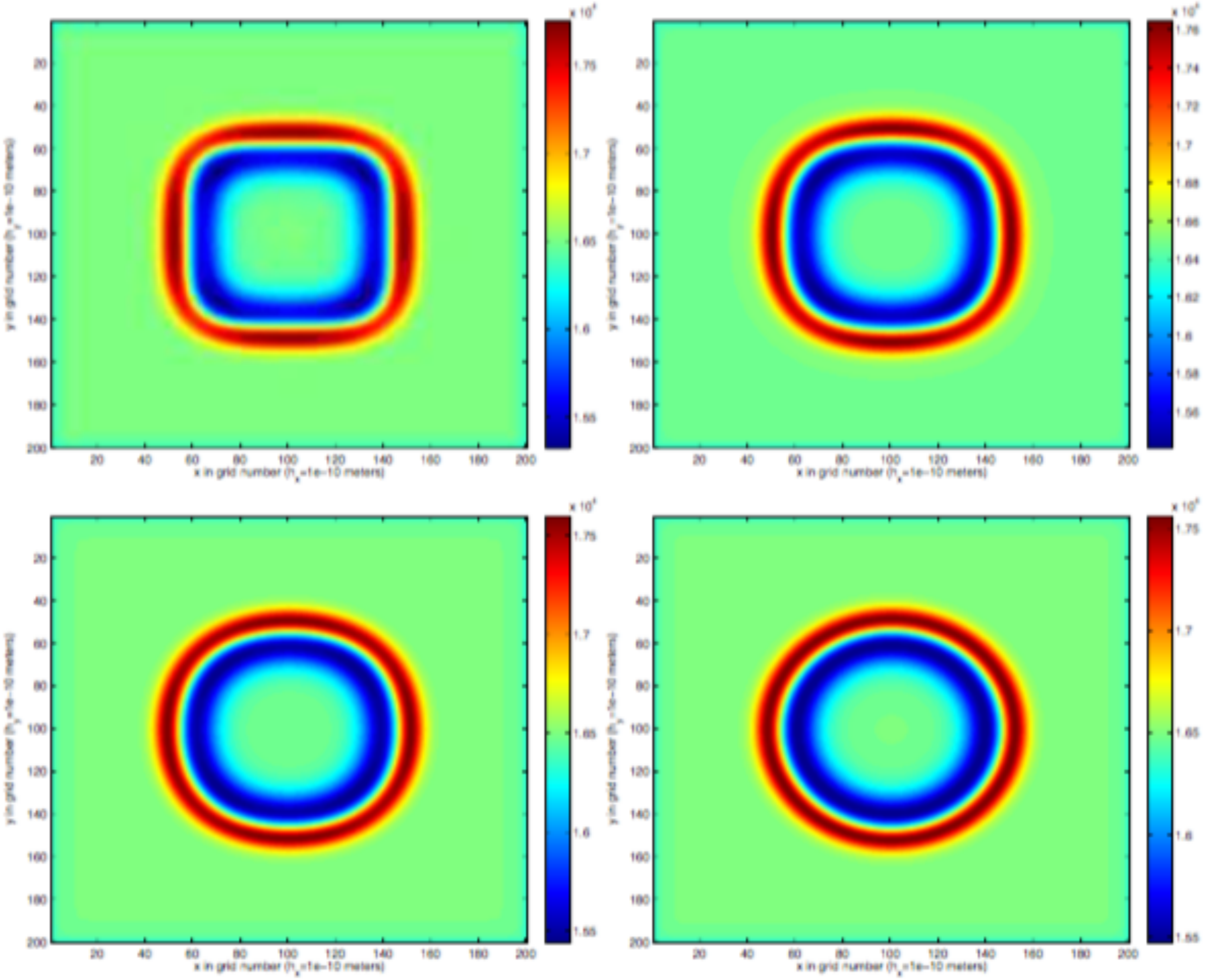


Figure: Homogeneous part of chemical potential profiles after 10, 20, 30, 77 iterations.

2D flash without gravity

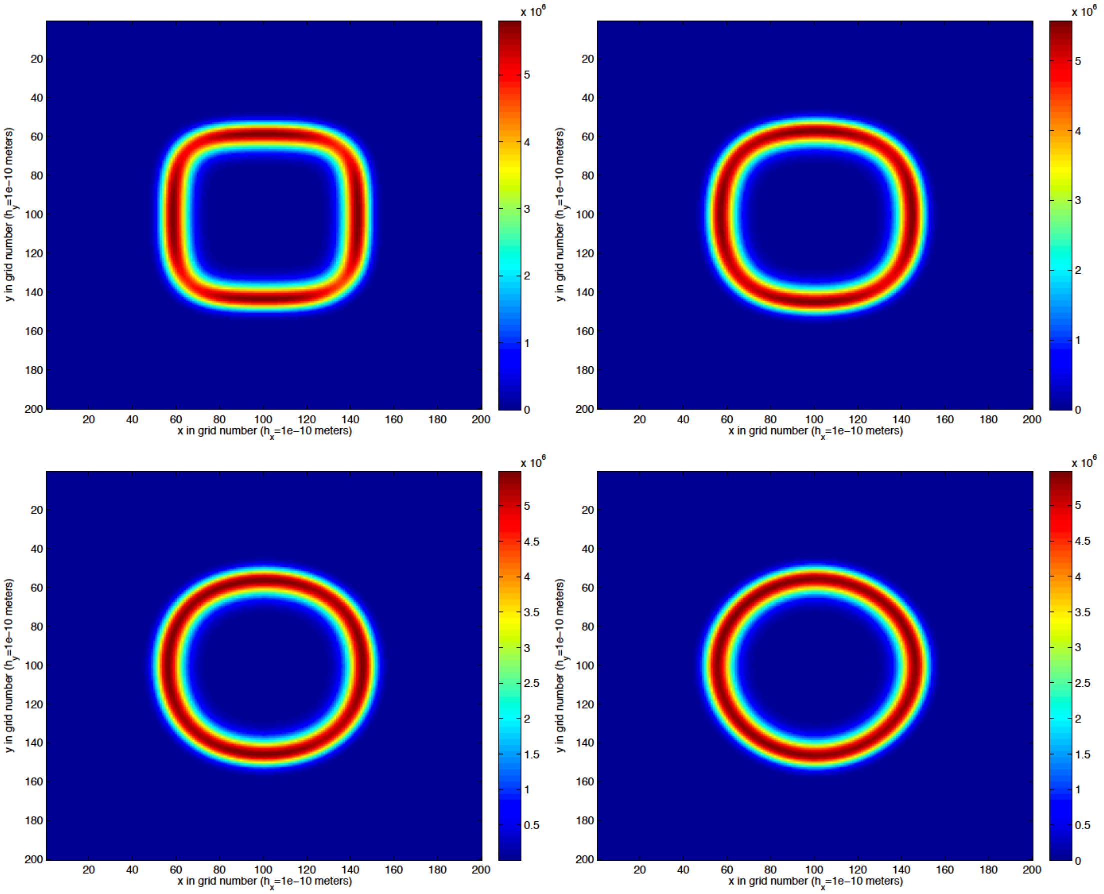


Figure: Interface tension density profiles after 10, 20, 30, 77 iterations.

2D flash without gravity

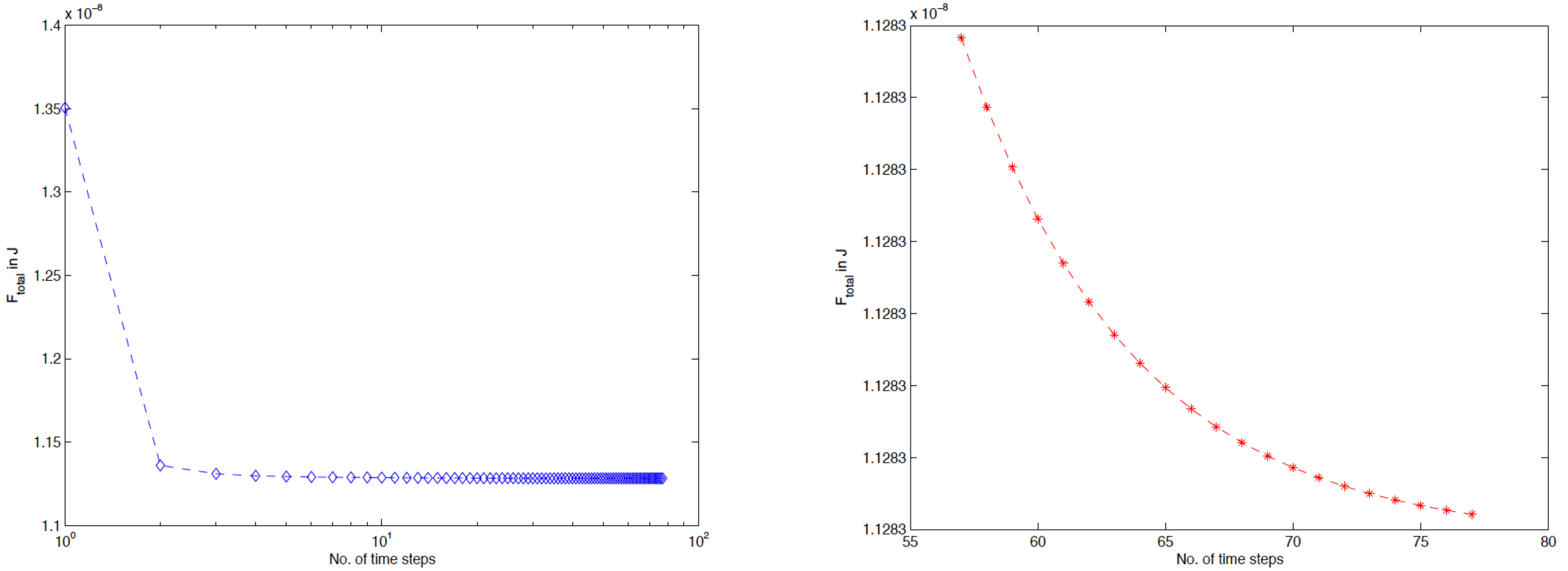


Figure: Convergence history (left: convergence since t_0; right: latest convergence).

