Thermodynamics and Basic Principles in Modern Hydrocarbon and Geothermal Energy Production from Subsurface Formations

A Rice University comprehensive course by:

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Location: Rice University, Houston;
Hybrid mode, much more effective in person

July 22 –26, 2024

Scope

This five day course covers a variety of topics on efficient energy production from conventional and non-conventional hydrocarbons, geothermal, and to a lesser degree, hydrogen in the subsurface. Superhot geothermal formations at depths less than 4 km may contain as much energy as hydrocarbon formations. Recent hydrogen discoveries in subsurface formations also look promising. In addition to topics of subsurface energy production, the topic of CO_2 sequestration in the subsurface and its widespread will be covered in detail.

Thermodynamic frameworks and theories will be used in formulation of most topics. There will be a concise presentation on bulk phase, interface between phases, and thin liquid films from both classical thermodynamics and statistical thermodynamics. The treatment of topics requires coverage of both equilibrium thermodynamics and thermodynamics of irreversible processes. Both classical thermodynamics and statistical thermodynamics concepts will be used to cover molecular simulations. Effective and accurate molecular simulations are facilitated by deeper knowledge of classical thermodynamics and statistical thermodynamics. Thermodynamics provides a framework for accurate calculation and numerical modeling and ultimately engineering of new effective molecules. There will be many recent examples covered by the course. There is a potential of using more effective molecules at much lower concentration (orders) for some of processes through molecular engineering from molecular simulations.

Fluid properties, as well as deformable solid properties, and the interface between fluids and fluid-solids, are major topics in the course, among others. There are important applications of fluid-solid interfacial energy in fracturing. Neglect of interfacial energy density of fluid-solods, which is often done in fracturing simulations, reduces prediction reliability. We also cover interfacial elasticity of fluid-fluid interfaces; recently it is observed that efficiency of fluid-fluid displacement can be greatly improved from increasing interface elasticity in brine-oil and brine-CO_2.

The context of the intensive course is energy production from the subsurface and environmental stewardship. Molecular structure in fluid phases and at the interface, and molecular engineering of functional molecules are covered to emphasize the advances that can lead to efficient processes. The context of presentations are shale light oil and gas reservoirs, low salinity water injection, improved oil recovery from fluid-fluid interface elasticity increase, flow assurance in relation to asphaltenes, waxes, and hydrates and

use of low concentration of functional molecules, CO_2 fracturing and CO_2 viscosification (in relation to mobility control in CO_2 injection and sequestration and CO_2 fracturing), and efficient calculations. Various molecular structures in bulk phases and at fluid-fluid and fluid-solid interfaces in hydrocarbon production, geothermal heat extraction, fracturing, are covered. Past climate changes (based on irreversible thermodynamics) are covered to the level that computations can be performed. The concepts will be presented through cartoons to facilitate understanding of a broad range of topics. All presentations and discussions will be based on materials (book, papers, and prepared write-ups) that will be provided to participants.

Items of discussion in the course include:

- Unique properties of CO_2 and hydrogen in comparison to nitrogen and methane and water in relation to improved oil recovery, and storage in subsurface formation and phase behavior.
- Efficient and safe CO_2 sequestration in saline aquifers.
- Multicomponent Fickian diffusion, and diffusion coefficient calculation based on irreversible thermodynamics.
- The strong connection between the Lagrangian and phase-field simulation of fracturing
- Mechanisms of low salinity water injection and effect of salinity and salts on wettability, dissolution, and in micellization and microemulsions
- Why low lab recovery may give high recovery in large scale and vice versa.
- Shale-gas and shale-light oil reservoirs and unique features of shale rocks
- Strength of cubic-plus-association EOS for a variety of complex problems in aqueous mixtures and asphaltene precipitation and variety of reservoir fluids
- CO_2 mixing with reservoir fluids; Modeling of diffusion flux in reservoir simulators based on gradient of chemical potentials
- Asphaltene and resin molecular structure and interaction with water
- Formation of nano-particles of asphaltenes and hydrates, and advantage of surface property changes to bulk phase property changes

- Why adsorption measurements at high pressure (say by gravimetric methods) do not provide relevant data and should be combined with molecular simulations to interpret the instrument measurements, and why shale swells from the contact with hydrocarbons and CO_2.
- Why flow in shale nano-pores is by diffusions and why flow in nano-pores can be one to three orders of magnitude higher than the calculations based on classical expressions.
- Effect of size of nano-particles on melting and on saturation pressure
- Efficient two- and three- and four-phase split computations based on incorporation of Gibbs free energy decrease.
- The link between irreversible thermodynamics and complex diffusion processes and past climate change modeling
- Species distribution in hydrocarbons and in geothermal formations with very high CO_2 content based on irreversible thermodynamics
- Accurate calculation of thermal diffusion in multicomponents from molecular simulations
- Hydrate particle stabilization and advancing hydrate flow assurance by small amounts of functionalized molecules
- Adsorption calculation of non-associating and associating molecules from molecular simulations
- Interfacial energy density of fluid-fluid and fluid-solids, and the vast difference between the two. Explore the effect of interfacial density in fracturing of rocks
- Interfacial elasticity and the effect on water displacement of oil and CO_2 displacement of brine.
- Thermodynamics of fracturing in rocks. Phase field method. Effect of different fluids on fracturing.

