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Lennard-Jones force field parameters for cyclic alkanes from cyclopropane to cyclohexane

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ABSTRACT

Lennard-Jones (LJ) force field parameters for cyclic alkanes from cyclopropane to cyclohexane are proposed. The molecular geometry is obtained from quantum mechanical calculations. The united-atom approach is applied by initially locating each site at the carbon atom position and subsequently changing the site–site distance; thereby, the LJ parameters and the site–site distance are optimized to vapor–liquid equilibrium (VLE) data, i.e., vapor pressure, saturated liquid density and enthalpy of vaporization. These new cycloalkane force fields are able to describe the VLE data with deviations of a few percent. Furthermore, self-diffusion coefficient, shear viscosity and thermal conductivity are calculated by molecular dynamics simulation and the Green–Kubo formalism. For the smaller two cycloalkanes, i.e., cyclopropane and cyclobutane, the predicted transport properties are in good agreement with the available experimental data. However, the force fields for cyclopentane and cyclohexane specified in this way do not predict transport properties with the desired accuracy. Therefore, they are re-optimized to experimental data on VLE properties and self-diffusion coefficient simultaneously. Then, also the other transport properties meet the experimental data well.

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1. Introduction

Molecular modeling and simulation is a powerful approach for studying static and dynamic thermophysical property data. Nowadays, it is widely employed to obtain thermophysical data of condensed phases under conditions which are difficult to handle experimentally. There are thus numerous molecular simulation applications of interest for process engineering, e.g., adsorption equilibria [1], vapor–liquid equilibria (VLE) [2] or chemical equilibria [3].

Cyclic alkanes and their derivatives are important for many chemical engineering applications, especially in the petrochemical and in the resin industries. E.g., napthenes (i.e., cycloalkanes) are dehydrogenated by catalytic reforming to aromatic hydrocarbons, such as benzene, toluene or xylenes [4]. Cyclopentane is used as a blowing agent for polyurethane foams that are employed for thermal insulation purposes, e.g., in domestic refrigerators and freezers [5]. Cyclohexanone, obtained by oxidation of cyclohexane, is converted by means of catalytic oxidation with air into dicarboxylic acids, which are essential raw materials to yield polyesters, polyamides, plasticizers and lubricating oils [6].

On the basis of accurate force fields, molecular simulation may yield thermophysical data for extending equations of state or proposing new ones from hybrid data [7]. To the best of our knowledge, there are no fundamental equations of state reported in the literature for cyclopropane and cyclobutane, because only few experimental data exist due to the poor chemical stability of these compounds. Fundamental equations of state are, however, available for cyclopentane and cyclohexane. The equation for cyclopentane by Gedanitz et al. [8] is valid in the temperature range 179.7–550 K up to a pressure of 250 MPa and a density of 12.11 mol l^{-1}. The equation for cyclohexane by Zhou et al. [9] is valid in the temperature range 279.47–700 K up to a pressure of 250 MPa and a density of 10.30 mol l^{-1}. These fundamental equations of state were used here as a reference to assess the simulation results of the present work.

Force fields consist of molecular geometric structure and interaction parameters. A widely accepted methodological route to devise force fields is to determine the molecular structure, i.e., bond lengths and angles, with quantum mechanical (QM) methods in a first step [10]. Subsequently, the intermolecular interactions are modelled by optimization of the Lennard-Jones (LJ) parameters

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to experimental VLE data [10–11]. Depending on the importance of conformational changes, the internal degrees of freedom are considered as well, and their parameters are typically transferred from QM calculations too [12–13].

Several force fields for cyclic alkanes are available in the literature. For cyclopropane, Lustig [14] proposed a three center LJ model which was fitted to experimental values for vapor pressure and saturated liquid density at 318.15 K. For the cyclic alkanes cyclobutane to cyclohexane, force fields based on the GROMOS96 family [15] were developed for biomolecular systems. For cyclopentane and cyclohexane, several LJ-based force fields which consider the internal degrees of freedom have been published [16–18]. The TraPPE-UA force fields [16] were fitted to vapor pressure, saturated liquid density and critical temperature. The force fields parameters proposed by Bourasseau et al. [17] were obtained by means of a rigorous optimization procedure, whereas in the work by Neubauer et al. [18], the LJ parameters were fitted to saturated liquid density by means of random search, keeping the bond lengths constant. There are also several rigid force fields for cyclohexane [10,19–21]. Eckl et al. [10] developed a set of non-polarizable force fields, which included a cyclohexane model. These force fields are based on information from QM calculations to specify geometry and electrostatics, the LJ parameters were fitted to VLE data with a Newton scheme. Errington and Panagiotopoulos [19] proposed a model based on the Buckingham exponential-6 potential, which was optimized to vapor pressure, saturated densities and critical point. The force field by Hoheisel and Würflinger [20] is a LJ-based model which was fitted to reproduce the experimental pressure of liquid and solid states. In case of the all-atom model for cyclohexane by Milano and Müller-Plathe [21], the LJ parameters for carbon and hydrogen were fitted to experimental values of density and enthalpy of vaporization by means of the simplex method.

