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Individualized force fields for alkanes, olefins, ethers and ketones based on the transferable anisotropic Mie potential

Dominik Weidler, Joachim Gross*

Institute of Thermodynamics and Thermal Process Engineering, University of Stuttgart, D-70569, Stuttgart, Germany

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ABSTRACT

Transferable force fields allow the prediction of physical properties for substances with scarce or absent experimental data. For substances with a comprehensive experimental database, however, transferable force fields produce results with higher errors than desired, because the transferable force fields are designed to represent a compromise in correlating the properties of many substances. For applications in chemical engineering, where requirements for accurate vapor pressure correlations and predictions exist, the results from transferable force fields are sometimes insufficient. We individualize the transferable anisotropic Mie force field (TAMie) for 38 substances of various chemical families, by introducing a correction parameter that scales all van der Waals energy parameters ε_i of the considered substance. We find markedly reduced deviations, mainly in the description of vapor pressures while the errors in liquid density do not change significantly. For polar species, the improvement in vapor pressure is typically a factor four in absolute average deviation to experimental data, when compared to the original TAMie force field. The improved description of pure substances enables more reliable predictions of phase equilibria in binary mixtures. The concept of individualizing substances that are well-characterized by experimental data within a transferable force field is appealing, because the ability to predict mixtures with substances that are not covered by experimental data is preserved.

1. Introduction

Transferable force fields allow predicting physical properties and phase equilibria of pure substances and mixtures that are poorly described by experimental data. Among the most established transferable force fields are the Transferable Potentials for Phase Equilibria (TraPPE) [1–7], the Optimized Potential for Liquid Simulations (OPLS) [8–13] and the Assisted Model Building with Energy Refinement (AMBER) force field [14].

The AMBER force field as well as the TraPPE-UA force field are based on so-called united-atom models, where the van der Waals contribution of hydrogen atoms are lumped with interaction sites of neighboring atoms. The van der Waals interaction of a methyl-group (-CH_3), for example, is considered as one effective interaction site. Recent developments improved the description of properties like the vapor pressure by introducing additional degrees of freedom in the parameterization of transferable force fields. An additional degree of freedom can be introduced for united-atom approaches, by moving the interaction site of, say a CH_3 group, away from the position of the carbon atom to better (effectively) account for the presence of hydrogen atoms. This approach was proposed by Toxvaerd [15,16] and led to the Anisotropic United Atom force field [17–26] (AUA) by Ferrando, Boutin, Ungerer and coworkers. Shifting of interaction sites of non-terminal groups (say a CH_2-group) outwards requires more advanced configurational bias sampling schemes, as proposed by Smit et al. [27], because the location of the CH_2-interaction site is only defined once both neighboring interaction sites have a defined location. The method of Smit et al. introduces the small offset of the interaction sites as a last step in a configurational bias sampling scheme.

Other studies use intermolecular potentials other than the Lennard-Jones potential, e.g. the Buckingham potential with three adjustable parameters per van der Waals interaction site [28] or the Mie potential also with three adjustable parameters [29–32]. These works show that a united atom force field build up on potentials other than Lennard-Jones can provide good results for vapor pressures and densities for phase coexistance.

The Transferable Anisotropic Mie (TAMie) force field, recently developed in our group with emphasis on thermodynamic

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* Corresponding author.
E-mail address: gross@itt.uni-stuttgart.de (J. Gross).

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properties and vapor-liquid equilibria [33–35] adopts some of these ideas. It is a united-atom model and incorporates anisotropy in a simple manner by allowing an offset to terminal united-atom sites. With this simple approach sophisticated sampling schemes like the one proposed by Smit et al. [27] can be avoided. A Mie potential is used for the van der Waals contribution of inter- and non-covalent intramolecular interactions.

For the multidimensional optimization of the force field parameters an analytic equation of state, namely the Perturbed Chain Statistical Associating Fluid Theory (PC-SAFT) equation of state [36,37] was used. Although the molecular model of the PC-SAFT model is more coarse compared to the TAMie force field, it is possible to approximately map the objective function of TAMie to an analogous objective function of PC-SAFT. The procedure is iterative but converges rapidly [38] and the final converged force field parameters are not biased by the PC-SAFT model [33].

Another approach of coupling an equation of state with molecular simulations was proposed by Ghobadi and Elliott who applied a SAFT with molecular parameters taken from force fields that were originally proposed for molecular simulations [39–41]. Recently, Müller and Jackson with coworkers derived force field parameters directly from a physically based equation of state (the SAFT-γ equation of state) [42]. Their procedure is appealing because it is non-iterative and leads to good results for thermodynamic properties and phase equilibria. The molecular model is limited, of course, to the molecular model underlying the analytic equation of state. Their molecular model considers molecules as tangentially bonded Mie interaction sites without bond-angle potentials. The usefulness of analytic equations of state for conducting molecular simulations has in another context been demonstrated by Gospodinov and Escobedo, who showed how probability distributions can be estimated from equations of state [43,44]. Sanchez et al. [45] used the PC-SAFT model for estimating bias potentials that allow sampling across the energetic barrier between a vapor and a liquid phase in open ensembles.