Fees and Registration

The fee for attendance is USD $2,500. For the staff from companies who are members of our *Energy Production Consortium***,** the fee is USD $2,000. Faculty and PhD student fees will be discounted to USD $2,000. The course fee includes a copy of the 2016 book, *Thermodynamics and Applications in Hydrocarbon Energy and Production*, the relevant write-ups and papers, as well as the lunch. Please register and pay the course fee by May 15th. The cost of the course will increase by 5% starting May 16th, raising it to $2625 for normal admission and $2100 for faculty and PhD students, and members of our research consortium RERI.

Please fill out the Google Registration Form to sign up for the course. We will reach out to you to confirm your attendance and collect the registration fee. We will accept wire transfers for the payment, please contact us at info@rerinst.org for any questions.

Schedule

The course will begin at 9:00 a.m. on July 22 and will end at 12:30 p.m. on July 26. Daily sessions will be from 9:00 a.m. to 4:30 p.m. with a lunch break from 12:30 p.m. to 1:30 p.m. Lunch will be provided. Part of the last session in the afternoon will be devoted to discussions.

General course agenda

Day 1

9;00 a.m. –9:30 a.m.

- Brief class introduction. Overview of molecular structures in bulk-fluid phases and fluid-fluid and fluid-solid interfaces. Formulations based on basic knowledge, modeling, and modern techniques from thermodynamics in efficient oil and gas and geothermal energy production and stewardship of the environment.
- Use of thermodynamic principles in the study of shale gas, shale-light oil, flow assurance, improved oil recovery, CO_2 sequestration in aquifers, geothermal heat extraction, and engineering of new molecules.

- Use of functional molecules and drastic change of properties at low concentration
- Property change with size in nm scale.

9:30 a.m. – 10:45 a.m.

- Brief review of bulk phase equilibrium thermodynamics and various thermodynamic functions
- Unique features of grand potential in comparison to other thermodynamic functions.
- Brief introduction to chemical potentials and various features for flow from lower pressures to higher pressures in mixtures.
- Removal of fluids from a constant -volume container at constant temperature and observation of pressure increase!
- Isobaric heating of a liquid and freezing!

10:45 a.m. – 11:00 a.m.

Coffee break

11:00 a.m. – 12:30 p.m.

- General theory of bulk-phase equilibrium thermodynamics with gravity and interfacial effects
- Effect for gravity on compositional variation across a column
- Effect of curvature on bubble point, dewpoint, condensation and vaporization. Effect of size and confinement on phase behavior
- Why condensation and vaporization can be drastically different in single components and in multicomponents? Sometimes the opposite of each other!

12:30 p.m. – 1:30 p.m.

- Lunch break

1:30 p.m. – 2:30 p.m.

- Phase behavior and volumetric description of fluids and fluid mixtures and petroleum fluids from cubic equations of state (EOS) including waxes and asphaltenes.

- Nature of delay and kinetics in various processes including vaporization, condensation, crystallization, and melting
- Why kinetics of vaporization is so different from condensation: the same is true in crystallization and melting
- Phase behavior description of fluid mixtures including petroleum fluids by the PR-EOS

2:30 p.m. – 3:15 p.m.

- Concept of molecular association
- Phase behavior of water and water-CO_2 mixtures and water-hydrogen by the cubic-plus-association (CPA) EOS
- Phase behavior in asphaltene precipitation by CPA-EOS

3:15 p.m. – 3:30 p.m.

- Coffee break

3:30 p.m. – 4:30 p.m.

- Characterization of reservoir fluids for modeling of various processes, including equilibria of vapor-liquid, vapor-liquid-liquid, wax precipitation, and asphaltene precipitation.
- Effect of brine salt on dissolution of CO_2 and hydrogen.
- Brief review and discussion of various topics of the day.

Day 2

9:00 a.m. –10:45 a.m.

- Thermodynamic stability, and criticality concepts and criteria. Applications in problems of hydrocarbon reservoirs and production. High concentration of CO_2 and methane in water at metastable conditions. Application in molecular simulation calculations.
- Gibbs free energy surface analysis; How rugged is Gibbs free energy surface? Tangent plane distance analysis
- Two-, three-, and four-phase phase split computations, stability testing, and how to perform phase-split computations with any number of phases with large number of components.

10:45 a.m. – 11:00 a.m.

- Coffee break

11:00 a.m. – 12:30 p.m.

- Brief presentation on phase behavior calculations in different thermodynamic spaces and applications
- General theory of irreversible thermodynamics; Entropy production expression, Fickian, thermal, and pressure diffusion flux expressions; How can oil float on top of lighter gas forever! Example is Yufutsu field in Japan. This is possible through thermal diffusion.
- Species distribution in hydrocarbon reservoirs and geothermal formations; Past climate changes from irreversible thermodynamics

12:30 p.m. – 1:30 p.m.