2D flash without gravity

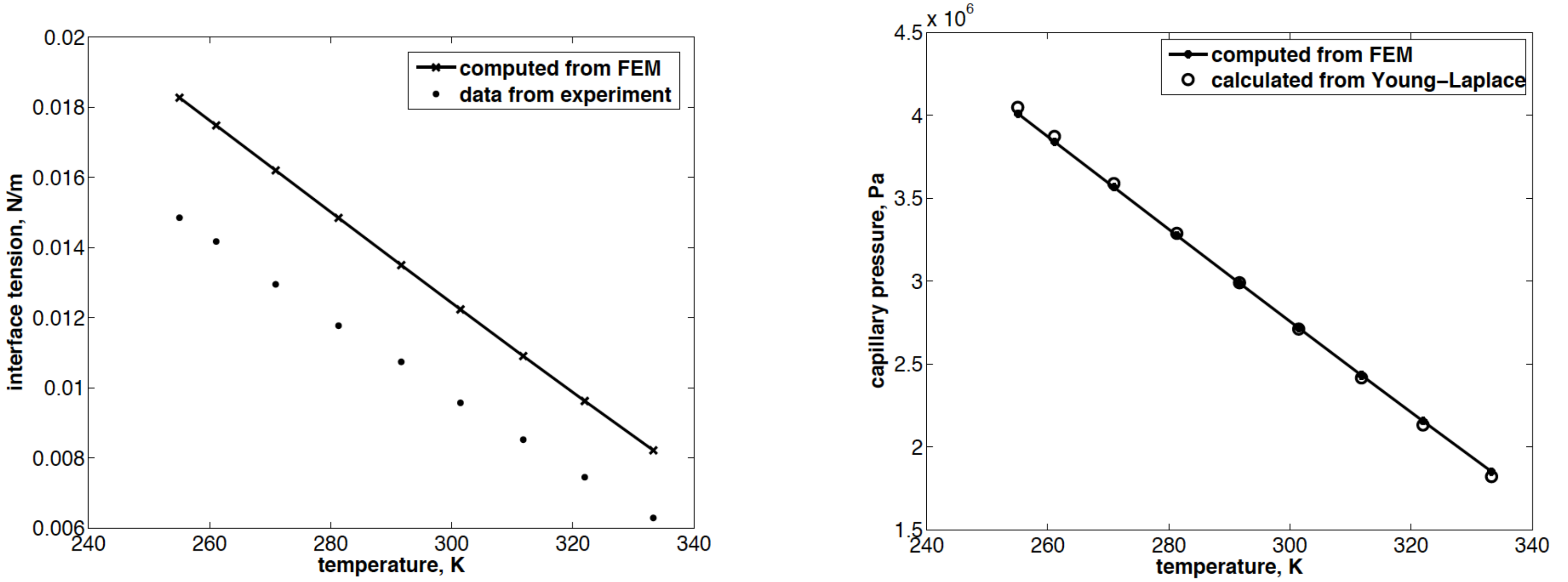


Figure: Comparison with lab data (left) or with Young-Laplace equation (right).

Numerical example with gravity

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- At the temperature of 350 K; No gravity;
- The volume is specified by a two-dimensional domain =(0, L)x(0, L), where L = 2 × 10^(–8)meters.
- Initial condition: 16 percent of the total volume is saturated liquid in the region of (0.3L, 0.7L)x(0.3L, 0.7L), while the rest (84%) is saturated gas.
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2D flash with gravity

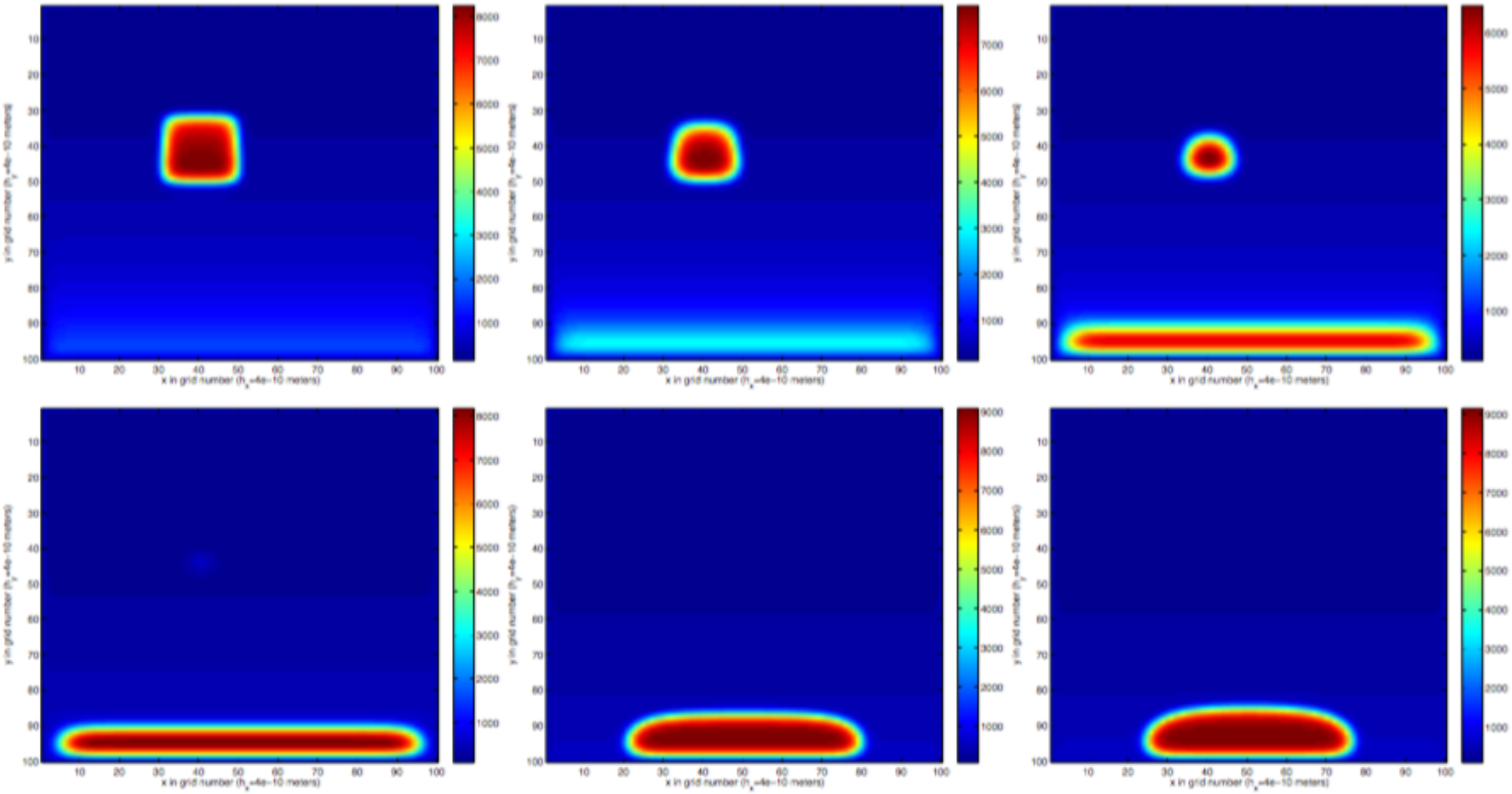


Figure: Molar density profiles after various iterations.

2D flash with gravity

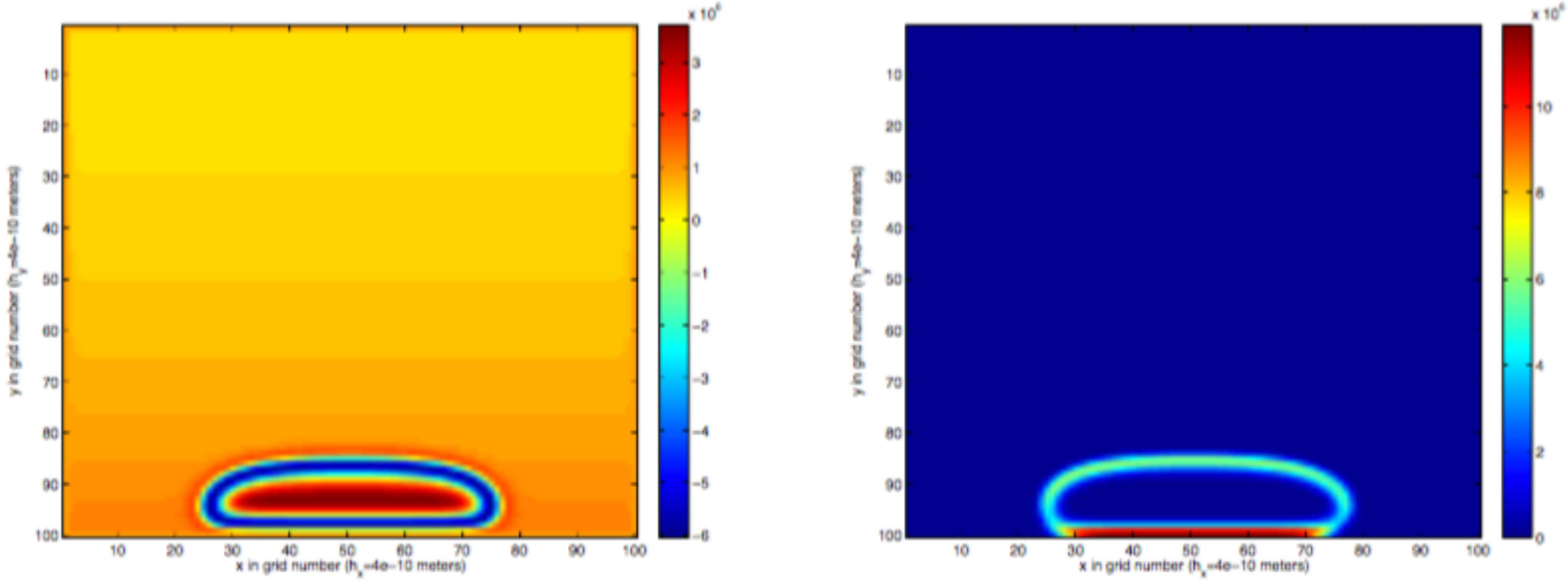


Figure: Pressure (left) and interface tension density (right) after convergence.

