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Molecular modelling and simulation of the surface tension of real quadrupolar fluids

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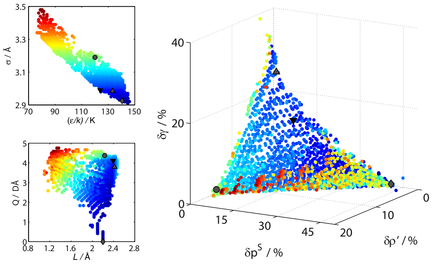
HIGHLIGHTS

- The vapor–liquid surface tension is computed for quadrupolar molecular models.
- On average, literature models overestimate the actual surface tension by about 20%.
- A multi-criteria optimization approach is applied to molecular models of CO_2.

GRAPHICAL ABSTRACT



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ABSTRACT

Molecular modelling and simulation of the surface tension of fluids with force fields are discussed. Twenty-nine real fluids are studied, including nitrogen, oxygen, carbon dioxide, carbon monoxide, fluorine, chlorine, bromine, iodine, ethane, ethylene, acetylene, propyne, propylene, propadiene, carbon disulfide, sulfur hexafluoride, and many refrigerants. The fluids are represented by two-center Lennard–Jones plus point quadrupole models from the literature. These models were adjusted only to experimental data of the vapor pressure and saturated liquid density so that the results for the surface tension are predictions. The deviations between the predictions and experimental data for the surface tension are of the order of 20%. The surface tension is usually overestimated by the models. For further improvements, data on the surface tension can be included in the model development. A suitable strategy for this is multi-criteria optimization based on Pareto sets. This is demonstrated using the model for carbon dioxide as an example.

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1. Introduction

In classical phenomenological thermodynamics following Gibbs (1876), interfacial properties are considered as excess contributions which are assigned to a formal dividing surface. In this way, the surface tension is obtained from the excess free energy with respect to a hypothetical system that does not contain an interface, consisting of the bulk phases in thermodynamic equilibrium only. Theorems that hold for the bulk properties can be immediately applied to interfacial thermodynamics, yielding fundamental relations such as the Gibbs adsorption equation (Gibbs, 1876; Alberty, 1995).

In interfacial thermodynamics, the Gibbs dividing surface represents the highest level of abstraction. Being strictly two-dimensional, the dividing surface does not have any volume, and its internal structure is not considered. While this simplifies the

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theoretical framework, it neglects physical phenomena which are important for understanding fluid interfaces. Since van der Waals (1873), it has been understood that such a purely empirical description can benefit from a theory of the fluid interface as a continuous region connecting two phases.

Thermodynamically, the internal structure of the interface, such as its thickness, can be considered by generalized versions of the Gibbs approach, e.g. as devised by Guggenheim (1940) or from more recent work (Frolov and Mishin, 2009; Laird and Davidchack, 2010). Furthermore, investigations based on statistical mechanics can provide a more detailed insight by describing the thermodynamics of interfaces in terms of their molecular structure (Henderson et al., 1976; Xu et al., 2012). In particular, the density functional theory (DFT) in combination with molecular equations of state was found to be a viable approach for interfacial properties of pure fluids (Jain et al., 2007; Gross, 2009) as well as mixtures (Kahl and Enders, 2002; Jain et al., 2007). In combination with simple expressions for the free energy, DFT yields analytical results such as the well-known approximation of the density profile by a hyperbolic tangent (Felderhof, 1970).

Molecular dynamics (MD) simulation, on the other hand, is based on the equations of motion from classical mechanics. While it is computationally more expensive, systems containing up to trillions of molecules can today be simulated on supercomputers, employing numerically convenient pair potentials (Germann and Kadau, 2008; Eckhardt et al., 2013). With relatively few model parameters, which can be adjusted to experimental data, molecular pair potentials are highly reliable for extrapolating and predicting a wide variety of fluid properties consistently (Ungerer et al., 2007; Eckl et al., 2008; Merker et al., 2012). Both static and dynamic properties can be computed by MD simulation (Bhatia and Nicholson, 2003; Allen et al., 2009; Guevara Carrión, 2012), for bulk phases as well as for heterogeneous systems (Vrabec et al., 2006; Müller, 2013). Even heat and mass transfer at fluid interfaces are well accessible to molecular dynamics (Strotos et al., 2008; Lotfi et al., 2014).

In a homogeneous bulk fluid, the long-range part of the force field acting on a single molecule averages out beyond a certain cutoff radius r_c, and straightforward mean-field approximations can be applied to compute the long-range contribution to the energy and the pressure (Allen and Tildesley, 1987). For simulations in the canonical ensemble, these corrections can be treated statically for the Lennard–Jones potential, and even for dipolar molecules (Saager et al., 1991), i.e. they have to be computed only once and do not change over time. However, molecular simulation of heterogeneous systems is more challenging, since the approximations behind the most straightforward techniques for homogeneous systems, e.g. the reaction field method (Onsager, 1936), break down in an anisotropic environment.