Substances that are comprehensively characterized by experimental data are less accurately described with a transferable force field compared to a force field individually adjusted to data of that substance. Deficiencies in describing individual substances are a result of a compromise that needs to be made in correlating force field parameters to many substances simultaneously. For the TAMie force field this compromise leads to a positive deviation in the vapor pressure curve of some substances and a negative deviation from the experimental vapor pressure for others, especially for polar substances. For chemical engineering applications, deviations in vapor pressure are critical for process safety and equipment design aspects and should be eliminated as much as possible. Fig. 1 visualizes the systematic offset in vapor pressure for ethers (di-ethyl-ether and di-n-propyl-ether) as calculated from the TAMie force field. The diagram shows relative deviations of calculated vapor pressure and the liquid density from experimental data for both substances. One observes overpredicted vapor pressure values for di-ethyl-ether and underpredicted values for di-n-propyl-ether, when using the optimum for the given degrees of freedom [34].

In this study we propose the concept of individualized transferable force fields. The concept preserves the strength of a transferable force field in predicting properties of substances that are weakly characterized by experimental data, while alleviating the problem of systematic deviations (mainly in vapor pressure) found for some species. We introduce a correction parameter ψ_A that scales all van der Waals energy parameters of a pure substance A and shifts the vapor pressure curve closer to experimental data. We present individualized force field parameters for 38 substances and show that mixture properties are better described.

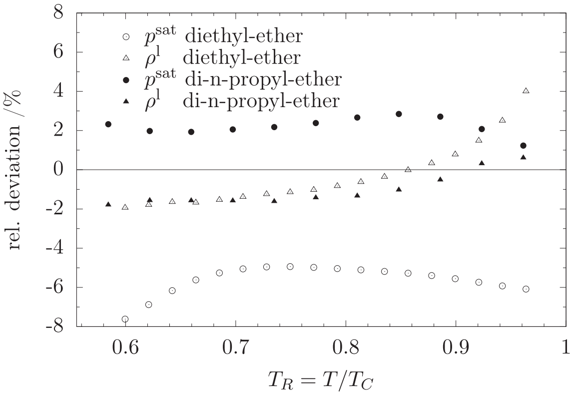

Fig. 1. Relative errors of the TAMie force field for ethers: spheres denote relative deviations concerning the vapor pressure, while the triangles symbolize the relative deviations of the liquid density. Filled symbols belong to dipropyl-ether and empty symbols to diethyl-ether.

2. Methodology

2.1. The TAMie force field

The TAMie force field is currently parameterized for n-alkanes and n-olefins [33], ethers [34], small cyclic alkanes, ketones, and aldehydes [35]. The pair potential between two interaction sites located either on different molecules, or more than three bonds apart in the same molecule writes as the sum of a Mie potential and an electrostatic potential, as

$$u_{ij} = c_n \cdot \varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{n_{ij}} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right] + \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}} \tag{1}$$

where r_{ij} is the distance between two interaction sites i and j, ε_{ij} is the van der Waals energy parameter, σ_{ij} is the corresponding size parameter, n_{ij} denotes the repulsive exponent, and q_i is the partial point charge. The partial charge or the energy parameter can be zero. Furthermore, ε_0 is the vacuum permittivity and the constant c_n ensures the minimum of the Mie potential at $-\varepsilon_{ij}$, with

$$c_n = \left(\frac{n_{ij}}{n_{ij} - 6} \right) \left(\frac{n_{ij}}{6} \right)^{\frac{6}{n_{ij}-6}} \tag{2}$$

The cross-wise parameters of the Mie potential are calculated using the Lorentz-Berthelot combining rules [46,47].

$$\sigma_{ij} = \frac{1}{2} (\sigma_{ii} + \sigma_{jj}) \tag{3}$$

$$\varepsilon_{ij} = \sqrt{\varepsilon_{ii} \varepsilon_{jj}} \tag{4}$$

and an arithmetic mean for the repulsive exponent n_{ij}

$$n_{ij} = \frac{1}{2} (n_{ii} + n_{jj}) \tag{5}$$

The force field optimization was carried out by minimizing the objective function

$$f(\mathbf{p}) = \frac{1}{N^{\mathrm{exp}}} \sum_{n=1}^{N^{\mathrm{exp}}} \left(\frac{\Omega_n^{\mathrm{sim}}(\mathbf{p}) - \Omega_n^{\mathrm{exp}}}{\Omega_n^{\mathrm{exp}}} \right)^2 \tag{6}$$

where Ω_n^{sim} and Ω_n^{exp} are simulated and quasi-experimental