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A Kinetic Description of Hydrate Systems Using Operator-Based Linearization Approach

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Summary

Gas hydrates are crystalline compounds of water and small guest molecules, relevant both as a hazard in hydrocarbon production and CO_2 sequestration, and as a potential energy resource in natural reservoirs. This work presents a kinetic simulation model for hydrate formation and dissociation in porous media, implemented using the Operator-Based Linearization (OBL) technique. We verify thermodynamic assumptions through Gibbs energy analysis, showing consistency between kinetic and equilibrium reaction models. The framework is validated against literature on methane hydrates and can be extended to CO_2 systems. Applications are demonstrated at core and field scales, including gas production by depressurization and thermal stimulation. Results highlight the strong influence of kinetic parameters on hydrate behavior, underscoring the importance of selecting appropriate reaction models for accurate physical and numerical predictions.

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Introduction

Gas hydrates are crystalline solids formed by hydrogen-bonded water cages encapsulating small gas molecules, stable at high pressure and low temperature. Their occurrence in subsea pipelines and reservoirs introduces operational challenges for hydrocarbon production and CO_2 sequestration, where near-wellbore hydrate formation can significantly impair injectivity. On the other hand, naturally occurring hydrate reservoirs in permafrost and marine sediments represent both a potential energy resource and a carbon storage option.(Sloan Jr & Koh, 2007)

Understanding hydrate dynamics in porous media requires robust simulation frameworks that can account for multiphase flow, thermal processes, and reaction kinetics. Traditional hydrate simulators (e.g., TOUGH+HYDRATE, CMG STARS) often approximate hydrate formation/dissociation using pressure–equilibrium differences, which limits applicability in non-equilibrium conditions. In this work, we extend the Delft Advanced Research Terra Simulator (DARTS) to include hydrate kinetics using the Operator-Based Linearization (OBL) approach. This method simplifies the implementation of highly nonlinear physics, allowing us to model hydrate systems under kinetic assumptions with a full thermodynamic description(Voskov et al., 2024; Michiel Wapperom et al., 2025).

Method and/or Theory

Hydrate-bearing porous media are modelled using a thermal–compositional–reactive formulation. Mass conservation for component c is expressed as:

$$\frac{\partial}{\partial t}\int_{\Omega} M^c d\Omega + \int_{\Gamma} F^c . n d\Gamma = \int_{\Omega} Q^c d\Omega$$

Here, M^cdenotes the accumulation term for the c^{th} component , F^crefers to the flux term of the c^{th} component , n refers to the unit normal pointing outward to the domain boundary; Q^c denotes the source/sink term of the c^{th} component.

We adopt a thermal–compositional–reactive formulation to model mass and energy conservation in hydrate-bearing porous media. The governing equations account for advective and diffusive fluxes, Joule–Thomson cooling, conduction, and hydrate pseudo-reactions. Hydrate is represented as an immobile solid phase occupying pore space, reducing porosity and permeability.

The kinetic model assumes instantaneous equilibrium between fluid phases but a non-equilibrium hydrate phase. Hydrate formation/dissociation is driven by the fugacity difference of water in fluid and hydrate phases, following an Arrhenius-type relation:

$$R = K . A_s(S_h) . \exp\left(\frac{-E_a}{RT}\right) . (f_{wH} - f_{wk})$$

Where A_s is hydrate surface area, E_a activation energy, and f_{wH}, f_{wk} are water fugacities in hydrate and fluid phases.

The Operator-Based Linearization (OBL) method represents nonlinear physical processes via algebraic interpolation operators, which are precomputed in a discrete parameter space and used during simulations. This avoids repeated flash calculations and simplifies Jacobian construction while retaining accuracy.

The accuracy and robustness of the hydrate simulation framework rely on a consistent thermodynamic description of all phases. At equilibrium, pressure and temperature are uniform and the Gibbs free energy of the system reaches a global minimum. The condition of equal fugacities for each component across all phases is imposed through stability analysis and phase-split routines, following the tangent plane distance criterion. This ensures that the correct number and type of phases are identified at any state point.

To achieve both accuracy and efficiency, a hybrid equation-of-state approach (M Wapperom et al., 2025) which improves the accuracy compared to full-cubic is used. Non-aqueous phases such as hydrocarbon gas and liquid are described with a cubic EoS (Peng–Robinson or Soave–Redlich–Kwong), which provides reliable predictions for nonpolar mixtures. The aqueous or brine phase is treated with a fugacity–activity model that captures the effects of salinity. Gas solubility in water is incorporated through Henry's law constants in combination with a dedicated water fugacity model, which allows accurate prediction of CO_2 and CH_4 solubility across a wide range of pressures, temperatures, and salinities. This hybrid scheme retains the efficiency of cubic-EoS based flash calculations while significantly improving thermodynamic consistency for water-rich phases.

For the hydrate phase, a modified van der Waals–Platteeuw model is applied. In this formulation, the fugacity of water in the hydrate is calculated from guest–host interactions and cage occupancies. The hydrate stability condition corresponds to the equality of water fugacity in the hydrate and fluid phases. This description is integrated into the overall flash calculation, so that hydrate equilibria are coupled consistently with the fluid phase equilibria. In kinetic simulations, the hydrate equilibrium provides the thermodynamic reference state that governs the driving force for formation and dissociation.

