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A classical density functional theory for vapor-liquid interfaces consistent with the heterosegmented group-contribution perturbed-chain polar statistical associating fluid theory

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ABSTRACT

A Helmholtz energy functional consistent with the heterosegmented group-contribution perturbed-chain polar statistical associating fluid theory (GC-PCP-SAFT) is developed in this study and is applied to predict interfacial properties of planar vapor-liquid interfaces. Predicted surface tensions of pure substances are in very good agreement with experimental data for systems of non-polar as well as polar compounds including biodiesel systems where the group-contribution approach proves especially advantageous. The average deviation of the proposed model from experimental data is only 5% for these substances. Short hydrogen-bonding compounds, such as methanol and ethanol, are not predicted convincingly well. For longer hydrogen-bonding molecules the results are satisfying and deviations decrease to values of 3–10% for the entire liquid-vapor region. The orientation of hydrogen-bonding molecules at the vapor-liquid interface is reproduced qualitatively by the proposed model. Surface tensions for mixtures (including mixtures with hydrogen-bonding components) are predicted surprisingly well, with average deviations from experimental data of 5%. For mixtures, transferable group-group interaction parameters are adjusted to binary vapor-liquid equilibria data. The description of vapor-liquid phase equilibria is thereby significantly improved, however, the improvement of predicted surface tensions is mild. Further, in order to compensate for a weakness of group-contribution equations of state, we propose a concept for individualizing the group-contribution approach for substances that are well characterized by experimental data. We introduce a component-specific parameter. This concept improves the description mostly of vapor pressures, especially for short and multi-functional molecules. The effect of this measure on predicted surface tensions, however, is very modest.

1. Introduction

In many technical applications, interfacial properties play a determining role. For the calculation of surface tension, many simple methods have been developed [1–7]. Most of these simple methods are only applicable to certain classes of systems, lack predictive capabilities, especially for mixtures, and require input values for densities or critical properties of the components under study, which need to be known experimentally or provided by auxiliary models. There is a clear need for self-contained, predictive models with a more general range of applicability. Beyond prediction of interfacial tensions, a detailed description of the interface is important for example in the development of theories for interfacial mass transfer beyond the simple two-film model, taking into account implications from the enrichment of certain species at the interface [8].

Density gradient theory (DGT) and classical density functional theory (DFT) are two methods that can be applied to describe interfacial properties. The fundamental difference between both methods is that DFT is entirely predictive for interfacial properties, whereas DGT requires a component-specific adjustable parameter (referred to as influence parameter), which is usually adjusted to experimental data of surface tensions. In this study we apply DFT without adjustable parameters.

An approximate expression for the Helmholtz energy functional $A[\rho(\mathbf{r})]$, where the square brackets denote a functional dependence on the spatially varying density profile $\rho(\mathbf{r})$, is at the core of any DFT approach. The development of the Statistical Associating Fluid

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Theory (SAFT) led to equations of state for non-spherical and hydrogen-bonding (i.e. associating) interactions [9]. SAFT models are based on Wertheim's Thermodynamic Perturbation Theory (TPT) [10–13] and were natively developed in a functional form [14], as worked out by Chapman and coworkers [15–17] with contributions of Kierlik and Rosinberg [18,19]. Jain et al. [20] modified the interfacial SAFT (iSAFT) form earlier proposed by Tripathi and Chapman [17] to account for the chain formation of single segments. The theory can be used to build heteronuclear chain fluids with individually tagged segments, which means that the density profile of all segments within a chain can be individually calculated.

In several studies, Helmholtz energy functionals consistent with SAFT-type equations of state have been applied successfully to study vapor-liquid interfaces and predict surface tension or study fluids in confined media. This includes the studies of Jackson and co-workers [21–24,24–26], Schindler et al. [27] and Malheiro et al. [28] who applied Helmholtz energy functionals consistent with the Statistical Associating Fluid Theory for potentials of variable range (SAFT-VR) or Kahl and Winkelmann [29] who applied a functional consistent with Lennard-Jones-SAFT. A review of current DFT applications can be found in the articles of Davis [30], Löwen [31], Wu [32], Emborsky et al. [33] or Landers et al. [34].

A Helmholtz energy functional consistent with the Perturbed-Chain Polar Statistical Associating Fluid Theory (PCP-SAFT) [35] [36] [37] [38] has been developed in our group [39–41]. Surface tension predictions from DFT calculations using the most recent Helmholtz energy functional are in excellent agreement with experiments [41] [42]. The required input for these calculations are the pure-component PCP-SAFT parameters and possibly binary interaction parameters. These parameters are commonly regressed to pure component and mixture vapor liquid equilibria, respectively, without considering interfacial properties.

In order to further increase the predictive capabilities of the DFT approach, a Helmholtz energy functional consistent with an accurate group-contribution (GC) equation of state is desirable. Group-contribution methods assume that the properties of a molecule can be determined as a function of the distinct functional groups that make up the given molecule. Such an approach makes the need for component-specific equation of state parameters obsolete. The range of applicability of DFT thus increases to compounds for which no or not enough experimental data is available to retrieve model parameters.