2D flash with gravity

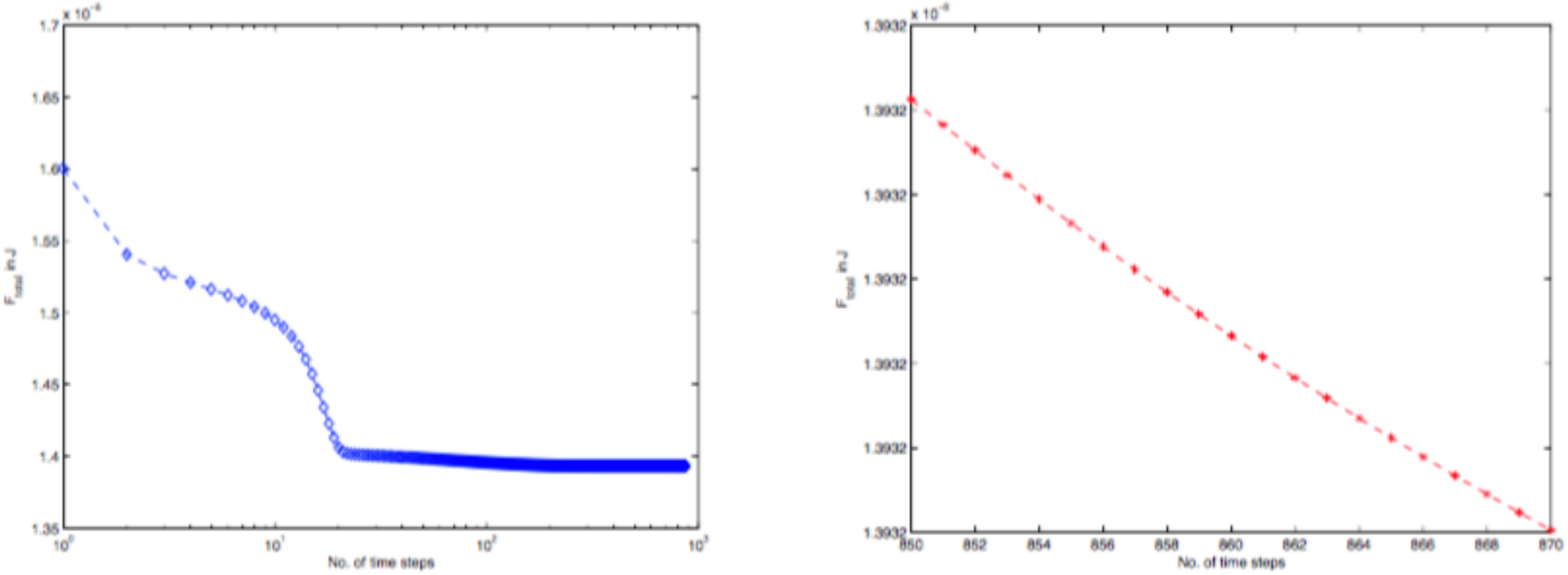


Figure: Convergence history (left: convergence since t_0; right: latest convergence).

Convex splitting treatment of multi-component PR fluid

- **Bad news:** the Hessian matrix arising from the second-order derivative of homogeneous contribution of total Helmholtz free energy is indefinite, and there is no an obvious convex splitting.

- **One approach** is to apply component-wise convex splitting strategy for numerical simulation of multicomponent two-phase fluid mixtures.

- We developed a component-wise convex splitting scheme by introducing a physics-preserving correction term, which is analogous to the attractive term in the Van der Waals EoS.

    - An efficient numerical algorithm is provided to compute the coefficient in the correction term.

The transient version of chemical equilibrium equations

- Add a time-derivative term into the right-hand side of

$$\sum_{j=1}^{M} c_{ij} \triangle n_j = \mu_i^b - \mu_i^c, \quad i = 1, \cdots, M$$

- then we can get

$$\frac{\partial n_i}{\partial t} - \sum_{j=1}^{M} c_{ij} \triangle n_j = \mu_i^c - \mu_i^b, \quad i = 1, \cdots, M$$

- with mass constraint

$$\int_{\Omega} n_i d\mathbf{x} = N_i.$$

- We adopt the Neumann boundary condition for no mass exchange condition. The initial condition is provided to give the total mass amount of each species in the closed system

$$\nabla n_i \cdot \nu_{\partial\Omega} = 0,$$

$$n_i = n_i^{ini}, \, t = 0.$$

The component-wise convex splitting of Helmholtz free energy

- Let

$$\tilde{f}_0 = f_0^{\text{ideal}}(\mathbf{n}) + f_0^b(\mathbf{n}) + f_0^a(\mathbf{n}) + \frac{1}{2}K\widehat{a}n^2 - \frac{1}{2}K\widehat{a}n^2,$$

- where

$$f_0^{\text{ideal}}(\mathbf{n}) = RT\sum_{i=1}^{M} n_i\left(\ln n_i - 1\right),$$

$$f_0^b(\mathbf{n}) = -nRT\ln\left(1 - bn\right),$$

$$f_0^a(\mathbf{n}) = \frac{\tilde{a}}{2\sqrt{2}\tilde{b}}\ln\left(\frac{1+(1-\sqrt{2})\tilde{b}}{1+(1+\sqrt{2})\tilde{b}}\right), \ \widehat{a} = \sum_{i,j=1}^{M}\sqrt{a_i a_j}\frac{n_i}{n}\frac{n_j}{n},$$

- and K is a constant to be determined.

The component-wise convex splitting of Helmholtz free energy

- It can be seen adding this term to the PR-EOS is physics-preserved and does not change the Helmholtz free energy density.
- More importantly, $\left(\widehat{a}_{ij}\right)_{M\times M} = \left(\sqrt{a_i a_j}\right)_{M\times M}$ is positive semidefinite,
- and $a_i = \widehat{a}_{ii} > 0$, which plays an essential role in our numerical algorithms.
- Rearrange $\tilde{f}_0(\mathbf{n})$ by

$$\tilde{f}_0(\mathbf{n}) = \left(f_0^{\mathrm{ideal}}(\mathbf{n}) + f_0^{b}(\mathbf{n}) + \frac{1}{2}K\widehat{a}n^2\right) + \left(f_0^{a}(\mathbf{n}) - \frac{1}{2}K\widehat{a}n^2\right).$$

- If the constant K is non-negative, then $f_0^{\mathrm{conv}} = f_0^{\mathrm{ideal}}(\mathbf{n}) + f_0^{b}(\mathbf{n}) + \frac{1}{2}K\widehat{a}n^2$ is component-wise convex with the molar density n_i .

An energy-stable component-wise convex splitting scheme

- For the PR model, with the newly-defined $\tilde{f}_0$, we can derive

$$\frac{\partial n_i}{\partial t} - \sum_{j=1}^{M} c_{ij} \Delta n_j = \mu_i(t) - \left(\mu_{0,i}^{\text{ideal}}(\mathbf{n}) + \mu_{0,i}^{b}(\mathbf{n}) + K \sum_{j=1}^{M} \widehat{a}_{ij} n_j \right) - \left(\mu_{0,i}^{a}(\mathbf{n}) - K \sum_{j=1}^{M} \widehat{a}_{ij} n_j \right), \ \mathbf{x} \in \Omega.$$

- We define $\widehat{a}_i$ as row vector $(\widehat{a}_{ij})_j$. The component-wise convex splitting procedure is shown below:

$$\frac{n_i^{k+\frac{i}{M}} - n_i^{k+\frac{i-1}{M}}}{\delta t} - c_{ii} \Delta n_i^{k+\frac{i}{M}} = \mu_i^{k+\frac{i}{M}} - \left(\{\mu_{0,i}^{\text{ideal}} + \mu_{0,i}^{b}\} \left(\mathbf{n}^{k+\frac{i}{M}} \right) + K \widehat{a}_i \mathbf{n}^{k+\frac{i}{M}} \right) - \left(\mu_{0,i}^{a} \left(\mathbf{n}^{k+\frac{i-1}{M}} \right) - K \widehat{a}_i \mathbf{n}^{k+\frac{i-1}{M}} \right) + \sum_{j \neq i} c_{ij} \Delta n_j^{k+\frac{i}{M}},$$

$$\int_{\Omega} n_i^{k+\frac{i}{M}} d\mathbf{x} = N_i.$$

The mixed finite element approximation for prediction

- We propose the RT0 mixed finite element approximation.

