Molecular Simulation of Hydrocarbon Occurrence and Phase Behavior in Nano Pores

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Abstract

Molecular simulation (MS) can mimic physical movements of interacting atoms and molecules in a complex system. The trajectories of atoms and molecules are determined by numerically solving the Newton's equations of motion where forces between atoms and molecules are defined by fields of molecular mechanics force. MS is able to deal with a vast number of particles and associated properties in complex systems numerically. In studying unconventional petroleum systems such as tight oil and shale gas, the occurrence and phase behavior of hydrocarbons in nano pores remain enigmatic. There are quite a few hypotheses on how hydrocarbons are stored in or adsorbed on the reservoir matrix but they cannot be adequately verified in the laboratory due to physical constraints. MS provides a valuable tool to numerically test various models from a molecular perspective. We applied MS to simulate light hydrocarbons and natural gas adsorption in zeolites, montmorillonite and quartz and have obtained the following understandings: (1) MS of a typical natural gas in SiO\textsubscript{2} at layer spacings of 1-2 nm and under 310°K and 0-15 MPa shows that the adsorption capacity on SiO\textsubscript{2} is affected by layer spacings and pressure; Propane and C\textsubscript{2}H\textsubscript{6} have stronger adsorption capacity than CH\textsubscript{4}. (2) MS of natural gas in Na-Otay montmorillonite in a layer spacing of 2 nm, at 353.5°K and 5-25 MPa shows that the mole fraction of CH\textsubscript{4} in the adsorbed phase is lower than in the bulk phase, but C\textsubscript{2}H\textsubscript{6} and C\textsubscript{3}H\textsubscript{8} in the adsorbed phase are higher; In Na-Otay Na\textsuperscript{+} is closest to CH\textsubscript{4} (3.2Å) followed by O (3.9Å) and Si (4.6Å); Water (7.15% wt) in Na-Otay reduces the adsorption capacity of CH\textsubscript{4} by 40%. (3) MS of CH\textsubscript{4} and CO\textsubscript{2} in FAU zeolites indicates that temperature has little effect on the adsorption at 1 MPa for CO\textsubscript{2} and 10 MPa for CH\textsubscript{4} with both having the same adsorption capacity. (4) MS of light hydrocarbons and quartz in a layer spacing of 20 nm at 350 K and 20 MPa shows that benzene is preferentially adsorbed onto the quartz by an order of magnitude over n-hexane. In nano pores, natural gas is adsorbed on the mineral surface as single layers. The aromatic fraction appears to be preferentially adsorbed on the mineral surfaces over the n-alkanes. Water has an adverse effect on the gas adsorption capacity. Those findings provide useful insights for understanding the occurrence of hydrocarbons in tight reservoirs and shales.
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Presentation Outline

- Challenges in studying unconventional resources
- Molecular simulation (MS)
- MS methods and model design
- Hydrocarbon adsorption on minerals
  - Quartz
  - Organics (coal)
  - Montmorillonite (Na-Otay)
  - Zeolite (FAU)
- Implications for tight oil and shale gas research
Complexity of the Unconventional Reservoirs

Tertiary Shale oil reservoir from the Biyang Sag
Pore Sizes of Conventional and Unconventional Reservoirs

- Water
- Glucose
- Antibody
- Virus
- Bacteria
- Barite
- Human hair
- Pencil tip
- Ant
- Tennis ball

Asphaltene

Pore sizes ranging from $10^{-1}$ nm to $10^8$ nm are shown with examples of materials and their respective pore sizes:

- Water: $10^{-1}$ nm
- Glucose: $10^0$ nm
- Antibody: $10^1$ nm
- Virus: $10^2$ nm
- Bacteria: $10^3$ nm
- Barite: $10^4$ nm
- Human hair: $10^5$ nm
- Pencil tip: $10^6$ nm
- Ant: $10^7$ nm
- Tennis ball: $10^8$ nm

20 nm

20 µm

500 µm
Presenter’s notes: This preliminary comparison of methane sorption isotherms measured in different laboratories in 2012 indicate that significant uncertainties are still associated with these tests in terms of consistency and reproducibility. Measurements of comparatively small sorption capacities are challenging with commercial instruments. The results should therefore be considered with due caution and not be over-interpreted. Much of the scatter must be attributed to differences in sample preparation.
Challenges in Direct Imaging Hydrocarbon Occurrence under Reservoir P/T Conditions

MS provides a way to visualize and quantify fluid-mineral interaction based on theoretical model + experiments.
Molecular Simulation

Molecular simulation (MS): Monte Carlo (MC) and Molecular Dynamics (MD) simulations

- Mimic physical movements of interacting atoms and molecules in a complex system
- Trajectories of atoms and molecules are determined by numerically solving the Newton's equations of motion where forces between atoms and molecules are defined by fields of molecular mechanic force
- Deal with a vast number of particles and associated properties in complex systems numerically

MS serves as a bridge between macroscopic & microscopic domains, experiment & theory
Molecules are put in a simulation box giving initial positions and velocities. Positions and velocities are updated by integrating the equations of motion. Use statistical mechanics to derive useful information from the detailed microscopic behaviour of the system. Relate the microscopic information to the macroscopic properties.

