Hydrocarbon Reservoirs and Production: Thermodynamics and Rheology

A comprehensive course by

Prof. Abbas Firoozabadi

Reservoir Engineering Research Institute

and

Prof. Gerald Fuller

Stanford University

Palo Alto, California USA

August 14 – 18, 2017

Shriram Center at Stanford University

Scope

This five-day intensive course offers a unified thermodynamic framework (bulk phase equilibrium, interfacial, and thin films), statistical thermodynamics and molecular simulations (mostly in relation to adsorption at the fluid-solid, and fluid-fluid interfaces, and wettability), and rheological aspects of a large number of topics in hydrocarbon energy production and environmental stewardship. Important topics from molecular structure in bulk and at the fluid-fluid and fluid-solid interfaces will be presented. The context of presentations is related to low salinity water injection, shale gas, shale light oil, heavy and super-heavy oil production, asphaltene deposition and removal, hydrate flow assurance, wax mitigation, CO_2 injection in light and heavy oil reservoirs, efficient and robust phase-split computations, emulsions, microemulsions, and past climate changes are covered to the level that computations can be performed. A focus of the course will be on thermodynamics of nano-particles and the vast opportunity that they offer for process improvement, efficiency, and safety. Efficient molecular dissolution of asphaltenes, and colloidal stabilization will be discussed in detail. The structures in various salt solutions in relation to micellization and microemulsion, and low salinity water injection will be covered. Viscoelasticity of bulk phase and fluid-fluid interface will be discussed but the focus will be on fluid-fluid interface elasticity. As a whole vast opportunities that functional molecules at some 100ppm concentration offer for improved hydrocarbon recovery and production will be a unique feature of this intensive course. The need for combining molecular simulations and molecular thermodynamics will be demonstrated in prediction of molecular structure and adsorption at the fluid-fluid and fluid-solid interfaces. 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 available to participants.

Items of discussion in the course include:

- Unique properties of CO_2 in comparison to nitrogen and methane and other fluids in relation to improved oil recovery in fractured and unfractured reservoirs containing light, heavy, and super-heavy oils. Field experiences from different parts of the world will be discussed.
- Mechanisms of low salinity water injection
- Effect of salinity and different types of salts on wettability, dissolution, and in micellization and microemulsion
- Why a chemical which gives a recovery in excess of 95% for water injection in the lab may fail in field applications.
- Shale-gas and shale-light oil reservoirs and unique features of shale rocks
- Phase behavior of mixtures of bitumen and various gases and normal alkanes and why normal alkane injection in heavy oils may encounter challenges.
- Strength of cubic-plus-association EOS for a variety of complex problems in aqueous mixtures and asphaltene precipitation
- Predictive capability of EOS and reservoir fluid characterization
- CO_2 mixing with reservoir fluids; Modeling of diffusion flux in reservoir simulators based on chemical potential driving forces
- Asphaltene and resin molecular structure and interaction with water and viscosity reduction
- Formation of nano-particles of asphaltenes and hydrates, and advantage of surface property changes to bulk phase property changes
- Why phase behavior 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. Why there is no hydrocarbon data except methane excess adsorption (and only one recent paper on ethane apparent adsorption) in shale media.
- Why flow in shale nano-pores is one to three orders of magnitude higher than the calculations based on the models in the current literature.
- Effect of size of nano-particles on melting and on saturation pressure
- Efficient two- and three-phase split computations
- The link between irreversible thermodynamics and complex diffusion processes and past climate change modeling
- Asphaltene removal from pipes and from rocks by efficient molecular dissolution
- Species distribution in hydrocarbon reservoirs from irreversible thermodynamics

- Hydrate particle stabilization and advancing hydrate flow assurance by small amounts of functionalized molecules
- Basic-level understanding of microemulsion and micellization and application to a variety of problems in hydrocarbon energy production.
- Interfacial Rheology
- Interfacial rheology measurement interpretation in relation to improved oil recovery

Schedule

The course will begin at 8:30 a.m. on August 14, and will end at 4:30 p.m. on August 18, 2017. Daily sessions will be from 8:30 a.m. to 4:30 p.m. with a lunch break from 12:15 p.m. to 1:30 p.m. Part of the afternoon sessions will be devoted to discussions.