The scheme is : to find a $\mathbf{n}_i \in W$ and $\mathbf{u}_i \in \mathbf{V}$ such that

$$\left(\frac{\partial n_i}{\partial t}, w_i\right) = (\mathbf{u}_i, \nabla w_i) - \sum_{E\in\tau_h} \langle \mathbf{u}_i \cdot \nu_{\partial E}, w_i\rangle_{\partial E} + (\mu_i(t) - \mu_{0,i}(\mathbf{n}), w_i)\,, \forall w_i \in W,$$

$$(\mathbf{u}_i, \mathbf{v}_i) = \left(\sum_{j=1}^{M} c_{ij} n_j, \nabla \cdot \mathbf{v}_i\right), \forall \mathbf{v}_i \in \mathbf{V},$$

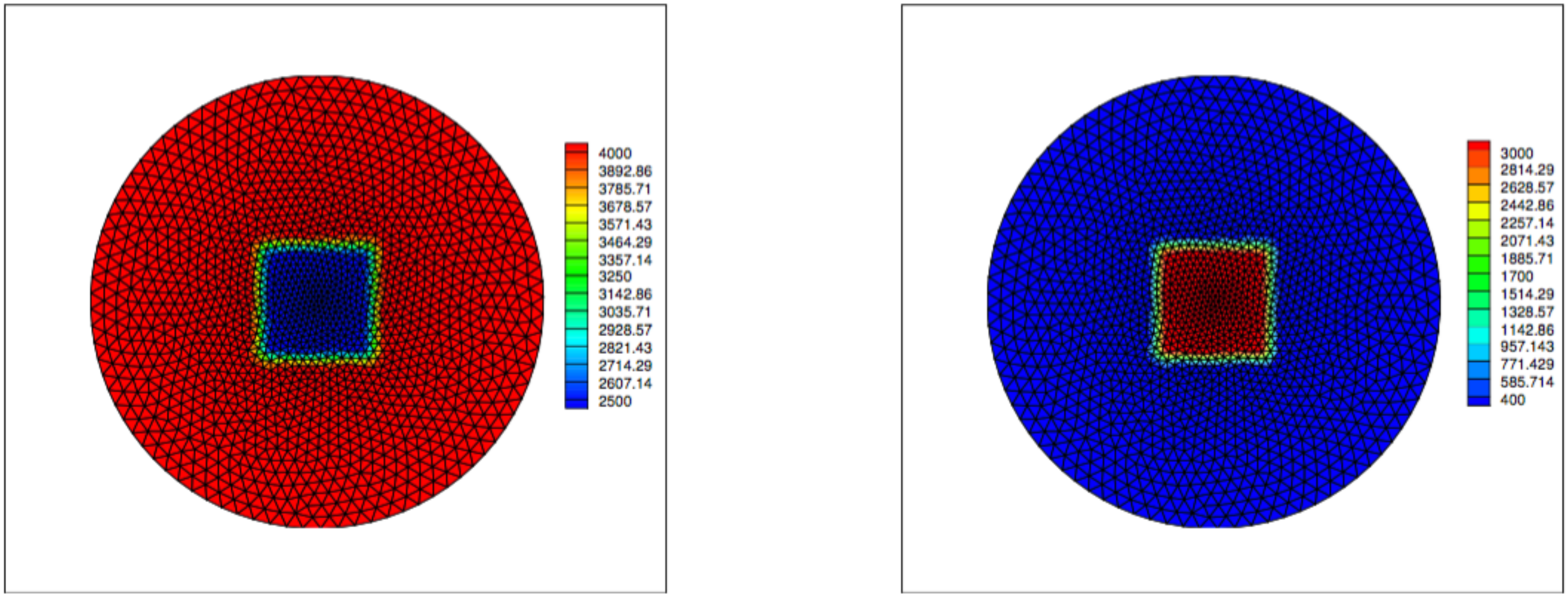
$$\int_\Omega n_i d\mathbf{x} = N_i,$$

$$(n_i, w_i) = \left(n_i^{\text{init}}, w_i\right), t = 0, \forall w_i \in W.$$

Numerical example for multicomponent system

- The mixture consists of methane (C1) and n-decane (nC10);
- At the temperature of 450 K; No gravity;
- The simulation is carried out on a disk domain with diameter L = 10^(–8)meters.
- The boundary condition is the Neumann type and the computational domain is divided into triangular meshes.

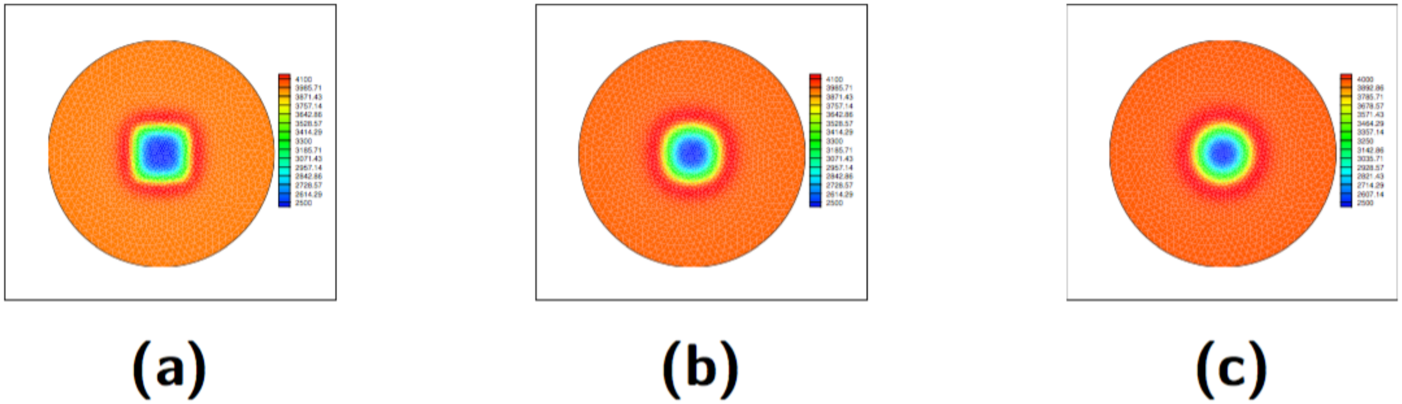
2D flash for multicomponent system



(a) **(b)**

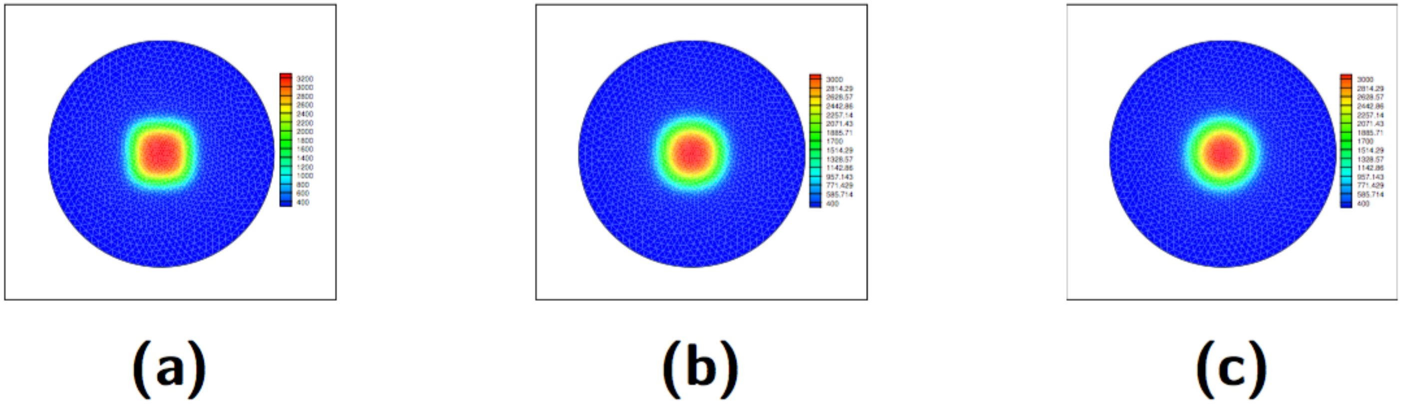
Figure 6: Initial condition (molar density distribution): (a) methane; (b) n-decane.

2D flash for multicomponent system



(a) (b) (c)

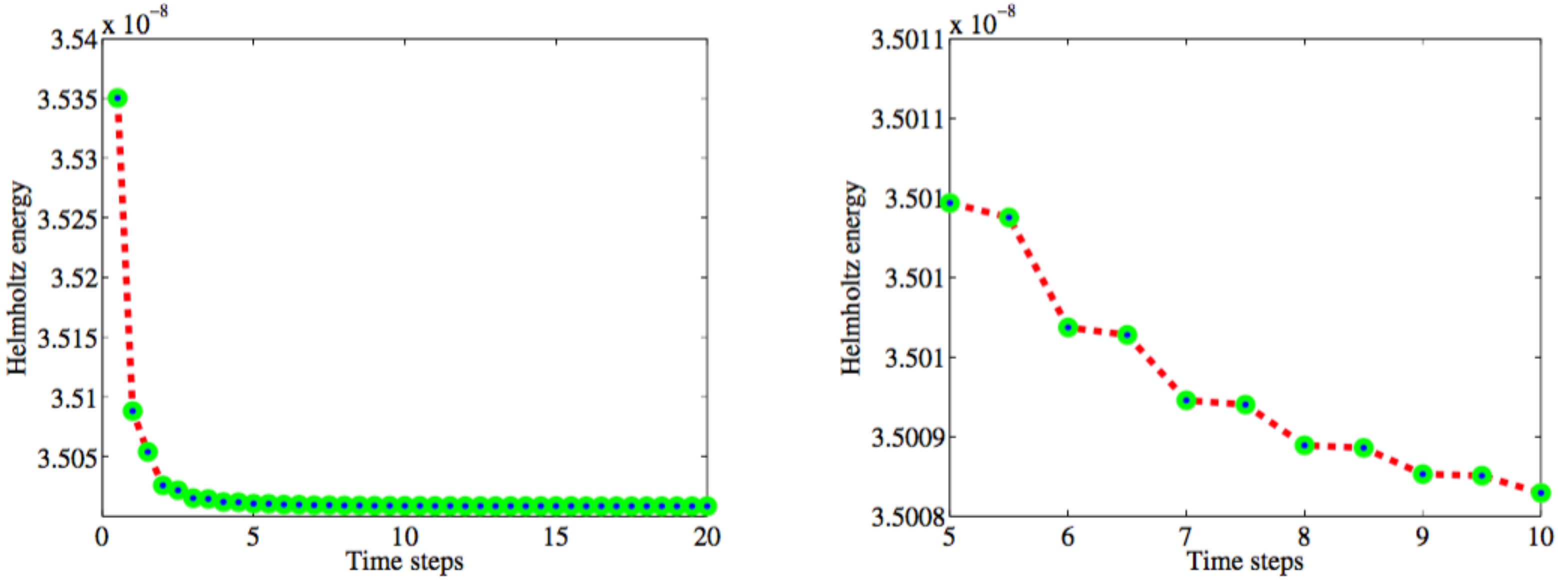
Figure 7: Molar density of methane: (a) 5th time step; (b) 10th time step; (c) 20th time step.



