The equation of state of n-pentane in the atomistic model TraPPE–EH

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Abstract. In this work, we study the vapor–liquid equilibrium in n-pentane. We use the TraPPE–EH (transferable potentials for phase equilibria–explicit hydrogen) forcefield, where each hydrogen and carbon atom is considered as independent center of force. The fluid behavior was investigated with different values of density and temperature by molecular dynamics method. The n-pentane evaporation curve was calculated in the temperature range of 290 to 390 K. The densities of the coexisting phases are also calculated. The compression curve at 370 K was calculated and isothermal bulk modulus was found. The simulated properties of n-pentane are in good agreement with data from a database of the National Institute of Standards and Technology, so the TraPPE–EH model can be recommended for simulations of hydrocarbons.

1. Introduction

The problems of fossil hydrocarbons extraction, storage and processing raise the interest to the numerical modeling of hydrocarbon fluids [1]. The hydrodynamic modeling of processes in oil-bearing rocks during oil or natural gas extraction requires proper account of two-phase flows of fluids through the pores [2].

The reasons for phase separation are the degassing of oils and retrograde condensation of natural gas at decompression. The retrograde condensation occurs in fluid mixtures containing a component with critical point lower than the temperature of mixture [3]. The phase diagram of such mixtures has a range of compositions where isothermal decompression from a supercritical state first leads to precipitation of liquid phase from a fluid, and then this condensate evaporates at further decompression [4]. As methane is the primary component of natural gas and its critical point is 190.6 K, retrograde condensation happens in natural gas with high amounts of high-boiling components in it [5]. Natural gas condensate is a liquid containing primarily hydrocarbons which are liquid at normal conditions, i.e. pentane and higher [6]. Optimization of natural gas extraction from condensate fields is an important technical problem [7].

Due to phase separation and two-phase flows during natural gas condensate extraction, knowledge of the equations of state and phase diagrams of the fluids is crucial for modeling [8]. Additionally, the account of capillary effects on the phase diagram is required due to porosity [9]. While the phase diagrams of hydrocarbons in free space are known from the experiments, the phase diagrams in pores can be calculated by numerical simulations [10]. The methods of
atomistic simulations, such as molecular dynamics (MD) or Monte Carlo (MC) are nowadays widely used to study the interactions of fluids with mineral surfaces [11]. The most crucial part of getting reliable results from MD or MC simulations is the choice of interatomic interaction model which accurately reproduces the properties of studied systems [12].

The TraPPE (transferable potentials for phase equilibria) potential family [13] was especially designed to accurately reproduce experimental data on vaporization curves of molecular liquids, including hydrocarbons. There are two potentials in the TraPPE family. The TraPPE–UA (united atom) is a simplified model which uses pseudoatoms CH, CH$_2$, CH$_3$, CH$_4$ which are considered point particles [14]. TraPPE–EH (explicit hydrogen) is an all–atom potential which uses separate force centers for each atom in the molecule. While TraPPE–EH gives a more realistic description of molecular interaction, the united–atom model gives about threefold reduction in computational cost. It has been shown that the united–atom approach does not give satisfactory accuracy for multicomponent phase diagrams and therefore is unsuitable for quantitative modeling [15]. The TraPPE potentials are designed for use in MC simulations. Some adaptations are needed to use them for the MD simulations with popular software such as LAMMPS [16] or GROMACS [17]. In this work, we adapt the TraPPE–EH potential for the MD simulations with the LAMMPS package and test it on the properties of n-pentane.

The rest of the paper is as follows. First, we describe the modifications we had to make to the originally published potential [18]. Then, we explain the simulation procedure. After that, our results for vaporization curve and compression curve of pentane are presented. In the end, the conclusions are given [19].

2. Model and calculation method

2.1. Force field

The potential energy of molecular system is expressed as a sum of nonbonded van der Waals interactions, bond stretching terms, angle vibration terms and energy of dihedral torsions around C–C bonds:

$$U = U_{vdW} + \sum_{\text{bonds}} U_b(r_b) + \sum_{\text{angles}} U_a(\theta_a) + \sum_{\text{dihedral}} U_d(\phi_d).$$

Nonbonded interaction is taken in the Lennard-Jones form. Nonbonded interactions are only calculated between atoms belonging to different molecules and between pairs of atoms separated by more than 3 bonds within the same molecule. Additionally, nonbonded interactions between carbon and hydrogen atoms separated by 4 bonds and between two hydrogen atoms separated by 5 bonds are excluded in the original TraPPE–EH formulation. Because LAMMPS package does not support nonbonded interaction exclusion for atoms which are farther than 3 bonds apart, we had to introduce additional fictive bonds that contribute to the topology but not to energy and forces. Those fictive bonds serve only to ensure proper exclusion of nonbonded interactions. The Lennard-Jones interactions are calculated with 14 Å cutoff radius. Original TraPPE models use rigid bonds. Due to complications in numerical integration of equations of motion with a large number of geometrical constraints, we use harmonic potential for bonds [20]:

$$U_b = K_b(r_b - r_{0,b})^2,$$

where b is the type of bond (C–C, C–H), $r_{0,b}$ is the equilibrium bond length, $r_b$ is the current bond length. The force constants $K_b$ are taken from the AMBER forcefield [21]. Such a workaround was suggested by the TraPPE authors if a fully flexible model is needed.