General course agenda

Day 1

8:30 a.m. – 9:30 a.m.
- Overview of molecular structures in petroleum fluids and fluid-fluid and fluid-solid systems and various issues in oil and gas production from thermodynamics and rheology concepts and modern techniques
- Use of thermodynamic principles in the study of shale gas, shale-light oil, flow assurance, and improved oil recovery
- Use of functional molecules to drastic change of properties
- Property change with size in the nm range

9:30 a.m. – 10:30 a.m.
- Brief review of bulk phase equilibrium thermodynamics
- Removal of fluids from a container and observation of pressure increase!

10:30 a.m. – 10:45 a.m.
- Coffee break

10:45 a.m. – 12:15 p.m.
- General theory of bulk-phase equilibrium thermodynamics in relation to gravity and interfacial effects, and electric field
- How we increase or decrease normal boiling by the size of the confinement and type of fluids?
- Why condensation and vaporization can be drastically different in single components and in multicomponents! Sometimes the opposite of each other!
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12:15 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)
- 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
- Why the PR-EOS works so well for reservoir fluids

2:30 p.m. – 3:15 p.m.
- Concept of molecular association
- Phase behavior of water and water-CO_2 mixtures 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.

- Phase behavior of bitumen with CO_2 and normal alkanes by CPA-EOS and PR-EOS
- Discussions and presentation of examples

Day 2

8:30 a.m. – 8:45 a.m.

- Characterization of reservoir fluids for modeling of various processes, including equilibria of vapor-liquid, vapor-liquid-liquid, wax precipitation, and asphaltene precipitation

8:45 a.m. – 10:30 a.m.

- Stability and criticality concepts and criteria, and applications in problems of hydrocarbon reservoirs and production; Gibbs free energy surface analysis; How rugged is Gibbs free energy surface? Tangent plane distance analysis

10:30 a.m. – 10:45 a.m.

- Coffee break

10:45 a.m. – 12:15 p.m.

- Two- and three-phase split computations; Stability testing; How to perform phase-split computations with any number of phases with large number of components

12:15 p.m. – 1:30 p.m.

- Lunch break

1:30 p.m. – 2:30 p.m.

- General theory of irreversible thermodynamics; 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 effects.

2:30 p.m. – 3:15 p.m.

- Species distribution in hydrocarbon reservoirs; Past climate changes
- Why mixing can separate the components in a hydrocarbon reservoir? The result is a high variation of horizontal composition change in a connected domain.

3:15 p.m. – 3:30 p.m.

- Coffee break

3:30 p.m. – 4:30 pm

- Introduction to interfacial thermodynamics
- New phase formation and driving force. Induction time.
- Effect of charge on bubble nucleation and condensation
- Discussions and examples

Day 3

8:30 a.m. – 9:15 a.m.

- Solution-gas drive in permeable media
- Thermodynamics of thin liquid films. Thin film description.
- Effect of size on melting point due to thin films

9:15 a.m. – 10:30 a.m.

- Introduction to shale-gas and shale-light oil reservoirs
- Condensation and vaporization in nano-pores less than 10 nm
- Phase behavior and flow in shale nano-pores; Adsorption and desorption in shale media by gravimetric method

10:45 a.m-12:15 p.m.

- Introduction to statistical thermodynamics, molecular simulations and molecular dynamics simulations; Grand potential and not Gibbs free energy is the thermodynamic function of choice in some nano-scale problems. One key advantage is that there is no need for knowledge of pressure! Simple concepts and vast applications

12:15 p.m. – 1:30 p.m.
- Lunch break

1:30 p.m. –2:30 a.m.
- Modeling of phase behavior and adsorption in shale porous media and in pores less than 10 nm; Complexities from hysteresis in shale media; no theory yet!
- Why use of EOS with adjusted T_C and P_C should be avoided in phase behavior in shale small nano-pores.

2:30 p.m. – 3:15 p.m.
- Modeling of flow in shale nano-pores
- Limitations of Knudsen and Klinkenberg flow expressions

3:15 p.m. – 3:30 p.m.
- Coffee break

3:30 p.m.- 4:30 p.m.
- Introduction to micellization and emulsion
- Thermodynamics of micellization and microemulsion; Effect of different salts; Why different salt molecules are so different in their effectiveness?
- Emulsion flow in porous media. Higher flow rates give lower pressure drops. This makes use of Dacry's law inappropriate! Detrimental effect of water-in-oil emulsion in oil revovery.
- Discussions

Day 4

8:30 a.m. – 9:15 a.m.
- Thermodynamics of adsorption in fluid-solid and fluid-fluid adsorption.