(a) (b) (c)

Figure 8: Molar density of n-decane: (a) 5th time step; (b) 10th time step; (c) 20th time step.

2D flash for multicomponent system



(a) **(b)**

Figure 11: Convergence of total Helmholtz free energy: (a) the component-wise total Helmholtz free energy during the whole simulation; (b) zoom in of 5th-10th time steps.

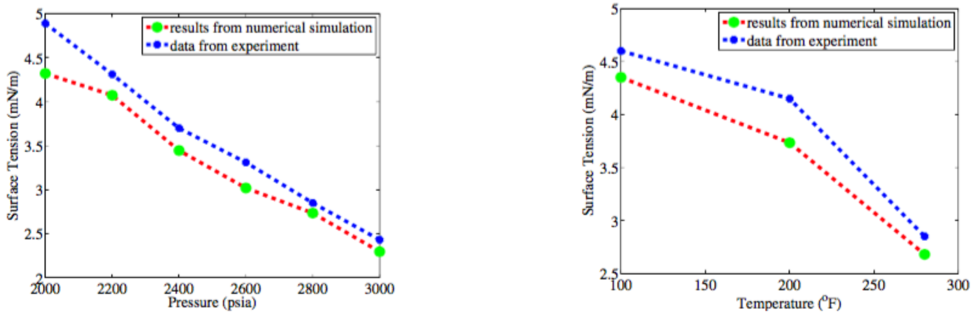
Simulation result vs. experiment

- The surface tension is computed through the formula

$$\sigma = \frac{F(\mathbf{n}) - F_0(\mathbf{n}^{\text{init}})}{A}$$

- where the interface tension is assumed to be constant in the interface.

- The simulation results fit well with the measured data to some extent in range of model, measurement and machine errors.



(a) **(b)**

Figure 12: Comparison of surface tension between simulations and experimental data: (a) at temperature $T = 280^\circ$F; (b) at pressure $P_0 = 2800$ psia.

Compositional Grading by Convex Splitting Methods

Gravity effect on fluid composition

- The effect of gravity is usually neglected in mixture theories.
  - A (single-phase) solution of chemicals is assumed to homogeneous in all spatial directions;
  - This homogeneity assumption is very accurate for single-phase fluid at a lab scale.
- Gravity is also sometimes negligible in a field scale.
  - Particularly if the thickness of the reservoir is small.
- Gravity can cause (pronounced) compositional variation in hydrocarbon reservoirs.
  - Particularly if the thickness of the gas/oil reservoir is large.
  - This is knowns as **compositional grading.**

New formulation of compositional grading

- As a consequence of the second law of thermodynamics, the total Helmholtz energy for a NVT system achieve its minimum at equilibrium.
- The total Helmholtz energy of an inhomogeneous fluid can be modeled by

$$F(\mathbf{n}) = \int_{\Omega} \left(f_b(\mathbf{n}) + f_g(\mathbf{n},\mathbf{x})\right) d\mathbf{x}, \quad f_g(\mathbf{n},\mathbf{x}) = M_w n g h.$$

- We have ignored the gradient contribution, as the contribution is very small at the reservoir scale.
- We add a time derivative term to convert the Euler-Lagrange equation to a transient problem.
- This dynamic model describes the evolutionary process of isothermal compositional grading and meanwhile satisfies the minimum energy principle.

Equilibrium equation with gravity

- Now we consider the problem of minimizing the total energy

$$\min F(\mathbf{n})$$

- under mass constraints

$$\int_\Omega n_i d\mathbf{x} = N_i,\ n_i > 0.$$

- By applying variational calculus, the minimization problem can be reduced to the following equilibrium condition

$$\mu_i(\mathbf{n}) + M_{w,i} g h - c_i = 0,\ i = 1, 2, \ldots, M,$$

- where $M_{w,i}$ is the molecular weight of component i .

The transient version of equilibrium equations

- A time-derivative term is added to the left-hand side of the gravity/chemical equilibrium equation

$$\lambda \frac{\partial n_i}{\partial t} + \mu_i(\mathbf{n}) + M_{w,i} g h - c_i = 0$$

- where   is a coefficient to enforce unit consistency.
- It can be proved the time dependent of chemical equilibrium equation has the energy-decaying property.
- The total Helmholtz free energy satisfy

$$\frac{dF(\mathbf{n})}{dt} = -\int_\Omega \sum_{i=1}^{M} \left(\frac{\partial n_i}{\partial t} \right)^2 d\mathbf{x} \leq 0$$

- Details see:
  - Y Li, J Kou, S Sun, "Numerical modeling of isothermal compositional grading by convex splitting methods", Journal of Natural Gas Science and Engineering, in print, 2017.

Convex-splitting for compositional grading

- Our algorithm based on convex-splitting of PR EOS:

$$\lambda \frac{n_i^{k+1} - n_i^k}{t^{k+1} - t^k} + \mu_i^{\text{convex}}(\mathbf{n}^{k+1}) + \mu_i^{\text{concave}}(\mathbf{n}^k) + M_{w,i} g h - c_i^{k+1} = 0.$$

- The convex and concave part of chemical potential has the following form

$$\mu_k^{\text{convex}}(\mathbf{n}) = \frac{\partial f_h^{\text{convex}}(\mathbf{n})}{\partial n_k} = RT \ln n_k - RT \left(\ln(1 - bn) - \frac{n b_k}{1 - bn} \right),$$

$$\mu_k^{\text{concave}}(\mathbf{n}) = \frac{\partial f_h^{\text{concave}}(\mathbf{n})}{\partial n_k} = \frac{2\tilde{a}_k b - a b_k n}{2\sqrt{2} b^2 n} \ln \left(\frac{1 + (1 - \sqrt{2}) bn}{1 + (1 + \sqrt{2}) bn} \right) + \frac{a(T) n}{2\sqrt{2} b} \left(\frac{(1 - \sqrt{2}) b_k}{1 + (1 - \sqrt{2}) bn} - \frac{(1 + \sqrt{2}) b_k}{1 + (1 + \sqrt{2}) bn} \right),$$

- where

$$\tilde{a}_k = \sum_{j=1}^{N} n_j (a_k a_j)^{1/2} (1 - k_{kj})$$

Convex-splitting for compositional grading

- Our algorithm based on convex-splitting of PR-EOS:

$$\lambda \frac{n_i^{k+1} - n_i^k}{t^{k+1} - t^k} + \mu_i^{\text{convex}}(\mathbf{n}^{k+1}) + \mu_i^{\text{concave}}(\mathbf{n}^k) + M_{w,i} g h - c_i^{k+1} = 0.$$

- Under certain condition, we can show

$$f_h(\mathbf{n}^{k+1}) - f_h(\mathbf{n}^k) \leq \sum_{i=1}^{N} \mu_i^{\text{convex}}(\mathbf{n}^{k+1}) \left(n_i^{k+1} - n_i^k\right) + \sum_{i=1}^{N} \mu_i^{\text{concave}}(\mathbf{n}^k) \left(n_i^{k+1} - n_i^k\right)$$

- As a consequence, our algorithm is unconditional stable; that is, for time step of any size, we have:

$$F(\mathbf{n}^{k+1}) \leq F(\mathbf{n}^k)$$

Comparison with fully explicit scheme and fully implicit scheme

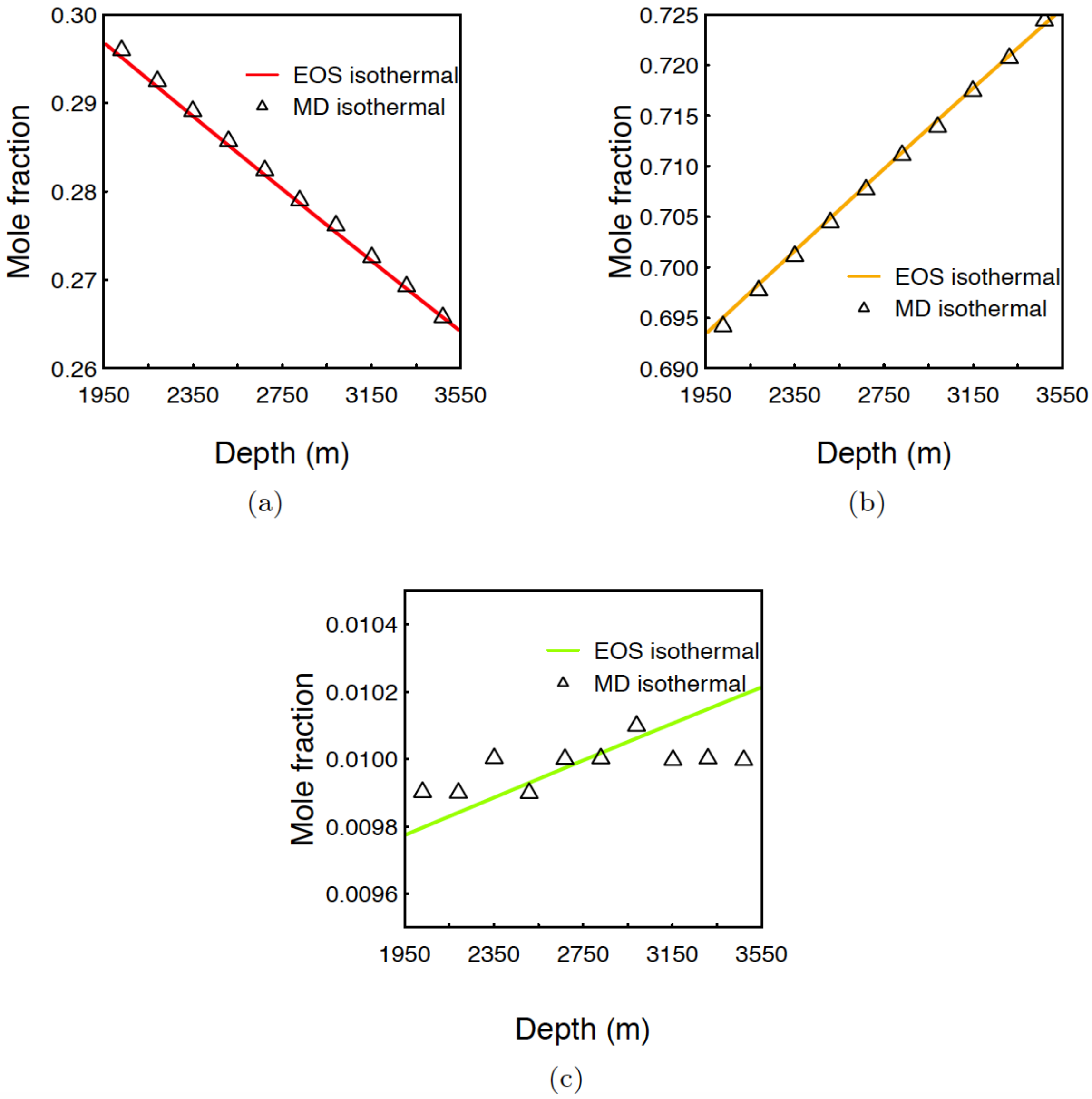
- For fully explicit scheme,
  - time step must be small enough. In binary mixture of methane(C1) and n-pentane(nC5) ay ambient temperature, the tilmestep size is no greater than 0,1.
  - The increase of molecular weight difference can lead to failure of convergence for a binary mixture of C1 and nC10 at the same condition, even with $\Delta t = 10^{-12}$.
- For fully implicit scheme,
  - the time step cannot be arbitrarily large.
  - The maximum time step for the synthetic oil case is 0.1

Compositional grading example 1: Acid gas

- This example is used to verify our model by comparing our numerical results with molecular dynamics(MD) results calculated by Galliero and Montel (Galliero et al., 2009).
  - We will see shortly that our numerical results match the MD data very well, especially for C1 and CO2.
- The acid gas mixture consists of methane(C1), carbon dioxide (CO2) and hydrogen sulfide(H2S) whose average mole fraction is 0.28, 0.71 and 0.01, respectively.
- The thickness of the vertical gas column is 1600 m, and the pressure and temperature at the reference depth is 40 MPa and 443.15 Kelvin.

Compositional grading example 1: Acid gas

Mole fraction distribution: (a) C1, (b) CO2 and (c) H2S along depth at 443.15 Kelvin



(a)

(b)

(c)

Compositional grading example 2: Real reservoir fluid

- To verify the applicability of the semi-implicit convex splitting method further, we use a test case proposed by Montel et al. (1985). In this case, the reservoir fluid consists of a condensate gas and a light oil.

- No GOC is found between the vapor and liquid phase.

- Table below presents gas composition with physical properties at reference depth:

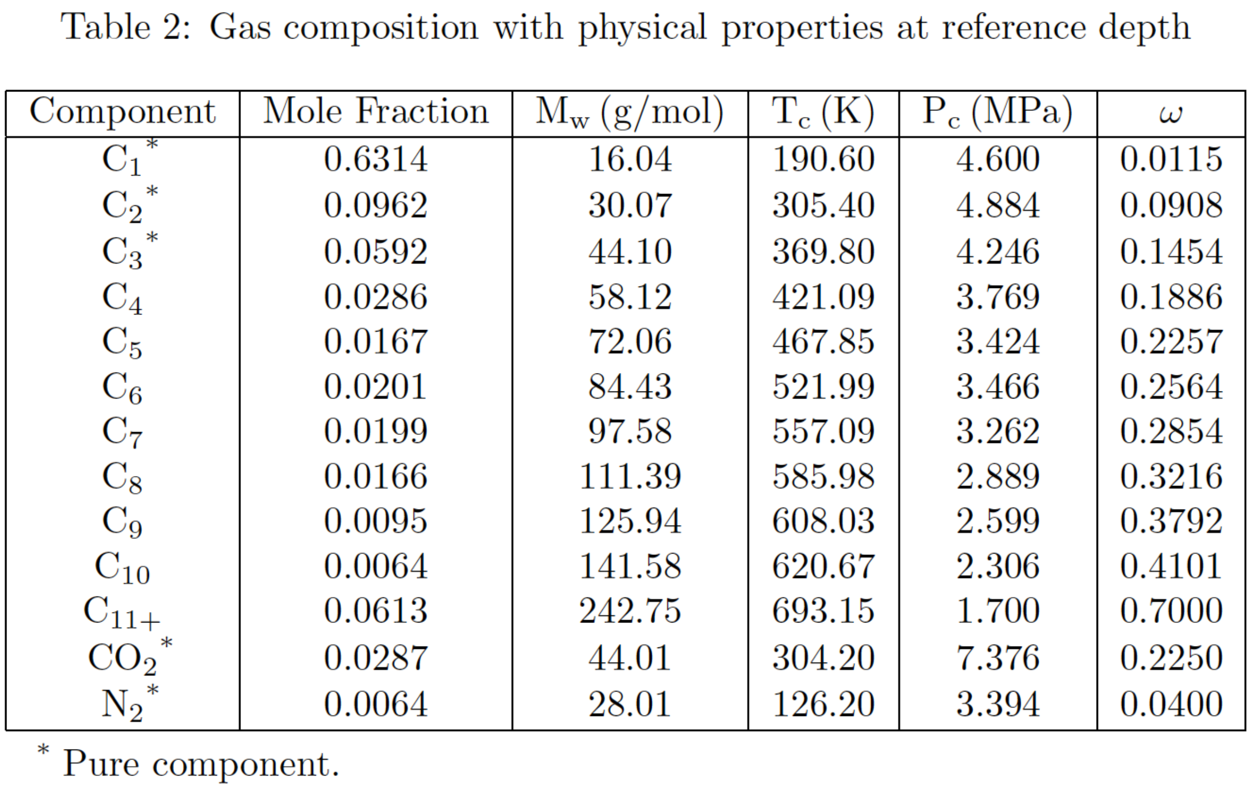


Table 2: Gas composition with physical properties at reference depth

Component	Mole Fraction	M_w (g/mol)	T_c (K)	P_c (MPa)	ω
$C_1{}^*$	0.6314	16.04	190.60	4.600	0.0115
$C_2{}^*$	0.0962	30.07	305.40	4.884	0.0908
$C_3{}^*$	0.0592	44.10	369.80	4.246	0.1454
C_4	0.0286	58.12	421.09	3.769	0.1886
C_5	0.0167	72.06	467.85	3.424	0.2257
C_6	0.0201	84.43	521.99	3.466	0.2564
C_7	0.0199	97.58	557.09	3.262	0.2854
C_8	0.0166	111.39	585.98	2.889	0.3216
C_9	0.0095	125.94	608.03	2.599	0.3792
C_{10}	0.0064	141.58	620.67	2.306	0.4101
C_{11+}	0.0613	242.75	693.15	1.700	0.7000
$CO_2{}^*$	0.0287	44.01	304.20	7.376	0.2250
$N_2{}^*$	0.0064	28.01	126.20	3.394	0.0400

* Pure component.

Compositional grading example 2: Real reservoir fluid

- To verify the applicability of the semi-implicit convex splitting method further, we use a test case proposed by Montel et al. (1985). In this case, the reservoir fluid consists of a condensate gas and a light oil.

- No GOC is found between the vapor and liquid phase.

- Table 1 presents composition variation along depth (field data).

