Comparison of forcefields for molecular dynamics simulations of hydrocarbon phase diagrams

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Abstract. Molecular dynamics calculations of vapor–liquid equilibrium of methane–n-butane mixture are performed. Three force-field models are tested: the TraPPE-UA united-atom forcefield, OPLS-AA all-atom forcefield and a fully flexible version of the TraPPE-UA all-atom forcefield. All those forcefields reproduce well the composition of liquid phase in the mixture as a function of pressure at the 300 K isotherm, while significant discrepancies from experimental data are observed in the saturated vapor compositions with OPLS-AA and TraPPE-UA forcefields. The best agreement with the experimental phase diagram is found with TraPPE-EH forcefield which accurately reproduces compositions of both liquid and vapor phase. This forcefield can be recommended for simulation of two-phase hydrocarbon systems.

1. Introduction

Natural gas extraction and storage problems require the knowledge of gas mixtures properties. Particularly, phase diagrams of the reservoir fluids are in many cases needed. Phase coexistence in multicomponent systems is defined by temperature, pressure and composition of two coexisting phases. The simple fact that coexisting phases have, in general, different compositions, has very profound consequences. One of them is the phenomenon of retrograde condensation, i.e. partial condensation of a supercritical fluid at isothermal decompression. It happens when the temperature of the fluid is between the lowest and the highest of critical temperatures of its constituent pure substances. Since the critical temperature of methane is 190.6 K, methane-containing mixtures at ambient temperatures always have some range of methane concentrations at which the retrograde condensation occurs. This condensation complicates gas fields operation, since it results in partial condensation of natural gas near a well bottom. It lowers a well yield and decreases the amount of recoverable hydrocarbons.

In hydrodynamic simulations of flows of hydrocarbon fluids, it is efficient to use tabulated or analytical equations of state for individual substances and mixtures [1–4]. The equations of state can be parametrized to give single-phase properties as well as liquid–vapor equilibrium curves. One of the widely used families of equations of state is the cubic equations of state [5,6]. They have analytical form similar to van-der-Waals equation and allow calculation of chemical potentials of individual substances in mixtures, therefore, the phase equilibria. The coefficients
for the equations of state are fitted to results of experimental studies of hydrocarbon fluids. The
bulk phase diagrams of pure hydrocarbons and mixtures are well known from the experiments.
However, phase diagrams in pores may be required for hydrodynamic modeling. An appealing
way to calculate such phase diagrams is the atomistic computer simulations by molecular
dynamics (MD) or Monte-Carlo (MC) methods. While MC method has more efficient techniques
for phase coexistence calculations, MD simulations have their merits. MD simulations provide
a unified approach for calculation of equilibrium properties (equation of state, phase diagrams,
moduli) [7, 8], transport coefficients [9, 10] and features of nonequilibrium processes [11].

Commonly used potential models used for atomistic simulations of molecular substances
are represented as the so-called forcefields, which include functional forms for interactions
between different types of atoms or groups of atoms, and coefficient sets for those functions.
The forcefields are subdivided into all-atom (AA), united-atom (UA) and coarse-grained (CG)
classes. AA forcefields treat every atom in a molecule as a separate interaction center. In the
UA approach, central heavy atom (C, N, O, etc) with all hydrogen atoms connected to it form a
united atom. CG models are mainly used for simulation of large biomolecules and provide even
larger structural elements as building blocks, such as whole functional groups, rings, or even
amino acids and nitrogenous bases.

In this paper, we study the accuracy of 3 forcefield models: LOPLS-AA (optimized potential
for liquid simulation–all-atom) [12, 13], TraPPE-UA [14] and TraPPE-EH [15] (transferrable
potential for phase equilibria–united atom and explicit hydrogen). Those forcefields are chosen
because they are developed using hydrocarbon properties as input parameters and so, expected
to be more accurate for hydrocarbon simulations than forcefields for biomolecules. We test
these models on the task of calculating the phase diagram of methane–n-butane system in
the retrograde condensation region. Those forcefields are adapted for molecular dynamics
simulations and are used in the LAMMPS package [16] to calculate phase equilibrium properties
by the direct coexistence method. We also compare the accuracy of the atomistic modeling and
analytical equations of state for phase diagram calculations.

