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Transferability of cross-interaction pair potentials: Vapor-liquid phase equilibria of n-alkane/nitrogen mixtures using the TAMie force field

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ABSTRACT

The van der Waals contribution of force fields designed for calculating phase equilibria and thermodynamic properties are usually adjusted to experimental data of pure components. Using these force fields for mixtures by applying combining rules for the cross-wise interaction potentials does not always lead to satisfactory results. This study considers the cross-wise van der Waals energy parameters $\varepsilon_{\alpha\beta}$ among individual pairs of (united-)atom groups as adjustable (but subsequently transferable) parameters. The cross-energy parameters are simultaneously adjusted to an experimental training set of several mixtures. An analytic equation of state, the Perturbed-Chain Polar Statistical Associating Fluid Theory (PCP-SAFT), is used for ensuring very swift convergence of the optimization procedure. As an example, we consider the phase equilibria of n-alkane/nitrogen mixtures. The cross-energy parameters (-CH_3 to N and -CH_2- to N) are adjusted to three mixtures as the training set. We explore the transferability of the so-obtained force field for varying temperatures and for mixtures that were not considered in the training set. Phase equilibria of nine n-alkane/nitrogen mixtures (each at various temperatures) are determined using Monte Carlo simulations in the grand canonical ensemble. Results for vapor-liquid equilibrium calculations show very good agreement with experimental data.

1. Introduction

Transferable force fields used in molecular simulations are appealing for engineering applications because they allow predicting physical properties in the absence of experimental data. Transferable force fields decompose the total interaction of molecules into van der Waals contributions, usually described as pair-wise interactions only, and static electrostatic interactions, commonly characterized by fixed (non-polarizable) partial point charges. One speaks of a united-atom model, when the van der Waals contribution of hydrogen atoms are considered together with larger neighboring atoms. The van der Waals interaction of a methyl-group (-CH_3) for example, is then lumped into one effective van der Waals interaction site.

What is needed for predicting physical properties of mixtures with transferable force fields are cross-wise van der Waals potentials. These cross-wise potentials should be determined by quantum mechanical calculations. When a unique functional form of potential is assumed for the van der Waals interactions, the cross-wise potential is determined by scalar-valued cross-coefficients (say $\varepsilon_{\alpha\beta}$ and $\sigma_{\alpha\beta}$). Simple combining rules, like the Berthelot-Lorentz combining rules [1,2], can be assumed for these coefficients. In fact, transferable force fields of united-atom groups are adjusted to pure components assuming the Berthelot-Lorentz rules or other combining rules to hold.

In simulations of mixtures it is then apparent to also assume combing rules for defining the cross-interactions between unlike van der Waals interaction sites of different molecules. The Berthelot-Lorentz combining rules for the interactions of unlike molecules lead to good predictions for some [3–7], but not generally for all mixtures, as several studies show [8–11]. In fact, considering the severe assumptions one has to make to derive combining rules, such as the Berthelot-Lorentz rules, it is somewhat surprising that they are at all valuable for practical applications.

Several studies analyze combining rules for the van der Waals cross-coefficients ($\varepsilon_{\alpha\beta}$ and $\sigma_{\alpha\beta}$) with focus on phase equilibrium properties and these studies arrive at different conclusions [3,8,10,12,13]. Potoff et al. study various mixtures and find the Kong combing rule [14] to yield better predictions for some mixtures

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compared with the Berthelot-Lorentz combining rules, whereas the Berthelot-Lorentz rule is to be preferred for other mixtures. Delhommelle and Millié [8] clearly articulate a recommendation for the Kong combining rule and point out deficiencies in the description of experimental mixture data for the Berthelot-Lorentz rule. These authors considered simple binary mixtures for more unambiguity. The finding is reemphasized in a subsequent study of Desgranges and Delhommelle [15]. A study of Schnabel et al. [10] compares eleven combining rule considering 44 binary mixtures. The authors show that no combing rule outperforms the Berthelot-Lorentz rule significantly. The study shows that the Lorentz rule (arithmetic combining rule for the van der Waals size parameter $\sigma_{\alpha\beta}$) gives results in good agreement to experimental mixture densities. That is a convincing and conclusive finding, because Rouha and Nezbeda [12] as well as Boda and Henderson [13] point out that mixture density data are very sensitive towards the cross-size parameter $\sigma_{\alpha\beta}$ (as compared to $\varepsilon_{\alpha\beta}$). Schnabel et al. further show that good results for phase equilibria of mixture require pairwise adjusted cross-energy parameters $\varepsilon_{\alpha\beta}$ [10].

When phase equilibria are targeted, it is intuitive to use binary phase equilibrium data for determining the cross-energy parameter [5,16–25]. Other choices, such as excess quantities (e.g. excess Gibbs energies), however, have also been proposed as suitable observables for adjusting cross-energy parameters [26–28]. Furthermore, second virial coefficients are regarded suitable for identifying cross-wise parameters [29,30]. The path is appealing, because second virial coefficients are well measurable or alternatively, it is often possible to use high-level quantum mechanical calculations for only single pairs of molecules. As a disadvantage, however, most force fields are not able to reproduce pure component virial coefficients, because emphasis is laid on liquid states in parameterizing effective (non-polarizable) charges and effective pair-wise van der Waals potentials.