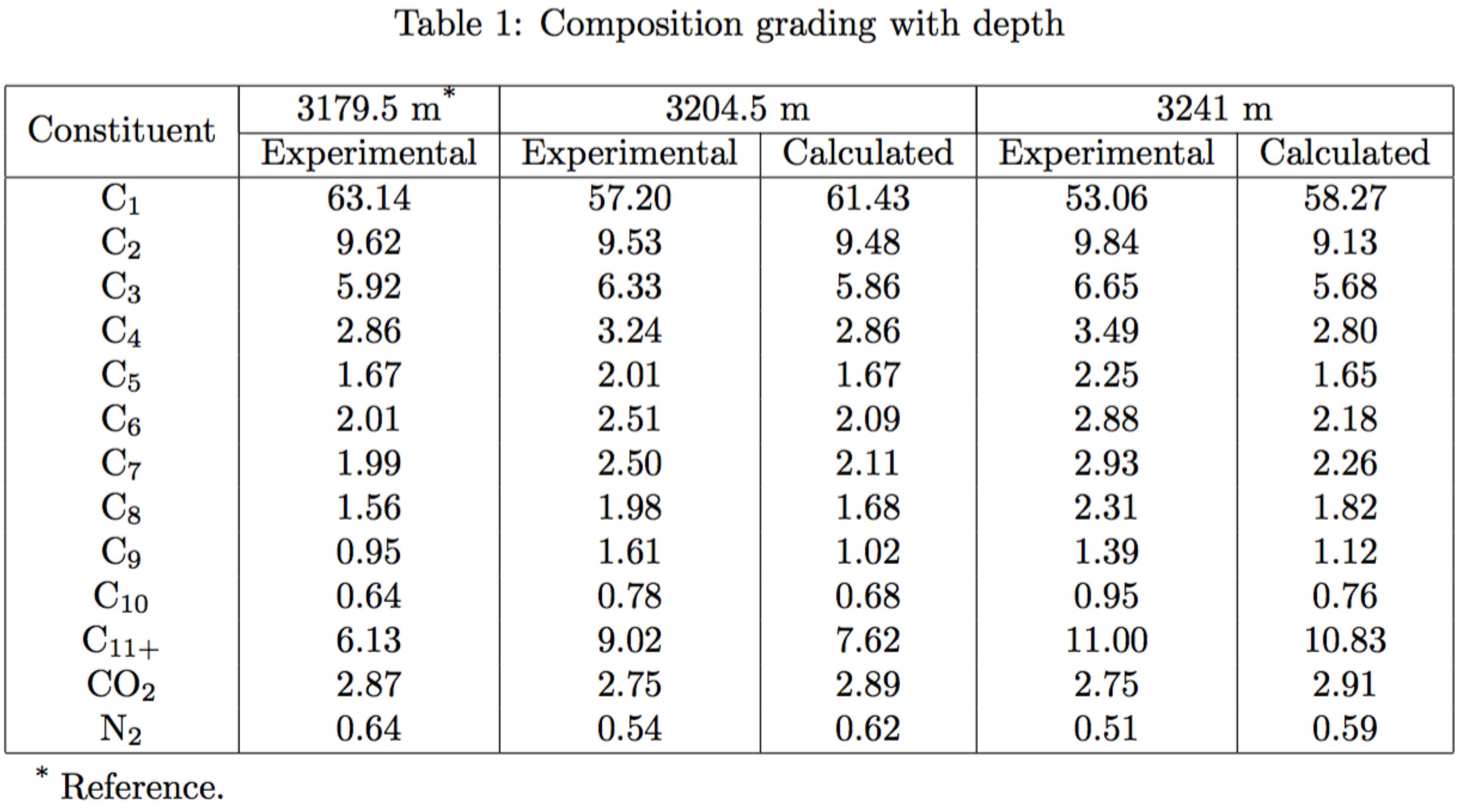


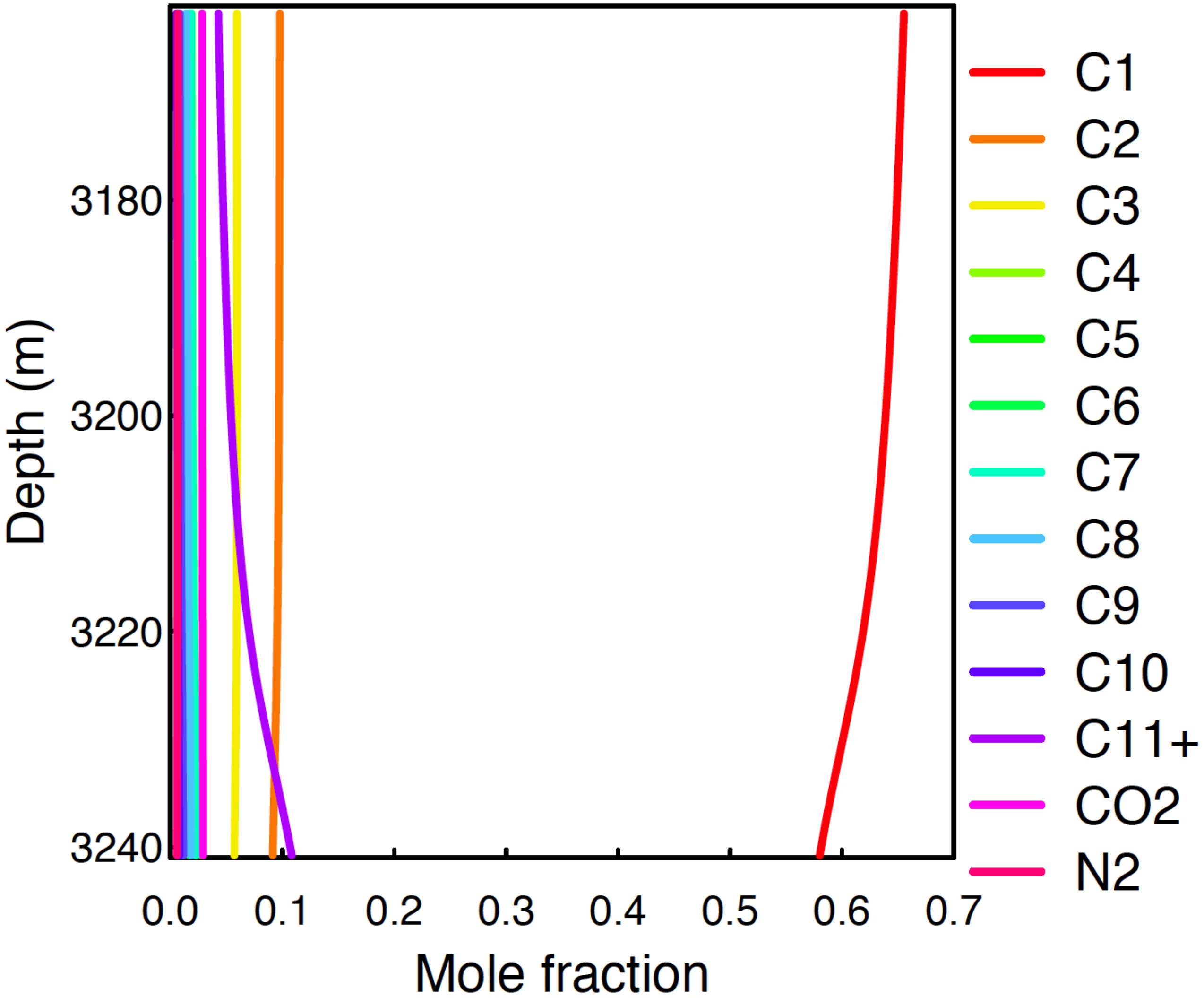
Table 1: Composition grading with depth

Constituent	3179.5 m*	3204.5 m		3241 m	
	Experimental	Experimental	Calculated	Experimental	Calculated
C_1	63.14	57.20	61.43	53.06	58.27
C_2	9.62	9.53	9.48	9.84	9.13
C_3	5.92	6.33	5.86	6.65	5.68
C_4	2.86	3.24	2.86	3.49	2.80
C_5	1.67	2.01	1.67	2.25	1.65
C_6	2.01	2.51	2.09	2.88	2.18
C_7	1.99	2.50	2.11	2.93	2.26
C_8	1.56	1.98	1.68	2.31	1.82
C_9	0.95	1.61	1.02	1.39	1.12
C_{10}	0.64	0.78	0.68	0.95	0.76
C_{11+}	6.13	9.02	7.62	11.00	10.83
CO_2	2.87	2.75	2.89	2.75	2.91
N_2	0.64	0.54	0.62	0.51	0.59

* Reference.

Compositional grading example 2: Real reservoir fluid

- Figure shows the mole fraction distributions of all thirteen components with depth.
  - It can be seen a phase change occurs at the lower part of the system and there is no apparent interface between two phases. This matches with the fact that no gas-oil contact is found between the condensate gas and the light oil.
  - By comparing our numerical results with the experimental data, our methods shows good accuracy.

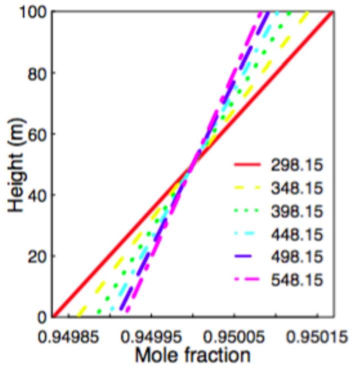


Compositional grading example 3: simplified natural gas

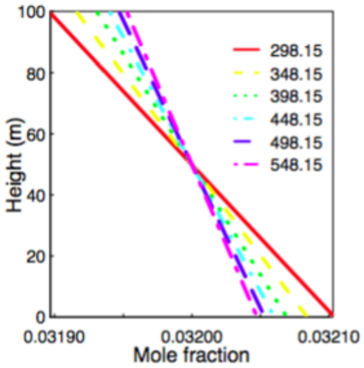
- This example is used to show compositional variation within single gas phase.
- The fluid mixture is composed of methane(C1), ethane(C2), propane(C3), carbon dioxide(CO2) and nitrogen(N2). The mole fraction of each component is 0.95, 0.032, 0.002, 0.006 and 0.01, respectively.
- The molar density of fluid mixture is assumed to be 2000 mol/m3.

Compositional grading example 3: simplified natural gas

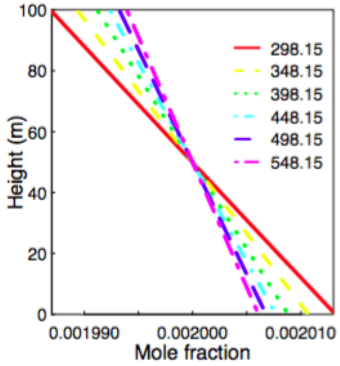
- Mole fraction distribution of C1, C2, C3, CO2, N2 when total molar density is 2000 mol/m3.



