Molecular dynamics analysis of compositional effects in hydrocarbon systems property calculations

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HIGHLIGHTS

- Proposed an engineering approach via MD to obtain fluid properties for EOR processes.
- Showed many advantages to generate PVT and non-equilibrium mixing properties.
- Illustrated subtle compositional microstructure phenomena from MD analysis.
- Quantified the complex compositional effects on diffusion and viscosity.

ARTICLE INFO

ABSTRACT

Fluid pressure–volume–temperature (PVT) properties are essential for enhanced oil recovery (EOR) process description, particularly for the development of new recovery processes such as solvent injection. However there remains significant uncertainty in laboratory experimental data, such as that associated with light and heavier components mixing processes. Much of this uncertainty may be attributed to the multicomponent nature of most oils and the existence of micro-structures in real dynamic systems.

Here, an alternate engineering approach is proposed and illustrated to obtaining this required data, which can be used as an alternative to, or in conjunction with, expensive and time-consuming direct experimental measurements. This method utilizes the molecular dynamics (MD) method to setup dynamic simulation models for a variety of hydrocarbon systems. More particularly, 16 single phase (both single and multicomponent) MD hydrocarbon systems are considered, as well as 3 biphasic (methane–decane) MD systems to quantify aspects of dynamic mixing. The impact of a variety of oil chemical structures (normal and branched alkanes, cycloalkanes, aromatic, and polar) on fluid property predictions is thereby highlighted, with implications for future additional complex oils analysis.

With these systems, a large range of equilibrium and non-equilibrium properties under different T, P and compositional scenarios have been predicted, and good agreement with available laboratory experimental data has been demonstrated here. Indications of subtle microstructure phenomena are also obtained from our MD analysis. As the resultant MD data represent many years of costly experimental measurements, this points to a new cost-efficient approach in obtaining necessary EOR parameters, to be used in conjunction with limited targeted experiments.

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1. Introduction

With the passing of the era of easy conventional oil resources, attention of the traditional oil and gas industry has been directed to unconventional resources (gas hydrate, shale gas and tight oil reservoirs, heavy oil and bitumen reserves) as well as extending the lifetimes of conventional reservoirs by using such new technologies and solutions. Both applications can be termed enhanced oil recovery (EOR) methods [1,2]. Such recovery schemes must be based on well-informed and well-parametrized reservoir simulation studies, utilizing verified pressure–volume–temperature (PVT) models and non-equilibrium properties such as viscosity and diffusion. Traditionally, these are obtained from time-consuming and expensive experimental studies. Furthermore, utilization of newer technology such as solvent processes and nanotechnology requires additional and harder to achieve data.

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A large volume of laboratory PVT experiments can be found for single and multicomponent systems. There is a strong motivation for continuing such tests with application to EOR process design (see for example AACI Research program, Alberta Innovates Technology Futures website, http://www.albertatechfutures.ca). Typically one experiment is designed to obtain one type of data only. While these experiments are costly and time consuming, one can often notice that there is significant variation in the literature data, especially with non-equilibrium properties for oil/gas mixing systems. This variation may be physical (or may be an artifact of experimental design). There is a need to quantify and reduce such uncertainty as the effect of such uncertainty in evaluating EOR processes can be significant.

Over this same time period, the capabilities of molecular modeling simulation protocols (including computational speed and analysis tools) for larger scale problems have also increased substantially. Numerous researchers have begun applying molecular modeling techniques to relevant problems in the oil and gas sector. Earlier work focused largely on expanding Monte Carlo (MC) techniques [3,4] while our interest is primarily in molecular dynamics (MD) approach. While similar force fields can be utilized in both techniques, the fact that both equilibrium and non-equilibrium physical properties can be generated with MD methods implies this is most useful here.

Wang and Hou [5,6] applied molecular dynamics method for molecular property predictions. Their first paper simulated bulk densities and heat of vaporizations of 71 organic molecules that cover the most common chemical functional groups. They concluded that simple van der Waals parametrization can significantly reduce the prediction errors. Their second paper simulated diffusion coefficients for several organic compounds in aqueous and non-aqueous solutions. They claimed that their sampling strategy of averaging the mean square displacement collected in multiple short-MD simulations is efficient in predicting diffusion coefficients of solute at infinite dilution.

Kunieda et al. [7] developed a molecular dynamics representation of 8 components oil (n-hexane, n-heptane, n-octane, n-nonane, cyclohexane, cycloheptane, benzene and toluene) and investigated the non-uniform distribution of the aromatic components near the water–oil interface. This same multi-component oil model was used to investigate oil spreading.