Usually the cross-energy parameter is written as a re-scaled Berthelot rule, $\varepsilon_{\alpha\beta} = \sqrt{\varepsilon_{\alpha\alpha}\varepsilon_{\beta\beta}}\cdot\xi_{ij}$, where i and j indicate species and α and β are for (united-)atom groups of these species, respectively. This form of writing the cross-energy on the one hand shows that the geometric Berthelot rule is already a good estimate that is modified with an adjustable parameter ξ_{ij}. On the other hand, this form clarifies, that the correction parameter ξ_{ij} is defined for species i and j, i.e. the same correction parameter is used for all (united-) atom groups α of the molecules i and atom groups β on species j, with $i \neq j$.

The scheme of adjusting a cross-energy parameter was used to describe the vapor-liquid equilibria of different binary systems with good results [5,11,19,31,32]. Applying the so-obtained binary parameters to ternary systems with no further adjustment to ternary mixtures leads to reliable results [33,34]. Applications range from molecular simulations of humid air [34] to aqueous solutions [35], electrolytes [36], pressure effects on homogeneous nucleation [37], gas storage in geological structures [25], carbon dioxide solubility [23], to composite analysis of Saturn's moon Titan [38].

As suggested by Schnabel et al. [10], in this work we use the standard Lorentz combining rule for the size parameter and an adjustable cross-energy parameter. However, we define transferable cross-energy parameters for each (united-)atom group individually: $\varepsilon_{\alpha\beta} = \sqrt{\varepsilon_{\alpha\alpha}\varepsilon_{\beta\beta}}\cdot(1-\kappa_{\alpha\beta})$, with $\kappa_{\alpha\beta}$ as an adjustable parameter. This approach defines adjustable cross-energy parameters for united-atom groups of different species, as corrections to the Berthelot combining rule. We show that this approach is transferable among alkane-nitrogen mixtures and how to adjust parameters $\kappa_{\alpha\beta}$ efficiently using the Perturbed-Chain Polar Statistical Associating Fluid Theory (PCP-SAFT) equation of state [39–41].

The PCP-SAFT model is an analytical equation of state that is suitable to accelerate convergence when adjusting force field parameters to experimental data. In previous work, we used PCP-SAFT for locally approximating the actual objective function and for minimizing the objective function in the parameter-space of the force field. The objective function from the PCP-SAFT equation of state is only approximate, which is why the procedure is iterative. Once convergence is achieved, however, the analytical model does not affect the final result anymore and the problem thus converges to the true minimum. The convergence is very swift, requiring only a few molecular simulation runs for evaluating the objective function, even for multidimensional optimization problems. The method has been applied to obtaining force field parameters of pure components [7,11,42,43] and of cross-interaction parameters of mixtures [23]. The approach has not been applied to individual pairs of atoms or united-atom groups.

A different approach that is also using an analytical equation of state was proposed by Müller and Jackson together with coworkers [44,45]. Their method relies on the SAFT-γ equation of state [46] and uses parameters of the analytic model directly as force field parameters. The procedure is therefore not iterative, but limits the force fields to coarse-grained models, where molecules are represented as tangentially bonded spherical interaction sites without electrostatic contributions. Their force-field enables fast calculations on large systems and, in case of molecular dynamics simulations, long calculation times [45].

In this study we define cross-energy parameters $\varepsilon_{\alpha\beta}$ for individual (united-)atom groups, which are adjusted to experimental phase equilibrium data and investigate the transferability of these parameters. Phase equilibria of n-alkane/nitrogen mixtures are regarded as an example, whereby the cross-energy parameters $\varepsilon_{CH_3,N}$ and $\varepsilon_{CH_2,N}$ are adjusted to three mixtures (the training set) using Monte Carlo simulations in the grand canonical ensemble. The transferability of the force field is then confirmed for several n-alkane/nitrogen mixtures that were not member of the training set. The PCP-SAFT equation of state is used to make the parameter regression efficient.

2. Molecular model

This work extends work on the TAMie force field [7,11,43], wherein the van der Waals energy contribution is limited to pairwise potentials and where fixed (partial) point-charges are regarded, omitting static polarizability. According to the TAMie model, molecules are decomposed into united-atom groups, such as a methyl-group -CH_3. We thus consider a molecule i to be composed of interaction sites α that interact to the interaction sites β of molecule j, according to

$$\phi_{\alpha\beta}\left(r_{\alpha\beta}\right) = c_{\alpha\beta}\,\varepsilon_{\alpha\beta}\left[\left(\frac{\sigma_{\alpha\beta}}{r_{\alpha\beta}}\right)^{n_{\alpha\beta}} - \left(\frac{\sigma_{\alpha\beta}}{r_{\alpha\beta}}\right)^{6}\right] + \frac{q_\alpha q_\beta}{4\pi\varepsilon_0\, r_{\alpha\beta}} \tag{1}$$

with $r_{\alpha\beta}$ as the distance between interaction site α and site β. The first term is a Mie potential, where we fixed the attractive exponent to the value 6, because this represents the leading term in the expansion of attractive (dispersive) interactions. The repulsive exponent $n_{\alpha\beta}$ is treated as an adjustable parameter, just like the energy parameter $\varepsilon_{\alpha\beta}$ and the size parameter $\sigma_{\alpha\beta}$. The coefficient $c_{\alpha\beta}$ is defined to enforce a minimum value of the potential $\phi_{\alpha\beta}(r_{\min}) = -\varepsilon_{\alpha\beta}$, as

$$c_{\alpha\beta} = \frac{n_{\alpha\beta}}{n_{\alpha\beta}-6}\left(\frac{n_{\alpha\beta}}{6}\right)^{6\,/\,(n_{\alpha\beta}-6)} \tag{2}$$

The second term of eq. (1) represents the electrostatic potential between the (partial) charges q_α and q_β separated by distance $r_{\alpha\beta}$