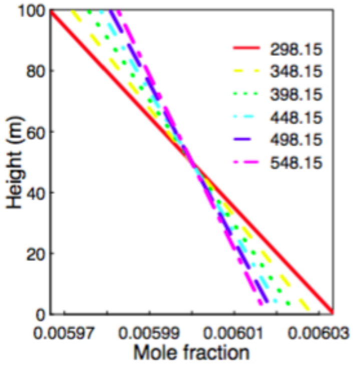
(a) C_1



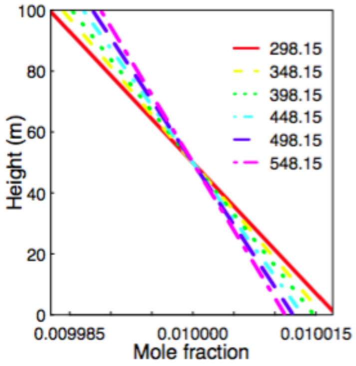
(b) C_2



(c) C_3



(d) CO_2



(e) N_2

Compositional grading example 4: synthetic oil

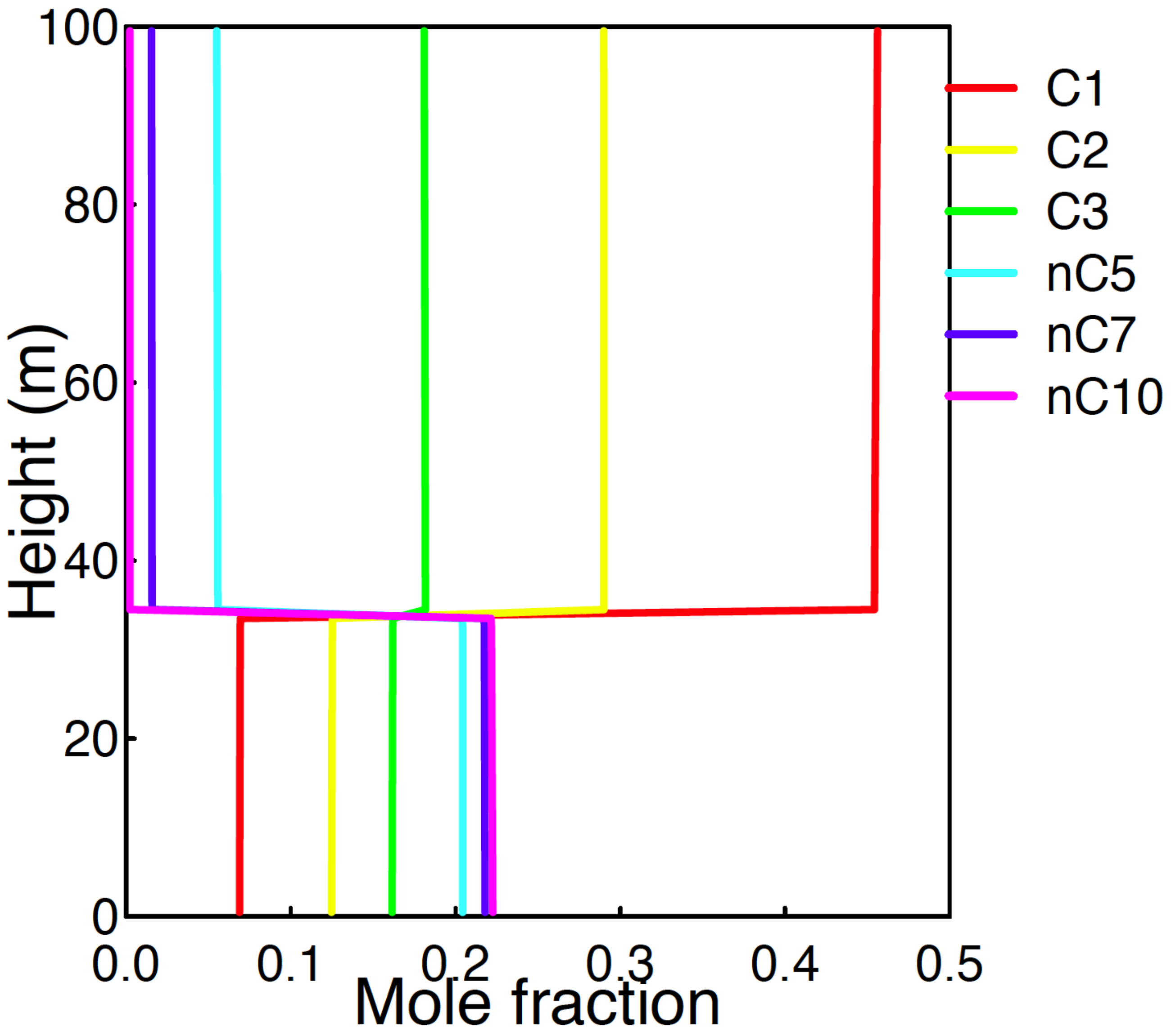
- This example is used to show the capability of our method to simulate the isothermal compositional grading of two phases with gas-oil contact.

- The fluid mixture is composed of methane(C1), ethane(C2), propane(C3), n-pentane(nC5), n-heptane(nC7) and n-decane(nC10). We call it synthetic oil, although its composition is far from the real oil composition.

- Initially ,we assume the fluid mixture is in vapor phase. The system temperature is 378.15 K and the molar density of each component is 500 mol/m3.

Compositional grading example 4: Synthetic oil

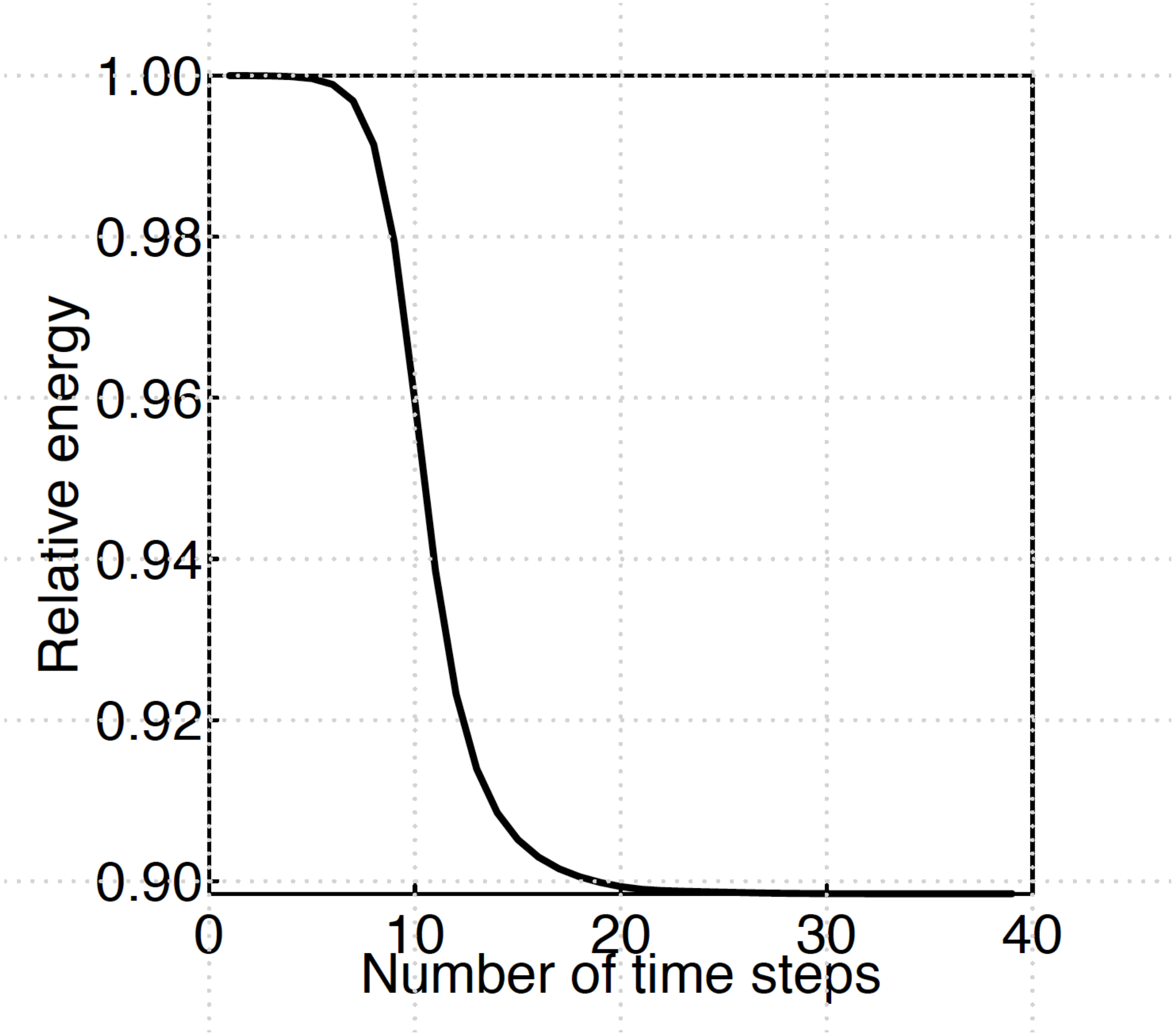
- Mole fraction distribution of C1, C2, C3, nC5, nC7 and nC10 at 378.15 K.



Compositional grading example 4: Synthetic oil

- **Figure: Relative energy change from non-equilibrium state to equilibrium state at 378.15 K.**

- Observations:
  - It is clear the total energy decreases with time steps.
  - At the first few steps, no phase splits so that energy decreases little. When two phases start to be generated, energy decays very quickly, resulting into high gradients in the middle, until it reaches the true equilibrium state.



Conclusions and future work

- **Conclusions**
  - A framework is established for diffuse interface modeling of two-phase systems with PR-EOS;
  - A semi-implicit time scheme is proposed to treat the volume exclusion effect of EOS implicitly while the pairwise attraction effect of EOS is calculated explicitly;
  - Adaptive FEM is developed for surface tension calculation;
  - A new modeling framework is established for compositional grading.
- **Future work**
  - Work in progress: The effects of wettability and geometry on the behaviors of fluid systems;
  - Near future work: To couple pore-network models with compositional two-phase flow in a single channel;
  - Future work: Moving contact line problems of compositional flow.

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