Zabala et al. [8] used molecular dynamics to predict diffusion coefficients in CO_2/n-alkane binary mixtures. They made the interesting argument that molecular simulation can be employed as a tool for the determination of Fick diffusivities in high pressure systems, like in oil reservoirs, without the need to construct complicated and expensive experiments. Wang et al. [9] extended these diffusion calculations to supercritical CO_2/alkyl benzene binary mixtures emphasizing the structural aspects. They also made a similar argument that molecular simulation technique is a powerful way to predict diffusion coefficients of solutes in supercritical fluids.

Several viscosity prediction approaches have been proposed and included in most of the available molecular dynamics programs. Palmer [10] used the transverse-current correlation function method (TCAF) to calculate the shear viscosity for the Lennard-Jones fluid, liquid carbon dioxide and the TIP4P model of water. He argued from his calculations that the use of TCAF's represents a viable alternative to the Green–Kubo relations for calculating the shear viscosity from equilibrium molecular dynamics calculations. Hess [11] compared the accuracy and efficiency of two equilibrium methods (Green–Kubo pressure fluctuation, transverse current auto-correlation-momentum fluctuation), and two non-equilibrium methods (periodic shear flow and sliding boundary condition SLLOD) and applied these methods to a Lennard-Jones fluid and the single point charge (SPC and SPC/E) water

models. He established the strengths and weaknesses of each approach.

Cui et al. [12] simulated the shear viscosity of liquid n-decane and n-hexadecane using the Green–Kubo method. They also emphasized that MD simulation can be a viable alternative of expensive and time consuming laboratory experiments in designing of high performance synthetic lubricants at various operating conditions. In a series of articles, Montello and Grest [13–16] investigated diffusion and especially viscosity of linear branched, high carbon number alkanes via molecular dynamics. In particular they showed the equivalence of the Green–Kubo and Stokes–Einstein approach for calculating high viscosity systems, and the crossover to Rouse model behavior for diffusion, viscosity, and equilibrium structure for higher carbon number alkanes. Later work by Gordon [17–19] investigated transport properties of isoparaffins via MD and the use of Stokes–Einstein relationships.

Headen et al. [20] studied asphaltene nanoaggregation in heptane and toluene from MD simulations. Li and Greenfield [21,22] used classical MD simulations to calculate physical properties for the model asphalt systems. Their simulated densities and viscosities for their model asphalt system were close to experimental data. They proposed an alternate method for calculated viscosities of very heavy oil systems by combining diffusion, rotational relaxation and viscosity.

In our recent work, Uddin and Coombe [23], MD techniques have been successfully applied to quantify gas hydrate dissolution kinetics as a multiphase problem (solid hydrate, water and CH_4/CO_2 gas). Gas diffusion in water and gas bubble evolution were quantified (and existence of micro-structures). This latter effect is not readily available from experiment.

Now appears an appropriate time to increase the scope of MD-investigated problems applied to the oil and gas sector. Here the use of molecular dynamics to quantify the equilibrium and non-equilibrium properties of complex oils and their mixing with light solvents is discussed, with the intention of complementing or avoiding tedious and expensive experimental studies. A protocol for phase property generation is utilized while developing a new MD methodology for initialization, utilizing a mixing process analogy. As such, this represents a new rapid and reliable engineering approach to MD model building. 19 large simulations representing a range of pure component and multi-component mixtures are presented, including several examples of light solvent mixing under single phase and 2 phase conditions. (The conventional terminology of oil and gas systems is utilized to describe our simulations, recognizing that MD does not utilize this distinction – the phase properties are a direct result of the system forces and pressure/temperature conditions).

2. Oil chemistry

Oil chemistry is made of a mixture of many different isomers of alkanes, cycloalkanes and aromatics, as well as high molecular weight polar heteroatom hydrocarbons. The bulk properties (e.g. specific gravity, density, viscosity) of each different petroleum source are defined by the percentage of different boiling point ranges of hydrocarbons found within petroleum as part of the petroleum composition. The percentages for these hydrocarbons can vary greatly, giving the crude oil quite distinct property characteristics depending upon geographic region.

Reservoir oil is categorized based on the molecular weight distribution of their constituents, and distinctions are made between light, medium, and heavy crude oil, based on the American Petroleum Institute's measure of oil density, API gravity and specific gravity SG. In general, if it has an API gravity ($API° = \frac{141.5}{SG} - 131.5$) higher than 20°, it is considered light. The oils from the Weyburn