9:15 a.m. – 10:30 p.m.
- Adsorption of ionic and nonionic surfactant at the fluid-solid interfaces; Adsorption of ionic and non-ionic surfactants at the fluid-fluid interfaces and interfacial tension.

10:30 a.m.–10:45 a.m.
- Coffee break

10:45 am-11:45 a.m.
- Asphaltene colloidal stabilization in petroleum fluids by functional molecules ; Molecular dissolution of asphaltenes in petroleum fluids with very low concentration of acidic surfactants; Dissolution of deposited asphaltene molecules back into petroleum fluids
- Effect of water and brine on asphaltene precipitation and deposition and mitigation

11:45 p.m. –12:15 pm.
- Natural gas hydrates
- Driving force in hydrate formation
- Hydrate anti-agglomeration; Hydrate slurry and hydrate powder by functionalized molecules at low concentrations

12:15 p.m. – 1:30 p.m.
- Lunch break

1:30 p.m.–2:30 p.m.
- MD simulation of hydrates; MD simulation of hydrate anti-agglomeration; Effect of salt on hydrate anti-agglomeration; tuning hydrate ani-agglomerants for effectiveness

2:30 p.m.- 3:15 p.m.
- Wax mitigation by crystal modifiers and dispersant. Effect of water

3:15 p.m. – 3:30 p.m.
- Coffee Break

3:30 p.m.- 4:45 p.m.

- Low salinity water injection; Mechanisms; Wettability change from salt concentration, measurements and MD simulations. Comparison from very low concentration chemical injection;
- Discussion on contact angle from MD simulations. Effect of CO_2 on wettability

Day 5

8:30 a.m. – 9:30 a.m.
- The class will be introduced to the science of rheology, which concerns the flow and deformation of complex, non-Newtonian liquids. This subject, which links together fluid mechanics and material science, has great application in the recovery of oil from porous media, wax and hydrate flow assurance, drilling operations that employ complex muds, the design of fracturing fluids, and the stability of oil-water emulsions.

9:30 a.m. – 9:45 a.m.
- Introduction to rheology, the stress tensor in flowing liquids and the rate of strain tensor. Definition of rheological material functions (viscosity, normal stress differences, compliance, dynamic moduli). Shear rheometry and constitutive models.

9:45 p.m. – 10:15 p.m.
- The design of rotational shear rheometers

10:15 p.m. – 10:30 p.m.
- Coffee break

10:30 a.m. – 11:30 a.m.
- Application of rotational shear rheometry to fluids in the production of oil
- Extensional rheometry. The extensional viscosity of mobile liquids. The design of extensional rheometers and their application to liquids used in enhanced oil recovery.

11:30 a.m. – 12:15 p.m.
- Interfacial rheology. Classification of complex fluid interfaces. Interfacial rheological material functions.

12:15 p.m. – 1:30 p.m.
Lunch Break

1:30-2:00 pm
Design of interfacial rheometers. Application to emulsion stability. The role of asphaltenes in emulsion stability.

2:00- 3:15 p.m.
- Review and applications of rheological measurements in oil production.

3:15-3:30 p.m.
Coffee Break

3:30-4:30 p.m.
Discussions and review of the course

Fees and Registration

The fee for attendance is US $2,600. For the staff members of those companies who are members of the Institute, the fee is US $2,200. The course fee includes a copy of the 2015 book, *Thermodynamics and Applications in Hydrocarbon Energy and Production*, and a file containing relevant write-ups and papers. A limited academic discount for PhD students and faculty members is available.

Payments should be made by wire transfer or check before July 1, 2017. Please make checks payable to Reservoir Engineering Research Institute and mail your payment to RERI | 595 Lytton Avenue, Suite B | Palo Alto, CA 94301. To arrange a payment by a wire transfer, please email us at info@rerinst.org. Payments may be refunded upon cancellation at least 30 days prior to the beginning of the course.

We ask prospective participants to register by completing our [Online Registration Form]