Extension of SAFT equation of state to include calcite wall effect in water properties within water-calcite interface using molecular dynamic simulations

Abstract

On the fluid-rock interface, the order of the molecular structure and dynamical properties of fluid deviates from that of the bulk phase and the fluid exhibits a different thermodynamic behavior. To develop an understanding of the fluid-rock interface molecular dynamic (MD) simulations is conducted for water-calcite system. In this study, the results of MD simulations explicitly exhibit the layering transition of water on water-calcite interface. To predict the water properties near calcite wall, we have defined a contribution for Helmholtz energy extended from SAFT equation of state (EOS). The new energy contribution depends on the dimensionless length-ratio (L/σ) presenting the confinement size. In addition, the confined water molecules interact with calcite surface through a square well energy (ε) estimated by MD simulation at a certain temperature (T). The outcomes of MD simulations confirm the serious deviation of Helmholtz, in confinement, corresponds to the small values of L/σ where the calcite electrostatic field overcomes the bulk water field. In this approach, the modified SAFT shows a good agreement with MD observations. Furthermore, the introduced model can predict the thermodynamic properties of water at systems with low water content.

Keywords: Molecular Dynamic, SAFT,

1. Introduction

The improved recovery from oil and gas reservoirs and cost-effective design of downstream facilities requires accurate knowledge of phase behavior and thermodynamic properties. The equation of states (EOS) are suitable tools performing the thermodynamic calculation and phase analysis. The EOSs facilitates calculation of Helmholtz free energy via defining a mathematical relationship between the pressure (P), volume (V) and temperature (T). Definitely, with known Helmholtz free energy, all thermodynamic properties are computable. The EOSs are classified in three main categories i.e. virial, cubic and molecular-based. The virial EOS of high order are precise enough to cover a wide range of fluid types but they are not efficient because they need a large database for convergence [1]. The most widely used EOSs in engineering applications are cubic EOSs which originally introduced by Van der Waals [2]. The conventional cubic EOSs although predict the behavior of pure components precisely but they suffer from lack of accuracy in describing the complex mixtures. Considering many attempts for curing the performance of the cubic EOSs, still they fail on analysis of complex hydrocarbons. Because, the complex hydrocarbons such as oil and gas contain non-similar molecules with different intermolecular interactions. Therefore, a robust and reliable thermodynamic model for analysis of the oil and gas phase behavior is highly demanded for industrial applications.

The molecular based EOSs so-called SAFT-type EOSs are constructed based on the statistical associating fluid theory and they formulate dispersive and associative interactions upon Barker-Henderson and Wertheim theories [3-4]. Furthermore, SAFT has shown great success in simulation of non-ideal interactions inside the polar fluids [5-7]. For example, the developed approach to model the hydrogen bonding with SAFT is the most recognized method to date, for simulation of non-ideal interactions in real systems [8].

The interaction between reservoir rock and hydrocarbons so-called interfacial effect is a non-ideal interaction and its significant role in thermodynamic modeling is indisputable [9]. On one hand, it is imperative to develop our understanding about fluid-rock governing interactions for precise assessment of hydrocarbon recovery from oil and gas reservoirs. On the other hand, cubic EOSs are not suitable candidates to capture fluid-rock molecular interactions. In this regard, SAFT-type EOSs with some modifications and tunings are probably able to capture the fluid-rock mutual interactions. However, a valid data set illustrating fluid-rock interactions is required for SAFT modification.

One theoretical method is using molecular simulations (Monte Carlo technique) to provide insights on confined fluid properties [10-11]. Actually, this approach considers the simulation outcomes as pseudo experimental data to develop a new model [12]. For example, Li et al. have investigated capillary condensation and evaporation of confined phase in slit-like pores. They reported that the phase transfer under pore confinement occur at pressure lower than bulk pressure [13]. Zhang et al. investigated the fluid-solid interaction on the critical point change. They found the critical point increases for weak fluid-solid interactions and decreases for strong interface interactions [14]. Barbosa et al. modified Travalloni [15] model by evaluating the effect of different confinement degree on the fluid structure [16].