The rest of the paper is structured as follows. At first, we describe the forcefields and the
modifications made to adapt them for MD simulations, give the details on simulation setup.
Then we present the results of the phase diagram calculations by MD method. Then we
compare the accuracy of atomistic modeling to the analytical equations of state. After that, the
conclusions are presented.

2. Simulation details

2.1. Potential models

The forcefields represent the potential energy of a molecular system as the sum of nonbonded
interactions, bond stretching, angle bending and dihedral rotation terms:

\[
U = U_{\text{nonbond}} + \sum_{\text{bonds}} K_b (r_b - r_{0,b})^2 + \sum_{\text{angles}} K_a (\theta_a - \theta_{0,a})^2 + \sum_{\text{dihedrals}} U_d (\phi_d),
\]

where \( r_b \) and \( r_{0,b} \) are current and equilibrium lengths of bond \( b \), \( \theta_a \) and \( \theta_{0,a} \) are current and
equilibrium values of angle number \( a \), \( \phi_d \) is the value of dihedral angle number \( d \), \( K_a \) and \( K_b \)
are forcefield coefficients. The dihedral interactions in all studied forcefields are represented in
the Fourier form:

\[
U_d = C_{0,d} + C_{1,d} \cos \phi_d + C_{2,d} \cos 2\phi_d + C_{3,d} \cos 3\phi_d,
\]

where \( C_i \) are forcefield-specific coefficients. The nonbonded interactions include short-range pair
interaction and Coulomb interaction. Short-range potential in the form of Lennard-Jones (LJ)
function is used both in OPLS and TraPPE forcefields. Coulombic interaction is only present
in the OPLS hydrocarbon description.
In the UA approach, methane molecules are presented by point particles and butane molecules are reduced to four-particle models. AA models include 5 atoms in a methane molecule $CH_4$ and 14 atoms in a butane molecule $C_4H_{10}$.

LOPLS-AA forcefield is used in the present work as it is described in [12, 13]. AMBER coefficients are used for bond and angle vibrational constants. TraPPE family forcefields are supposed to use rigid bonds and geometrical constraints for H–C–H and H–C–C angles. Due to complications with rigid bonds in the MD method, fully flexible methane butane molecule models are used instead of rigid bonds suggested in the original TraPPE forcefield. Missing force constants for the bonds and angles are taken from the AMBER forcefield [17]. Forcefield authors claim that phase diagrams are determined mainly by the intermolecular forces so such augmentation would still give the correct phase equilibrium [15].

Another feature of TraPPE-EH forcefield is that LJ interaction centers are situated on carbon atoms and in the middle of C–H bonds. Since LAMMPS does not support off-atom force centers, hydrogen atoms are placed as the interaction centers, and the C–H bond length is half of the normal in TraPPE-EH model.

Screened Coulomb potential is used in LOPLS-AA forcefield to reduce the computational cost of the model. As shown by Wolf in [18], screened Coulomb potential with a sufficiently large cutoff radius must give result consistent with the full potential in electrically neutral systems. Another reason to choose truncated potential for electrostatics was that the hydrocarbon molecules have zero charge and zero dipole moment, so intermolecular electrostatic forces should be short-range even with unmodified potential.

For the TraPPE-UA forcefield, LJ cutoff radius is 16 Å, and the potential and its derivative are smoothed to zero from 16 to 18 Å. For the TraPPE-EH and OPLS-AA forcefields, LJ potential truncated at 18 Å is used.

2.2. Equilibration

The approach to create a two-phase gas–liquid system is analogous to what was used in [7]. A long simulation box is used with $L_x : L_y : L_z = 1 : 1 : N$ where $N \sim 10$. The butane molecules are first placed in the center filling the volume $L_x \times L_y \times 0.5L_z$. The $Z$ axis is a preferential direction in this configuration, which is normal to the interface. The whole box volume is filled then with randomly distributed methane molecules. Energy minimization is then applied to relax the structure and move apart the particles which are generated unphysically close to each other. The numbers of methane and butane molecules define the mixture composition. Mixtures with 25 to 70 molar percentage of methane are considered.