- Lunch break

1:30 p.m. – 3:15 p.m.

- Species distribution in hydrocarbon reservoirs and geothermal formations; Past climate changes from irreversible thermodynamics
- Formulation of diffusion in numerical simulations.
- Interfacial thermodynamics. Gibbs adsorption equation. New phase formation and driving force. Induction time. Line tension. Effect of size on contact angle. Bubble nucleation. Induction time. Thermodynamics of adsorption in fluid solid interfaces

3:15 p.m. – 3:30 p.m.

- Coffee break

3:30 p.m. – 4:30 pm

- Thermodynamics of thin liquid films. Disjoining pressure concept.
- Effect of thin liquid film on melting point of solid nanoparticles.
- Brief review of the topics of the day and discussion

Day 3

9:00 a.m. – 10:15 a.m.

- Solution-gas drive in permeable media

- Introduction to deformable solids and definition of various key solid mechanical properties. Linear viscoelasticity
- Mechanical and thermal stability of deformable solids in failure and comparison to stability of fluids
- Basic expression of momentum balance in deformable solids

10:15 a.m. – 10:45 a.m.

- Basic concepts of statistical thermodynamics. Fluctuation theory

10:45 a.m.-11:00 am

- Coffee Break

11:00 a.m.-12:30 p.m.

- Molecular and atomistic simulations. Molecular models. Molecular dynamics simulations. Monte Carlo simulations. Various algorithms and ensembles. Potential functions. Basic concepts in conducting molecular and atomistic simulations.

12:30 p.m. – 1:30 p.m.

- Lunch break

1:30 p.m. – 2:30 p.m.

- Hydraulic fracturing by water and by CO_2. Griffith's idea of deformable media failure from tension; critical energy release rate.
- Lagrangian and the Euler-Lagrange equation
- Phase field formulation of fracturing and fracture propagation

2:30 p.m. – 3:15 p.m.

- Fluid-solid interfacial energy density. Molecular simulations.
- Thermal stress
- Hydraulic fracturing by CO_2 and by water: breakdown pressure, fracture intensity. Effect of thermal stress on fracturing.

3:15 p.m. – 3:30 p.m.

- Coffee break

3:30 p.m. – 4:30 p.m.

- CO_2 viscosification and effectiveness in displacement of brine and oil by viscosified CO_2.
- Basic requirements of CO_2 viscosifier molecules
- Brief review of the topics of the day and discussions

Day 4

9:00 a.m.-10:00. a.m.

- Molecular simulation of adsorption in CO_2 viscosifier oligomers
- Viscosity calculation by molecular simulations

10:00 a.m.-10:45 a.m.

- Introduction to flow assurance: waxes, hydrates, and asphaltenes.
- Asphaltene colloidal stabilization in petroleum fluids by functional molecules; Molecular dissolution of asphaltenes in petroleum fluids at very low concentration of functional molecules;
- Effect of water and brine on asphaltene precipitation, deposition, and mitigation

10:45 a.m.-11:00 a.m.

- Coffee Break

11:00 a.m. –12:300 a.m.

- Wax mitigation by crystal modifiers and dispersant. Effect of water
- Natural gas hydrates. Various molecular structures
- Driving force in hydrate formation. Hydrate anti-agglomeration; Hydrate slurry and hydrate powder by functional molecules at low concentrations

12:30 p.m. – 1:30 p.m.

- Lunch break

1:30 p.m.- 2:15

- Molecular simulation of hydrates and hydrate anti-agglomeration. Effect of salt and hydrocarbons on hydrate anti-agglomeration

2:15- 3:00

- Introduction to shale-gas and shale-light oil reservoirs. Kerogen media.

- Adsorption and desorption in shale and kerogen media. Swelling from CO_2 and hydrocarbons in kerogen media

3:00 p.m. – 3:15 p.m.

- Coffee break

3:15 p.m. – 4:30 p.m.

- Flow and Separation of species in shale nano-pores. Flow in shale media.
- Molecular simulations of adsorption and swelling in kerogen media
- Review of the topics of the day and discussions

Day 5

9:00 a.m.-10:15 a.m.

- Molecular simulation of wettability and contact angle.
- Molecular simulation of mutual solubility in different fluid phases.
- Molecular simulations of Fickian and thermal diffusion in multicomponent mixtures
- Molecular simulations of CO_2-brine and H_2-brine at superhot conditions

10:115 a.m-10:45 a.m.

- Introduction to rheology and interfacial rheology.

10:45-11:00

- Coffee break

11:00 a.m. – 12:30 p.m.

- Low salinity water injection
- Major effect of fluid-fluid interfacial elasticity on displacement in porous media
- Increase in oil recovery from increase in interfacial elasticity in porous media
- Course Wrap-up

12:30 p.m – 1:30 p.m.

Lunch