At a vapor–liquid interface, a volume integral over a short-range interaction such as dispersion, which decays with r_{ij}^{-6} in terms of the intermolecular distance r_{ij}, can yield a significant contribution, of the order of r_c^{-3}, to the potential energy as well as the surface tension (Janeček, 2006). Various algorithms have been devised to compute such effects efficiently and in a scalable way (Tameling et al., 2014; Werth et al., 2014a), facilitating the massively parallel MD simulation of heterogeneous systems with large numbers of particles (Arnold et al., 2013; Isele-Holder et al., 2013).

On the molecular level, the surface tension γ can be considered in different ways, based on mechanical and thermodynamic approaches. Thermodynamically, the surface tension is defined by the free energy change related to a differential variation of the surface area. Such differential excess free energies can be determined by test-area simulation (Gloor et al., 2005; Ghoufi and Malfreyt, 2012), whereas approaches based on grand-canonical sampling yield the absolute excess free energy associated with the interface (Binder, 1981, 1982; Schrader et al., 2009; Das and Binder, 2011; Tröster et al., 2012).

Mechanically, an interfacial tension causes a local stress, i.e. a negative pressure, which acts in the direction tangential to the interface. For the vapor–liquid surface tension at curved interfaces, mechanical and thermodynamic methods lead to contradicting results (Sampayo et al., 2010; Malijevský and Jackson, 2012; Tröster et al., 2012), and thermodynamic statements cannot be based on the mechanically defined value of γ directly. In case of planar fluid interfaces, however, the mechanical and thermodynamic approaches are rigorously equivalent, and the mechanical approach, which is employed here, can be straightforwardly implemented in terms of the intermolecular virial (Salomons and Mareschal, 1991). If periodic boundary conditions are employed and the canonical ensemble is simulated, the surface tension is immediately related to the deviation between the normal and tangential components of the pressure tensor.

Accurate molecular simulation results for the surface tension require an adequate consideration of the long-range contribution, which is sometimes nonetheless absent from works reporting such values (Eckl et al., 2008; Braun et al., 2013). Molecular models for which the surface tension has recently been evaluated reliably include carbon dioxide (Ghoufi et al., 2008; Kraska et al., 2009), which is also considered in the present work, water models (Vega and de Miguel, 2007; Ghoufi et al., 2008), and several other molecular fluids (Neyt et al., 2011; Eckelsbach et al., 2014). Comparing model predictions to experimental data, deviations were found to be of the order of 10–20% for various molecular models from the literature (Ghoufi et al., 2008; Neyt et al., 2011; Eckelsbach et al., 2014) and typically of the order of 50% for water models (Vega and de Miguel, 2007).

However, no systematic evaluation of γ by MD simulation of an entire class of molecular models has been conducted so far. This is the aim of the present work, focusing on a simple, but powerful class of models for real fluids from the literature. Vrabec et al. (2001) and Stoll et al. (2003) developed molecular models of the two-center Lennard–Jones plus point quadrupole (2CLJQ) type for 29 real compounds, including air components, halogens, hydrocarbons, and refrigerants. In previous work, these models were also applied successfully to binary (Vrabec et al., 2009) and ternary mixtures (Huang et al., 2009). The vapor–liquid equilibrium (VLE) behavior of the 2CLJQ model fluid has been studied systematically (Stoll et al., 2001), serving as the basis for a molecular equation of state which contains an explicit contribution of the quadrupole moment (Gross, 2005).

A correlation for the surface tension of the 2CLJQ model fluid from the previous work (Werth et al., 2014b) is extended by new MD simulations in the present work. On this foundation, the predictive capacity regarding the surface tension of the planar vapor–liquid interface is assessed here for these models, which were adjusted to VLE properties of the bulk fluids only (Vrabec et al., 2001; Stoll et al., 2003), i.e. interfacial properties were not taken into account for the parameterization.

For the present MD simulations of the surface tension, an efficient algorithm is employed to compute the contribution of the long-range correction (Werth et al., 2014a), combining an integration over planar slabs (Janeček, 2006) with a center-of-mass cutoff for multi-site models (Lustig, 1988). The obtained vapor–liquid surface tension is entirely predictive, and a comparison with experimental data can serve to validate or improve the molecular models. The surface tension predicted by these models has not been studied previously, except for molecular nitrogen and oxygen, where Eckelsbach et al. (2014) found a deviation of about 15% between model properties and experimental data. The present work confirms this result and considers the whole set of 2CLJQ models of real fluids systematically.

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