In this study we develop a Helmholtz energy functional consistent with the heterosegmented group-contribution PCP-SAFT equation of state [43] [44], i.e. when applied to a homogeneous system, this functional reduces to the expressions of heterosegmented GC-PCP-SAFT.

The Helmholtz energy functional is based on modified iSAFT to account for the chain formation of single segments. Predictions of the surface tension as obtained from the DFT approach for pure components as well as mixtures for non-polar and non-associating, polar as well as associating compounds are compared to experimental data. Furthermore, it is shown that the level of detail accessible by calculating density profiles for individual segments offers the possibility to qualitatively reproduce the orientation of hydrogen-bonding molecules at the interface. This is exemplified for 1-alcohols.

2. Heterosegmented group-contribution PCP-SAFT

In the heterosegmented group-contribution PCP-SAFT equation of state, the Helmholtz energy A is calculated as the sum of several contributions [43] [44]

$$\frac{A}{NkT} = \frac{A^{IG}}{NkT} + \frac{A^{HS}}{NkT} + \frac{A^{HC}}{NkT} + \frac{A^{Disp}}{NkT} + \frac{A^{Assoc}}{NkT} + \frac{A^{Dipole}}{NkT} \tag{1}$$

where the summands are the Helmholtz energy of an ideal gas, the contribution of the hard-sphere fluid, of chain formation, of dispersive attraction, of association, and of dipole-dipole interactions. In the following paragraph, we present modifications to the dispersive contribution of eq. (1). For details on the remaining Helmholtz energy contributions, we refer to the original work on the group-contribution PCP-SAFT equation of state by Sauer et al. [43] and Gross et al. [44].

The defining advantage of group-contribution methods is their predictive capability: properties of compounds where no experimental data is available to adjust component-specific parameters can be derived from the molecular structure of the compound and parameters for the groups constituting the molecule. A drawback of GC methods, on the other hand, is that methods using compound-specific parameters, where applicable, usually fare better than group-contribution approaches. In an attempt to improve results of heterosegmented GC-PCP-SAFT for compounds with a large body of experimental data we introduce a parameter ϕ_i to the dispersive contribution which is adjusted to experimental vapor pressure data of component i. As a consequence, we improve the representation of well-known substances, while preserving the ability to predict substances with no or limited experimental characterization, and mixtures thereof. The choice to use vapor pressure data rather than liquid density to regress ϕ_i is based on the results presented in Ref. [43] which show that values of heterosegmented GC-PCP-SAFT for liquid density are already convincingly accurate whereas larger deviations occur for vapor pressure. Furthermore, transferable group-group interaction parameters $k_{\alpha\beta}$ are introduced to improve the description of mixtures. The parameters $k_{\alpha\beta}$ have values $\neq 0$ only for segments of unlike types α and β which are located on different chain molecules. The dispersive contribution to the Helmholtz energy for a mixture of N components at temperature T and density ρ is then obtained as

$$\frac{A^{Disp}}{NkT} = a_1 + a_2 \tag{2}$$

where

$$a_1 = -2\pi\rho I_1 \sum_{i=1}^{N} \sum_{j=1}^{N} x_i x_j \sum_{\alpha} \sum_{\beta} n_{i\alpha} n_{j\beta} m_\alpha m_\beta \sigma_{\alpha\beta}^3 \varepsilon_{i\alpha,j\beta} \Big/ kT \tag{3}$$

$$a_2 = -\pi\overline{m}\rho I_2 C_1 \sum_{i=1}^{N} \sum_{j=1}^{N} x_i x_j \sum_{\alpha} \sum_{\beta} n_{i\alpha} n_{j\beta} m_\alpha m_\beta \sigma_{\alpha\beta}^3 \left(\varepsilon_{i\alpha,j\beta} \Big/ kT\right)^2 \tag{4}$$

The sums with indices α and β run over all group types and $n_{i\alpha}$ denotes the number of segments of type α on molecule i. Furthermore, m_α and σ_α represent the segment number and diameter parameter, respectively, of segments of type α, with the geometric condition $\overline{m} = \sum_i^N x_i \sum_\alpha n_{i\alpha} m_\alpha$, the combining rule $\sigma_{\alpha\beta} = 0.5(\sigma_\alpha + \sigma_\beta)$, and the combining rule for the cross-wise energy parameter

$$\varepsilon_{i\alpha,j\beta} = \sqrt{\varepsilon_\alpha \phi_i \cdot \varepsilon_\beta \phi_j}\left(1 - k_{\alpha\beta}\right) \tag{5}$$

where $k_{\alpha\beta}$ takes on the values presented in Table 1 only if $\alpha \neq \beta$ and $i \neq j$, otherwise it is defined as zero. Here ε_α is the dispersive energy parameter characterizing the attractive van der Waals interaction