However, the molecular simulations inspired by Monte Carlo procedure, are not able to incorporate a certain chemistry as the fluid and solid phase. Herein, Molecular dynamic (MD) simulations are introduced which are able to simulate a fluid-solid interface with known chemistry. MD simulations are suitable tools to generate the reliable data sets prospecting the fluid-rock interactions under the fluid-rock confinement. MD simulations have emerged as a suitable technique to study the interfacial effects in systems containing complex fluids [17]. Recently, the study of fluid-rock interface with MD simulation has gained numerous contributions in the literature [18-20]. Kirch et al. have studied the mutual effect of calcite interface and electrolyte ions (Na, Cl, and Ca) on water structure with MD modeling and NMR. They illustrated the strong ordering of surface water on calcite interface inhibits the adsorptions of chemical species [21]. Ricci et al. investigated the water-calcite interface with AFM experiment and MD simulations. With MD simulation, they observed the shorter residence of Ca2+ ions than Na+ on calcite surface and they validated this finding with AFM experiment [22]. However, very few researches have employed the advantage of MD simulations to modify the EOSs.

In this study, we used MD technique to model water-rock interface. We chose calcite (1014) surface and water as the representative of rock formation (oil reservoir rock). Calcite is the most abundant and ubiquitous mineral in oil and gas reservoirs and water with permanent polar molecule is one of the petroleum constituents with strong polar behavior. The remainder of this paper is organized as follows. In Section2, we describe the details of MD simulation and theoretical method for SAFT modification. In Section 3, the modified SAFT model is validated with MD results. In Section 4, we summarize the list of findings and conclusions.

2. Theoretical background

2.1. Theory of MD simulation

The MD simulation applies Born-Oppenheimer approximation to model the dynamic of the multi particle systems built upon a certain thermodynamic ensemble [23]. In this approximation, Newton’s law of motion governs the dynamic of the nuclei corresponding to the atoms or molecules. Therefore, the non-relativistic Hamiltonian becomes an implicit function of nuclei positions and momentums [24]:

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|  | (eq-1) |

where:

*pi* and *ri* are set of particle momenta and positions, *KE* is kinetic energy, *U(r)* is potential energy, mi is particle mass, and *N* is total number of particles.

We used open source LAMMPS software as the classical molecular dynamic code for molecular dynamic simulation [25]. The Newtonian equation of motions developed by velocity Verlet algorithm adopting the time step of 1 fs incorporated for all simulations. Each MD simulation picked a certain T through the loop over temperature in LAMMPS code.

The developed force field by Raiteri et al. defined the internal forces between 480 calcite molecules [26]. These molecules sorted in 6 layers along (1014) perfect calcite plane with 42×43 [A2] surface area. The SPC/E model, described the internal interactions among molecules for water bulk [27-28]. Figure 1 shows the calcite-water layout in simulation box. As it is seen, we have built a molecular system including a water bulk mounted above the calcite slab along z direction. In the simulation box, the water bulk is designed for two different densities i.e. 950 and 1000 [kg/m3] and three different length along z direction i.e. 20, 40 and 70 [A]. The boundary conditions were periodic for x and y and for z direction the boundary conditions remained fixed. The Buckingham and Lennard Jones potentials with 12 [A] cut-off predicted the van der Waals interactions in our simulations.

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| Figure 1. Illustration of water-calcite system for MD simulation. Calcite slab includes 6 layers sorted along (1014) plane and overlaps with water bulk on xy plane. The water bulk has extended along z-axis with 20, 40 and 70 [A]. |

To wrap the molecules of calcite slab and water bulk, we applied the PACKMOL that compacts the molecules with a certain distance such that the structure of molecules remains intact [29]. Running the minimize function with conjugate gradient algorithm, let the molecules remain at reasonable distance and avoiding the energy flood during simulation run. The equilibration process in each simulation is fulfilled with initializing the particles velocity with 2T based on Boltzmann distribution because, almost 50% of the kinetic energy compensates the potential energy. Then, the equilibration followed with Nose-Hoover NVT thermostat until 5 [ns] in which temperature remains constant at T=300, 400 and 500 [K]. Finally, we measured the thermodynamic properties by averaging over total run time.