In this work, the united atom approach was applied to cyclic molecules from cyclopropane to cyclohexane. All molecules were considered as a set of methlylene (CH_2) sites, which are bonded according to their energetically most favorable geometric structure. The molecules were considered as non-polar fluids employing LJ sites only.

Having specified the geometry in terms of the bond angles, there are three parameters that can be fitted for each of the cycloalkane force fields. These are the LJ size and energy parameters for the methylene sites as well as the site–site distance. The site–site distances were varied to account for the absence of the hydrogen molecules following the approach proposed by Toxvaerd [22]. This approach has been used e.g., by Ungerer et al. [23] and Bourasseau et al. [17] to optimize the anisotropic united atoms (AUA) force field family. In this work, the relative magnitude of the site–site distance was kept constant, by taking the results from QM calculations as a starting point. All parameters were subsequently optimized with the reduced unit method by Merker et al. [24], which does not require additional molecular simulation runs.

The prediction of the transport properties of liquids by molecular simulation is particularly significant, because these data are generally difficult to model accurately, especially with phenomenological approaches. Thus, transport properties are considered as a challenging test for force fields. E.g., that predictive task was proposed for mixtures of type water + short alcohol as a benchmark for the development of water models [25]. Therefore, the capability of the present rigid cycloalkane models with respect to the prediction of the most important transport properties, i.e., self-diffusion coefficient, shear viscosity and thermal conductivity, was assessed.

2. Parameterization procedure

The parameterization procedure by Eckl et al. [10] was adapted here. First, the molecular structure of the considered cyclic molecules was determined by means of the open source code for computational chemistry calculations GAMESS (US) [26]. A Hartree–Fock calculation with a relatively small (6–31 G) basis set was chosen to determine the positions of all carbon and hydrogen atoms.

Next, the united atom approach was applied to the methylene groups that were initially located at the carbon atom positions of the molecular structure from QM. Then, the bond angles θ,ϕ and the site–site distances r between the methylene groups were calculated employing the equations reported by Essén and Svensson as implemented in the software EVCLID [27]

$$r(i,j) = |\boldsymbol{a}_j - \boldsymbol{a}_i|, \tag{1}$$

$$\boldsymbol{b}_{i,j} = \frac{\boldsymbol{a}_j - \boldsymbol{a}_i}{r(i,j)}, \tag{2}$$

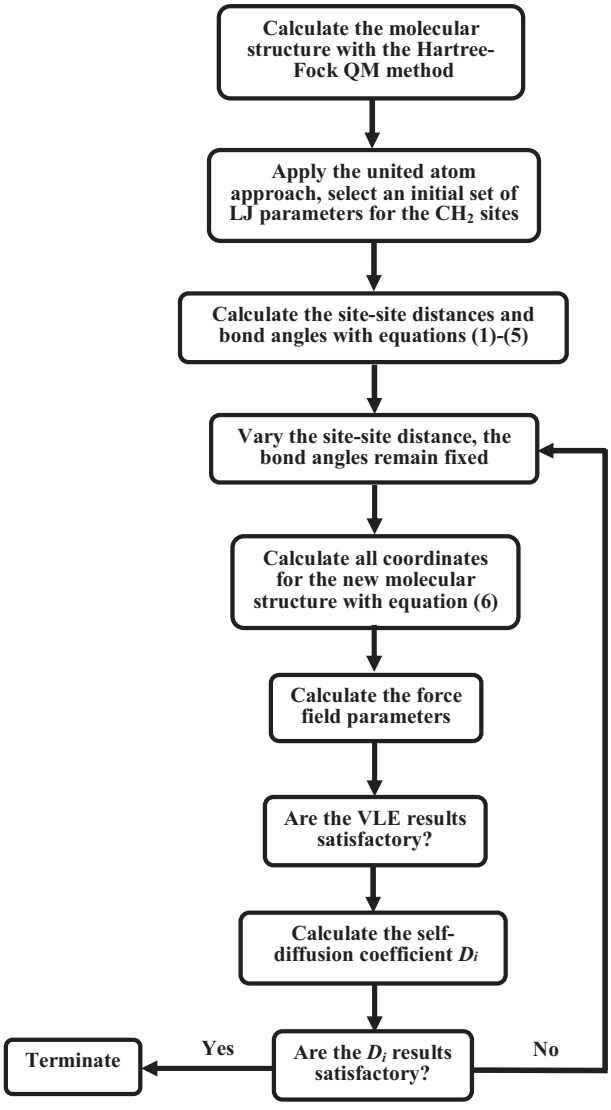

Fig. 1. Workflow of the present force field parameterization process.

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