

A comprehensive course

By

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Link

<https://glasscock.rice.edu/course?id=41822059>

Scope

This five-day course offers a unified framework from classical equilibrium and irreversible thermodynamics, and statistical thermodynamics, and molecular simulations to investigate bulk phases, interfaces, and thin liquid films. Rheology of bulk and interfaces is an integral part of the intensive course. The focus of the topics will be on molecule structure in bulk phase, adsorption at the fluid-solid and fluid-fluid interfaces, interfacial energy density of fluid-fluid and fluid-solid interfaces, wettability, viscosification of CO₂, hydraulic fracturing by water and by CO₂ in tight hydrocarbon and geothermal formations, and interfacial rheology. Many topics are covered in relation to efficient hydrocarbon energy and renewable 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 is 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, CO₂ fracturing in shale and in geothermal formations, and CO₂ viscosification (in relation to mobility control in CO₂ injection and sequestration and CO₂ fracturing). Various structures in bulk phases from micelles and emulsions in hydrocarbon production are covered. We will also cover efficient and robust phase-split computations in relation to CO₂ and fluid hydrocarbons and asphaltene rich-phase, and CO₂ and water, CO₂-brine, hydrogen-water, and hydrogen-brine. Past climate changes are covered to the level that computations can be performed. The course will go beyond nano-particles; at the atomic scale the vast opportunities that functional molecules can offer for process improvement, efficiency, and safety will be explored. Efficient molecular dissolution of asphaltenes, and colloidal stabilization will be discussed. A new improved oil recovery that may only require a concentration of 100 ppm functional molecules in brines of high salinity will be presented in detail. Various advantage of CO₂ fracturing of tight oil and gas formations and hot dry rock in geothermal formations will be discussed in detail. The need for combining molecular simulations and molecular thermodynamics will be demonstrated in prediction of molecular structure and adsorption at the 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 proved to participants.

A topic of major emphasis will be use of CO₂ : in CO₂ sequestration, CO₂-IOR, and CO₂ fracturing based on fundamentals. Direct CO₂ viscosification will facilitate the widespread use.

Items of discussion in the course include:

- Unique properties of CO₂ in comparison to nitrogen and methane and water in relation to improved oil recovery in fractured and unfractured reservoirs and fracturing of tight formations and geothermal formations. Lab results and field experiences from different parts of the world will be discussed.
- Efficient and safe CO₂ 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 a low lab recovery may give a 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. Basic concepts in electrolytes. E-CPA EOS.
- Predictive capability of EOS and reservoir fluid characterization
- CO₂ 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. Why shale swells from the contact with hydrocarbons and CO₂.
- Why flow in shale nano-pores is by diffusions. Why flow in nano-pores is 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
- 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
- Thermal diffusion in CO₂-water and CO₂-brine in CO₂ sequestration in aquifers
- 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
- New IOR by increase in interfacial elasticity.
- Thermodynamics of fracturing in rocks. Solid-fluid interfacial energy density. Phase field method

Schedule

Daily sessions will be from 9:0 a.m. to 4:30 p.m. in the first day and from 8:30 am to 4:30 p.m. in the last four day with a lunch break from 12:30 p.m. to 1:30 p.m. Part of the last daily 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 petroleum fluids and fluid-fluid and fluid-solid systems and use of basic knowledge, modeling, and modern techniques from thermodynamics and rheology 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, and improved oil recovery
- Use of functional molecules and drastic change of properties
- Property changes with size in the nm range
- Solubility increases in CO₂ at constant temperature and pressure with increase in size of one group of hydrocarbons!

9:30 a.m. – 10:30 a.m.

- Brief review of bulk phase equilibrium thermodynamics
- Unique features of the thermodynamics function grand potential in comparison to other thermodynamic functions.

- Removal of fluids from a constant -volume container at constant temperature and observation of pressure increase!
- Isobaric heating of a liquid and freezing!

10:30 a.m. – 10:45 a.m.

- Coffee break

10:45 a.m. – 12:30 p.m.

- General theory of bulk-phase equilibrium thermodynamics with gravity and interfacial effects
- 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!

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.
- 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 and brine-CO₂, H₂-water, and H₂-brine by the cubic-plus-association (CPA) EOS, and e-CPA
- 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 CO₂ and normal alkanes by CPA-EOS and PR-EOS
- Characterization of reservoir fluids for modeling of various processes, including equilibria of vapor-liquid, vapor-liquid-liquid, wax precipitation, and asphaltene precipitation
- Discussions of various topics of the day.

Day 2

8:30 a.m. – 10:30 a.m.

- Thermodynamic 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
- Two- and three- and four-phase phase split computations; Stability testing; How to perform phase-split computations with any number of phases with large number of components.
- Brief presentation on phase behavior calculations in UNV space and major difference with the PTN and VTN spaces.