2.2. Theory for SAFT modification

To modify the SAFT equation of state, first we start from original definition of partition function in equation (2) which gives the thermodynamic properties of the fluid [30]:

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|  | equation(2) |

30- Hill TL. An introduction to statistical thermodynamics. Courier Corporation; 1986.

where, in the left side the total number of particles, system volume and temperature are shown with N,VandTrespectively. While, in the right side, qint, λ, Vf and Econf were written as the internal partition function, the de Broglie thermal wave length, configurational energy and is Boltzmann constant respectively. Then, we show Helmholtz free energy and chemical potential as following:

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|  | equation(3) |
|  | equation(4) |

Within the confined geometry presented in figure 2, homogeneous and heterogeneous phases mainly control the fluid phase behavior. The interactions in homogeneous and heterogeneous phases imply to water-water and water-calcite interactions respectively. Equation (2) to (4) have defined the water-water interaction in homogeneous phase. Therefore, an additional definition is required for water-calcite interaction to complete the thermodynamics of the system. In this regard, we have split the configurational energy to fluid-fluid (Econf-ff) and fluid-wall (Econf-fw) contributions as bellow:

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|  | equation(5) |

The first three terms in equation (5) correspond to Helmholtz energy in bulk phase and the last term implies to Helmholtz free energy in confinement. Using equation (3) for different contributions gives:

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|  | equation(6) |
|  | equation(7) |

In figure 2, we have depicted the water-calcite interface schematically. Three classified zones are visible in this figure.

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| Figure 2. The sketch of water-calcite interface. Three different regions are visible here. Region I is bulk region that water-water molecule interactions exist. Lz is the distance of water bulk top layer from calcite surface, which is assumed 20, 40 and 70 [A] in MD simulations. Region II is surface-adsorbed region in which the molecular interactions are governed by water-calcite interactions. The thickness of this region is shown with δ. Region III is called forbidden region its thickness σ is supposed to be half of the molecular bond of water molecule. This region is very narrow such that cannot have the center of mass any water molecule. The absorbed water molecules on calcite surface interact with calcite molecules through an energy square well with depth=-ε and width=δ. |

Region I and II display zones which water-water and water-calcite interactions are dominant respectively. Lz presents the length of the water bulk above calcite surface which assumed to be 20, 40, 70 in MD simulations. Region III is free of any water molecule because its thickness less than half of water molecule diameter (σ ≤ 0.85 [A]). In the other words, there is not enough room for water molecules to settle. Hereafter the dimensionless ratio of Lz/σ is called length-ratio. The adsorbed water molecules interact with calcite through an energy square well energy the following condition:

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|  | equation(8) |

In equation (8), region III is assumed to have infinitive energy. This assumption says the energy level in this narrow region is very high such that the molecules cannot land there. That is why it is called forbidden zone.

3. Results and discussion

3.1. MD simulation for T=500 [K]

Figure 3 displays the profile of scaled density at three different length-ratio (Lz/σ) along z-axis. In this figure, we see the larger length-ratio, the lower the water bulk density that implies to the minor calcite wall effect on bulk density for large values of length-ratio. In the other words, the blue curve belonging to stabilizes at highest bulk density. Whereas, the green plot stands at the third rank with length-ratio of 70. The same regime is seen for max density peak on water-calcite interface. Therefore, the lowest length-ratio of water not only provides the highest density for bulk, but also keeps the layering density at maximum value near calcite surface.

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| Figure 3. This figure displays the effect of on water bulk density and layering zone at T=500 [K]. As it is seen, the blue curve with stabilizes at highest value of bulk density and red and green curves follow it respectively. In the zoom box at right side, the ranking of density max peak next to the calcite is same as bulk density. Therefore, the blue curve with lowest value of has the largest bulk density and highest max peak. While, the green curve with largest holds the lowest position at bulk and layering region above calcite. |

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| Figure 4. has not been generated yet (T=400) |

The profile of water density within bulk and layering zone are depicted for T= 400 and 300 [K] in figure 4 and 5. As it is observed, figure 4 and 5 show the same behavior as figure 3.