Applications of Molecular Simulation | Junfang Zhang | Page 4

How MS Is Performed

Prediction of Oil/Gas behavior in the Reservoir

Digital Oil

Digital Rock

Digital Oil Field

Time

Hydrodynamic properties

EOS

Computational chemistry

Thermodynamic properties

Quantum Mechanics

Molecular Dynamics

Lattice Boltzmann Method

Lab. Experiment (HPTP)

Reservoir Simulation

Need to know behavior of hydrocarbons at our reservoir (Matsuoka, 2014)
Applications of MS: Nano-fluids

Slip boundary

At nano scale atoms of minerals are no longer static
Polymer moving through a 2-nm channel
Hydrocarbon Adsorption on Minerals and Coal

- Quartz
- Coal
- Montmorillonite (Na-Otay)
- Zeolite (FAU)

Adsorbed Phase: CH$_4$, C$_2$H$_2$, C$_3$H$_6$, Benzene, n-C$_6$H$_{14}$, n-C$_{20}$H$_{42}$ and CO$_2$
Simulation Conditions

Surface Area: $24.55 \times 27.01 \text{ Å}^2$

Layer Interval: 10, 15, 20, 200 Å

T: 310-350 K

P: 0-25 MPa

Compositions: $C_1$ (92%), $C_2$ (6%), $C_3$ (2%)

Light HCs: Benzene, $C_6H_{14}$, $C_{20}H_{42}$
CH₄ Adsorption on SiO₂: Results

Simulated isotherm sorption curve vs channel dimensions
Gas Adsorption on SiO₂

Channel width: 10 Å; P=15 MPa

Radio Distribution Function

- CH₄ (methane)_O
- CH₃ (ethane)_O
- CH₃ (propane)_O
- CH₂ (propane)_O

![Graph showing RDF for various molecules](image)
CH$_4$ Adsorption on Coal

**Simulation Conditions**

308K; 0-10 MPa
Moisture contents: 0%-3%
Absolute adsorption of CH$_4$ [mmol/g] vs Pressure [MPa]

- **Simulation (coal with 0 wt% water)**
- **Simulation (coal with 1.2 wt% water)**
- **Simulation (coal with 3.0 wt% water)**
- **Langmuir fit (coal with 0 wt% water)**
- **Langmuir fit (coal with 1.2 wt% water)**
- **Langmuir fit (coal with 3.0 wt% water)**

**Simulated isotherm sorption curve vs Langmuir fit**

- **Dry**
- **30%**
- **3.0% water**
CH$_4$ Adsorption on Na-Otay (montmorillonite)

Simulation Conditions

353.5 K; 5-25 MPa

Moisture contents: 7%

Modeling box: 21X

18.28 X 6.56 Å$^3$

Interlayer: 2 nm

\[ \begin{align*}
M_x^+ & \left[ Si_{a} Al_{8-a} \right] (Al_{b} Mg_{4-b})O_{20}(OH)_4
\end{align*} \]

\[ x = 12 - a - b \]

a = 8; b = 3
Gas Adsorption on Na-Otay: Results

Gas isotherm sorption curve at $T=353.5$ K from MS

Adsorption isotherm [mol/kg] vs. $P$ [MPa]

- Methane ($\text{CH}_4$)
- Ethane ($\text{C}_2\text{H}_6$)
- Propane ($\text{C}_3\text{H}_8$)
CH$_4$ Adsorption on Montmorillonite

CH$_4$ adsorbed on the Na$^+$ of Na-Otay as a single layer
CH$_4$ Adsorption on Na-Otay: Results

CH$_4$ isotherm sorption curves at T=353.5 K with pressure for dry and moist Na-Otay from MS
CH₄ & CO₂ Adsorption on FAU-Zeolite

**Rationale:**
There is great controversy in the isotherm adsorption community on the CO₂ and CH₄ adsorption capacity and gas bulk density.

**Simulation Conditions**
288-328 K; 1-100 MPa

**FAU-Zeolite**: CaₓNa₈₈₋₂ₓAl₈₈Si₁₀₄O₃₈₄ , Si/Al=1.18
The adsorption capacity of CO₂ and CH₄ on Zeolite are the same at high pressure (>30 MPa) and temperature has no effect on the AC at HP.
CO₂ & CH₄ Adsorption on FAU-Zeolite: Results

At high pressure (>60 MPa) the density of adsorbed phase of CH₄ and the bulk density converge, temperature has no effect on both densities.

Bulk density = the average density of the free gas and adsorbed gas.
Gas \((C_1-C_3)\) adsorbed on minerals predominantly in single layer

- \(C_2H_4 \& C_3H_8\) have stronger adsorption capacity (AC)
- \(\text{CH}_4\) adsorption increases with pore sizes (1-2 nm)
- At high P, temperature has little effect on gas AC
- \(\text{CH}_4\) bulk density = density of adsorbed phase at HP
- \(\text{CH}_4\) and \(\text{CO}_2\) have similar adsorption capacity at HP
- Water has an adverse effect on gas adsorption
- Aromatics are preferentially adsorbed on mineral surface over n-alkanes
Implications

➢ Resource assessment (adsorption capacity)
  ➢ P/T effect on the gas adsorption capacity
  ➢ Bulk density of shale gas at high pressure
  ➢ Minimum pore size for gas storage
  ➢ H₂O on adsorption capacity

➢ Production and flow mechanism
  ➢ Single layer adsorption (pore throat)
  ➢ Water-wet minerals conducive for gas flow
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Thank you
Combined Monte Carlo and molecular dynamics simulation of methane adsorption on dry and moist coal

Junfang Zhang, M.B. Clennell, D.N. Dewhurst, Keyu Liu

Molecular Simulation of CO₂ Solubility and Its Effect on Octane Swelling

Junfang Zhang, Zhejun Pan, Keyu Liu, and Nick Burke

Thermodynamic Analysis of Molecular Simulations of CO2 and CH4 Adsorption in FAU Zeolites

Junfang Zhang, Nick Burke, Shuichang Zhang, Keyu Liu, Marina Pervukhina.