Thermodynamic models also supply the fluid and solid properties required in the conservation equations. Phase densities and viscosities are obtained directly from the cubic EoS or from empirical correlations where appropriate. Enthalpies are computed as the sum of ideal and residual contributions, with residual terms derived from Helmholtz free energy or fugacity derivatives. For the aqueous phase, enthalpy is obtained from the water fugacity model and Henry's law expressions for dissolved components. By conserving phase internal energies consistently, the simulator captures energy changes due to dissolution, mixing, phase transitions, and Joule–Thomson expansion.

Thermal processes play a central role in hydrate systems. The simulator includes conduction through both rock and fluids, advection of enthalpy with moving phases, cooling or heating effects associated with the Joule–Thomson expansion of gases, and the latent heat released or consumed during hydrate formation and dissociation. The strong nonlinear couplings between flow, thermodynamics, and heat transport present significant challenges for numerical simulation.

To validate the framework, we benchmarked against experimental data and existing hydrate simulators. Gibbs energy surface analysis was employed to confirm that, in the limit, kinetic models converge to equilibrium thermodynamics.

Results

We applied the model at both **core- and field-scale**:

- **Core-scale CH_4 hydrate formation**: Laboratory experiments on methane hydrate formation in sand packs were reproduced. The simulator captured spatial heterogeneity in hydrate saturation, driven by competing effects of boundary cooling, exothermic hydrate formation, and adiabatic expansion. Simulated hydrate distributions) closely matched experimental observations(Yin et al., 2018).

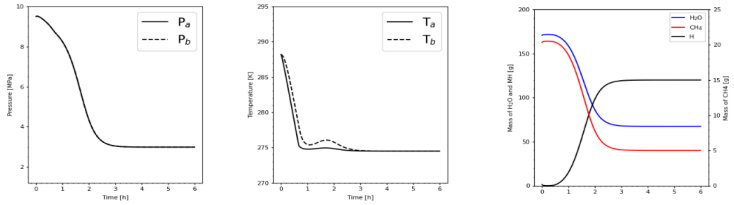

Figure 1 Results for CH4-hydrate formation experiment after 6 hours of simulation.) Time evolution of (a) pressure, (c) temperature and total mass of H_2O, CH_4 and MH components

- **Field-scale hydrate dissociation**: Two scenarios were tested in a radial reservoir:
    1. **Thermal stimulation** – a temperature increase at the well created a dissociation front. Gas production remained limited in early stages due to secondary hydrate reformation caused by pressure buildup(Kowalsky & Moridis, 2007).

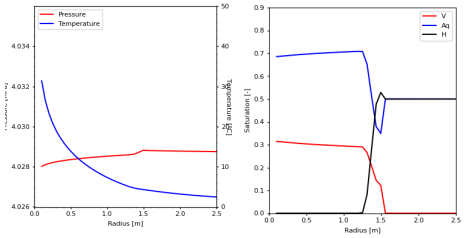

Figure 2 Results for Thermal stimulation after 30 days of simulation. Spatial distributions of pressure and temperature and saturations of V, Aq and H phases.

    2. **Depressurization** – lowering wellbore pressure produced widespread dissociation, with stronger gas release and cooling effects. Gas production rates depended strongly on initial hydrate saturation(Kowalsky & Moridis, 2007).

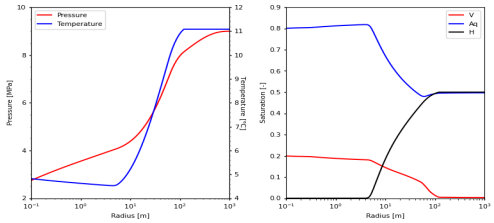

Figure 3 Results for Depressurization *case after 30 days of simulation. Spatial distributions of pressure and temperature and saturations of V, Aq and H phases.*

- **CO_2 hydrate formation**: We reproduced a core-scale CO_2 injection experiment, demonstrating the model's flexibility to extend beyond methane hydrates with minor modifications. You can find the place of temperature sensors in reference paper (Li et al., 2024).

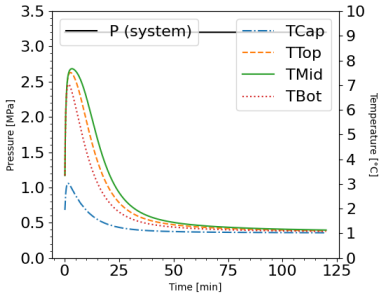

Figure 4 Pressure and temperature profiles in the CO2 hydrate formation simulation during first 2h.

Conclusions

We developed a kinetic hydrate model in porous media using the Operator-Based Linearization approach within the DARTS framework. Key findings include:

- The OBL technique effectively captures the nonlinear interactions of hydrate systems while simplifying implementation of kinetic and thermodynamic models.

- The model reproduces both laboratory-scale hydrate formation experiments and field-scale dissociation scenarios, showing consistency with published benchmarks.

- Results demonstrate strong sensitivity of hydrate behaviour to kinetic rate parameters, suggesting that calibration against experimental data is essential.

- Gibbs energy analysis confirms that kinetic and equilibrium models converge in the thermodynamic limit, supporting future comparisons of equilibrium-based and kinetic-based simulation strategies.

This framework provides a flexible tool for investigating hydrate-related risks in CO_2 sequestration operations and the feasibility of methane production from hydrate reservoirs.

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