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| Figure 5. This figure displays the effect of on water bulk density and layering zone at T=300 [K]. As it is seen, the black curve with stabilizes at highest value of bulk density and magenta and torques curves follow it respectively. The zoom box in right side, displays the same ranking as bulk density for density peak within layering region. Therefore, the black curve with lowest value of has the max bulk density and maximum layering peak. While, the torques curve with highest value of has minimum bulk density and its max peak holds the lowest position. |

Namely, the dominant density in bulk phase and layering confinement belongs to the minimum length-ratio and vice versa. The reason refers to the electrostatic field of calcite surface, which is stronger for small length-ratio and makes deviations from bulk within the interface confinement. Wherease, the longer water bulks along z-axis have stronger intermolecular cohesions, which can damp the calcite electrostatic field. Therefore, the density for large length-ratio within interface confinement peaks at closer values to the bulk density.

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| (a) |
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| (b) |
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| (c) |
| Figure 6. This figure compares the density profile within bulk and interface confinement for similar and different temperatures i.e. 300, 400 and 500 [K]. As it is shown, with a constant length-ratio, the large densities at bulk corresponds to the lower temperatures as expected. Whereas, lower density peaks within interface confinement belongs to high temperatures. |

Figure 6 compares the density profile of water within interface confinement and bulk at similar constant length-ratio and different temperatures i.e. 300, 400 and 500 [K]. As it is expected, high temperature decreases the water bulk density because of increase in bulk volume. Nevertheless, the density peak in layering zone belongs to high temperature. This fact refers to the control of density with existing electrostatic fields within the interface confinement. Namely, the electrostatic field of calcite surface within the interface confinement is more effective at high temperatures. Since, the intermolecular cohesions of bulk water weakens at high temperature, the effect of calcite field absorbs more water molecules and make larger peaks in density profile.

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| Figure 7. This figure displays the effect of on the total energy in water bulk density and interface confinement at constant temperature (T=300 [K]). As it is seen, the blue circles with have minimum rank within interface and bulk and red circles with have maximum energy at interface and within the bulk. |

Figure 7 displays the behavior of total energy for different length-ratio and constant temperature (T=300 [K]). As it is seen, the shortest length-ratio corresponds to the minimum total energy within bulk and confinement. However, according to the figure 3 and 5, the shortest length-ratio associated with maximum density in confinement and bulk. Comparing figure 3 and 5 with figure 7 explicitly reveals that at constant a temperature at water-calcite interface, largest density corresponds to lowest total energy. Since, total energy is equal to sum of potential and kinetic, one initially can guess the potential energy governs the total energy value. In the other words, at dens regions the distance between water molecules is short therefore the potential energy increases. To make sure about this idea, we have plotted potential energy profile at figure 8. The pattern of potential energy in figure 8 confirms that the distance between water molecules governs the profile of total energy. Now one might ask why the energy for is minimum at confinement compared with. As it has mentioned already, the electrostatic field of calcite on thin water bulk along z-axis is stronger and more water molecules are absorbed to the calcite surface, which gives high density and low total energy. Whereas, thicker water bulk with and 70 have stronger intermolecular interactions which cancels out the calcite electrostatic field.

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| Figure 8. This figure displays the effect of on the potential energy in water bulk density and interface confinement at constant temperature (T=300 [K]). As it is seen, the blue triangles with have minimum peak within interface and bulk and red circles with have maximum potential energy at interface and within the bulk. |

Furthermore, the tail of the density profile for saturated gas for 500, 400 and 300 [K] stands at top, middle and bottom with shorter threshold. The shorter threshold along z-axis gives smaller density for saturated gas after averaging. Hence, the high temperature gives lower gas density, which was expected.

3.2. Comparison of modified SAFT and MD simulation results

4. Conclusion

3.2. Comparison of modified SAFT and MD simulation results

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