Nose–Hoover thermostat [19] and Shinoda barostat [20] are applied at MD runs. As a fluid medium is simulated, the external pressure is established by changing only the $L_z$ size of the simulation box to fit the $P_{zz}$ pressure tensor component to the target value. The sizes $L_x$ and $L_y$ remain the same during the simulation, and the isotropic stress tensor is maintained hydrostatically by the fluid phases. The simulations are carried out for 1.5 million timesteps, or 6 ns, and component densities are then averaged over the last 500 000 timesteps in 100 bins along the $Z$ axis to obtain the profiles.

rRESPA scheme [21] is used for the numerical integration of motion equations. With the TraPPE-UA forcefield, 4 fs timestep is chosen for non-bonded interactions, 2 fs for dihedral torsions and 1 fs for bond and angle oscillations. With the AA forcefields, 2 fs timestep is used for non-bonded interactions, 2 fs for dihedral torsions and 0.5 fs for bond and angle oscillations to maintain stable simulation with explicit hydrogen atoms. Periodic boundary conditions are employed.
3. Simulation results
Density profiles of the hydrocarbon mixture components are calculated by MD simulations. The examples of the profiles are presented in figure 1 for temperature 330 K at two pressures. The liquid phase is butane-rich; the vapor phase is methane-rich. Butane density profiles have the shape quite typical to liquid films: high density in the film region and low density in the vapor region. In contrast, methane densities are roughly the same in liquid and vapor phases. Moreover, the absolute methane density in liquid can be lower than in vapor at high pressures. It is interesting to note that there is usually a maximum of the methane density near the phase boundary which points to the methane adsorption on the interface.

The phase equilibrium curve is calculated for the methane–n-butane mixture at 330 K (figure 2). All the forcefield models used reproduce experimental data [22] on methane solubility in liquid butane rather well up to 80 atm. They also reproduce the existence of the retrograde condensation region for the mixture under consideration at this temperature. The existence of the region follows from the fact that the phase equilibrium curve does not reach 100% methane molar fraction. However, the simplified TraPPE-UA model does not capture correctly the vapor composition. OPLS-AA, the most computationally expensive forcefield of three, also fails in capturing the phase diagram from the vapor side. The TraPPE-EH model gets the vapor and liquid compositions closest to the experimental data. This means that the fully flexible variant of the TraPPE-EH forcefield can be used for phase diagram calculations.

4. Comparison with the analytical equations of state
Figure 3 shows the comparison of the phase diagram calculated with the TraPPE-EH forcefield and phase diagrams calculated by cubic equations of state. We compare three analytical forms of equation of state: Soave–Redlich–Kwong (SRK), Peng–Robinson (PR) and the equation proposed by Brusilovskiy [5].

While there are some inaccuracies in the phase diagrams obtained both from atomistic simulations and from the equations of state, they are not large and have the same order of magnitude. This means that atomistic simulations can be used to provide the input for the equation of state fitting. It may prove useful when the phase equilibria are expected to be shifted. For example, the phase diagrams in porous media can be calculated by atomistic modeling and then fitted by a cubic equation of state to use in hydrodynamics.
Figure 2. Phase equilibrium curves of methane–n-butane at 330 K: MD models compared to the experimental data [22].

Figure 3. Phase equilibrium curves of methane–n-butane at 330 K: TraPPE-EH compared to cubic equations of state.

5. Conclusions
Phase equilibrium of methane–n-butane mixture is calculated from our MD simulations using 3 forcefield models: OPLS-AA, TraPPE-UA and TraPPE-EH. The 330 K isotherm is considered as a test.

All those forcefields reproduce well the composition of liquid phase in the mixture as a function of pressure, while significant discrepancies from experimental data are observed in the saturated vapor compositions with OPLS-AA and TraPPE-UA forcefields. The best agreement with the experimental phase diagram is found with TraPPE-EH forcefield which accurately reproduces
compositions of both liquid and vapor phase. This forcefield can be recommended for simulation of two-phase hydrocarbon systems.

The accuracy of TraPPE-EH forcefield is comparable to that of the cubic equations of state widely used for hydrocarbons. This allows us to use this forcefield in future to provide input for cubic equation of state fitting procedure. For example, a reparametrisation of known equations of state may be needed for description of phase equilibria in porous media.

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