10:30 a.m. – 10:45 a.m.

- Coffee break

10:45 a.m. – 12:30 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 diffusion.
- Species distribution in hydrocarbon reservoirs; Past climate changes from irreversible thermodynamics
- CO₂-water, CO₂-brine segregation in thermal and gravity fields

12:30 p.m. – 1:30 p.m.

- Lunch break

1:30 p.m. – 3:15 p.m.

- 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

- Defining parameters of deformable media; thermodynamics of deformable solids. Thermal stress
- Discussion of the topics of the day.

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 micellization and emulsions
- 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 Darcy's law inappropriate in some coreflooding! Detrimental effect of water-in-oil emulsion on flow
- Introduction to molecular simulation.

10:30 a.m.-10:45 am

- Coffee Break

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

- Molecular and atomistic simulations: basic concepts of statistical thermodynamics. Thermodynamic and molecular models. Molecular dynamics simulations. Monte Carlo simulations

11:45 a.m. – 12:30 p.m.

- Molecular and atomistic simulations (continued): Various algorithms and ensembles. Potential functions. Basic concepts in conducting molecular and atomistic simulations.
- Linear elasticity. Phase behavior and mutual solubility calculations by molecular simulations. Challenges in calculation of solubility of polymers in CO₂.

12:15 p.m. – 1:30 p.m.

- Lunch break

1:30 p.m. – 2:30 p.m.

- 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
- Fluid-solid interfacial energy density. Molecular simulations
- Comparison of hydraulic fracturing by CO₂ and by water: breakdown pressure, fracture intensity in shale and in geothermal formations.

2:30 p.m. – 3:15 p.m.

- CO₂ viscosification and effectiveness in displacement of brine and oil by viscosified CO₂.
- Why some oligomers may be effective in CO₂ solubility and viscosification

3:15 p.m. – 3:30 p.m.

- Coffee break

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

Introduction to flow assurance: waxes, hydrates, and asphaltenes.
Discussions.

Day 4

8:30 a.m.-9:30. a.m.

- Asphaltene colloidal stabilization in petroleum fluids by functional molecules; Molecular dissolution of asphaltenes in petroleum fluids at very low concentration of functional molecules; Dissolution of deposited asphaltene molecules back into petroleum fluids
- Effect of water and brine on asphaltene precipitation and deposition and mitigation
- Wax mitigation by crystal modifiers and dispersant. Effect of water

9:30 a.m.-10:30 a.m.

- Natural gas hydrates
- Driving force in hydrate formation
Hydrate anti-agglomeration; Hydrate slurry and hydrate powder by functional molecules at low concentrations

10:30 a.m.-10:15 am

- Coffee Break

10:15 a.m. –11:00 a.m.

- Low salinity water injection; Mechanisms

11:00 a.m.-12:00 pm

- Improved oil recovery by effective functional molecules at 100 ppm concentration through increase in interface elasticity
- Introduction to shale-gas and shale-light oil reservoirs

12:30 p.m. – 1:30 p.m.

- Lunch break

1:30 p.m.- 2:30 pm

- Condensation and vaporization in nano-pores more than 10 nm
- Phase behavior in shale nano-pores more than 10 nm
- Adsorption and desorption in shale and kerogen media. Swelling from hydrocarbons in kerogen media

2:30 p.m. – 3:30 p.m.

- Flow and Separation of species in shale nano-pores. Flow in shale media.

3:00 p.m. – 3:15 p.m.

- Coffee break

3:15 p.m. – 4:30 p.m.

- MD simulation of hydrates and hydrate anti-agglomeration; Effect of salt and hydrocarbons on hydrate anti-agglomeration
- Effect of droplet size on contact angle. MD simulations of contact angle
- Discussions

Day 5

8:30 a.m.-10:30 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. 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.

10:30-10:45

- Coffee break

11:45 a.m. – 12:30 p.m.

- Linear viscoelasticity

12:30 p.m. – 1:30 p.m.

- Lunch break

1:30 p.m. – 2:30 p.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.

2:30 p.m. – 3:30 p.m.

- Interfacial rheology. Classification of complex fluid interfaces. Interfacial rheological material functions.

3:30 p.m. – 3:45 p.m.

- Coffee break

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

Application of bulk and interfacial rheology to problems in oil production and manufacturing
Discussions

The lectures are based on Thermodynamics and Applications in Hydrocarbon Energy and Production, and a file containing relevant write-ups and papers.

Fees and Registration The fee for attendance is US \$2,900. For the staff members of those companies who are members of the Research Consortium, the fee is US \$2,300. Faculty and PhD student fee will be also US\$2,300. The course fee includes a copy of the 2016 book, *Thermodynamics and Applications in Hydrocarbon Energy and Production*, and a file containing relevant write-ups and papers as wells as the lunch.