In the original article, C–H bond length is equal to 1.1 Å. The Lennard-Jones nonbonded interaction sites are located at the carbon atom and at the center of carbon–hydrogen. Thus, the interaction site of the hydrogen atom is at the distance 0.55 Å from the carbon atom. In this
work, we use the interaction sites at the ends of bond with the length 0.55 Å. The configuration of the Lennard-Jones sites in the molecule therefore stays the same as in the original model.

Angle bending terms also have the harmonic form:

$$U_a = K_a(\theta_a - \theta_{0,a})^2,$$

where $a$ is the type of angle, $\theta_{0,a}$ is the equilibrium angle value, $\theta_a$ is the current angle value. Again, some angles use geometrical constraint in the original TraPPE, in which case we take missing coefficients $K_a$ from the AMBER forcefield. Dihedral torsions energy is represented in the Fourier form:

$$U_d = C_0 + C_1 \cos \phi + C_2 \cos 2\phi + C_3 \cos 3\phi.$$

Only the C–C–C–C dihedrals and X–C–C–H dihedrals where H is a hydrogen atom from a methylene group contribute to energy in TraPPE–EH model. Torsional energy is zero for dihedrals having hydrogen atoms from methylene groups only.

2.2. Simulation details

N-pentane in liquid and two-phase states are simulated. To get an amorphous state, pentane molecules are placed in random orientations into the nodes of simple cubic lattice which is unstable and decays quickly. To get the liquid phase, all the volume of simulation box is filled with molecules. To get the two-phase state, we fill $1/3$ of simulation box with 1344 molecules with approximately the density of liquid, and 100 molecules are placed at random in the rest of the simulation box (figure 1). Periodic boundary conditions are used in three directions, thus, simulations correspond to bulk liquid phase or to a slab of liquid in contact with vapor. Energy minimization is performed after the generation of the initial state to relax the structure and move apart the particles which are generated unphysically close to each other.

The rRESPA scheme [16] is used for the numerical integration of motion equations. The timestep is equal to 1 fs and has been chosen for non-bonded interactions, 0.5 fs for dihedral torsions and 0.25 fs for bond and angle oscillations.

Relaxation runs for 500 000 timesteps are performed after the energy minimization. Then, 2 million timesteps production runs are performed with Nose–Hoover thermostat maintaining the desired temperature. The stress tensor components and densities are then averaged over the last 500 000 timesteps in 100 bins along the $Z$ axis to obtain the profiles. Visualization of simulation cell is done using the AtomEye [22] and OVITO [23] software. The plotting is done using the SciDaVis program.

3. Results

The vapor–liquid coexistence curve calculated in the temperature range from 290 to 390 K (figure 2). The coexistence curve in the $P$–$T$ plane is close to data from a database of the
Figure 2. The saturated vapor pressure of n-pentane in temperature range from 290 to 390 K. Reference data are from [24].

Figure 3. (a) Equilibrium density profiles along the simulation box for vapor–liquid; (b) vapor–liquid coexistence curves for n-pentane. Calculated coexistence densities for the TraPPE–EH model are shown as black and red; reference data [24] are shown as green and blue.

National Institute of Standards and Technology (NIST) [24]. The atomistic model overestimates saturation pressures slightly, which effectively shifts the vaporization curve by about 10 K.

The densities of coexisting phases are calculated from the time-averaged density profiles in figure 3(a). The $V$–$T$ coexistence diagram is shown in figure 3(b). Overall, the densities of liquid and vapor are close to the database values in the temperature range studied. The relative discrepancies in liquid density lie within few percent. Discrepancies in vapor density are of order of tens percent which is still a good result considering rather strong dependence of saturated vapor density on temperature. As in the case of saturated pressures, the phase diagram appears
Figure 4. (a) Relative volumes of n-pentane at 370 K; (b) isothermal bulk modulus $B_T$ (in kilobar) for n-pentane. Reference data are from [25].

to be shifted by about 10 K compared to the NIST reference data. The critical temperature is therefore slightly underestimated in the atomistic model.

The calculated saturated vapor pressures lie in the range from 0.86 to 14.11 bar and do not exceed the reference critical pressure 33.70 bar.

Isothermal compression curve of liquid pentane is calculated at 370 K. Figure 3(a) shows the dependence of pressure on relative volume. Differentiation of this curve gives the isothermal bulk modulus:

$$B_T = -V \left( \frac{\partial p}{\partial V} \right)_T.$$ (5)

The differentiation is done by fitting the simulation data by a polynomial and taking the derivative of the fitting curve. The dependence of the bulk modulus on pressure is presented in figure 3(b). Both the compression curve and bulk modulus behavior are close to the reference data [25]. The least discrepancies are observed near the equilibrium density. The error increases at the increasing compression. This is probably due to the excessive stiffness of repulsion term in the Lennard-Jones potential.

4. Conclusion

We propose a fully flexible modification of the TraPPE-EH force field for compatibility with the LAMMPS molecular dynamics package. We show that the suggested modifications do not decrease the accuracy of calculations in comparison with the original model. The potential is verified on the n-pentane simulation. The evaporation curve of n-pentane is calculated in the temperature range from 290 to 390 K. The isothermal bulk modulus of liquid pentane at 350 K is calculated. The simulated properties of n-pentane are in good agreement with the NIST reference, so the suggested TraPPE-EH modifications can be recommended for MD simulations of hydrocarbons. The theoretical results are of great interest for simulations of fossil fuels extraction processes from natural reservoirs.

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