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A new force field for H_2S and its binary and ternary mixtures with CO_2 and CH_4

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ABSTRACT

We present a new force field for H_2S, based on an exponential-6 functional form for the repulsion–dispersion interactions and a charge distribution. This force field is used in a series of Expanded Wang–Landau (EWL) simulations, which allow to obtain an accurate estimate for the partition function and thus provides access to all thermodynamic properties of the system. The simulation results show that this new force field yields accurate values for the VLE properties of pure H_2S. For binary mixtures of H_2S with CH_4, EWL results, obtained with this force field and the standard combining rules, are in excellent agreement with the experimental data. In line with previous work, no combining rules were found to perform well for the H_2S–CO_2 binary mixture and parameters for the interactions between unlike sites were optimized to obtain an excellent agreement for this mixture. We finally extend the EWL simulation method to simulate phase equilibria for ternary mixtures of H_2S with CH_4 and CO_2 and show that the parameters obtained in this work model accurately the vapor–liquid coexistence in these ternary mixtures.

1. Introduction

In recent years, natural gas has been increasingly produced from acid gas fields, with a higher content of acid gases, including H_2S and CO_2. Regulations impose that these acid gases be removed from the natural gas, prompting new avenues of research to treat natural gas. This can be achieved either through the adsorption of H_2S [1–6], e.g. in alkanolamines solutions, or through an acid gas injection process. As discussed by Chapoy et al. [7], the latter approach requires a wealth of data and models to predict accurately the phase equilibrium data involved in the process.

Molecular simulation, combined with the use of force fields based on an exponential-6 functional form, have recently been shown to model accurately the behavior of CO_2-H_2O mixtures under a wide range of conditions [8]. This is especially important in view of the rising interest in CO_2 geological storage [9,10], since H_2S is thought to be a significant impurity in the CO_2 stream to be sequestered in the acid gas injection process [7]. The first goal of this work is therefore to extend this force field to model pure H_2S. To carry out a thorough test of the model, we use the recently developed Expanded Wang–Landau (EWL) simulation method [11–13]. Rather than determining the properties of the system for a given set of conditions of temperature and pressure, the EWL method gives a highly accurate estimate of the partition function of the system and only requires the temperature as an input parameter. Once the value of the partition function is known, all properties of the system can be readily calculated using the statistical mechanics formalism. The second goal of this work is to use the newly parameterized force field to model binary mixtures of H_2S with CO_2, with CH_4, as well as the ternary mixture H_2S–CO_2–CH_4, providing the first application of the EWL method to the study of a ternary mixture.

The paper is organized as follows. In the next section, we briefly review the principles underlying the EWL approach, discuss the functional form used for H_2S and give the simulation details. We then present the results obtained for pure H_2S and for the binary and ternary mixtures studied in this work. In each case, we assess the performance of the force field by comparison with the experimental data. We finally draw the main conclusions from this work in the last section.

2. Simulation method

2.1. Expanded Wang–Landau simulations

The Expanded Wang–Landau (EWL) approach [11–13] is a Monte Carlo (MC) simulation method that consists in determining, with great accuracy, the partition function of the grand-canonical

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ensemble for a system of molecules in a given volume and at a given temperature. We briefly outline the method here and refer the reader to our prior work [11–13] for a full account of the EWL approach. The great advantage of the method lies in the fact that, once the grand-canonical partition function has been determined, the formalism of statistical mechanics [14] provides access to all properties of the system for a wide range of conditions, including e.g. the conditions for phase coexistence. The method is based on the Wang–Landau sampling, which was initially devised to obtain numerical estimates for the density of states in the microcanonical ensemble [15–21], i.e. at fixed number of molecules N, at fixed volume V and at fixed energy E. The Wang–Landau sampling was recently extended to calculate estimate for the partition function in other ensembles, including the isothermal–isobaric partition function [22–24,26,25,27–29] and the grand-canonical ensemble [11–13]. When studying molecular fluids, the insertion and deletion MC steps are divided into M stages (M being an integer), in line with the expanded ensemble approach [30–38]. This means that the system actually simulated consists of N full (regular) molecules plus one fractional molecule at stage l (l being an integer, whose value is between 0 and $M-1$). This is found to improve the acceptance rate of the insertion/deletion steps and, in turn, to increase greatly the accuracy of the partition function and of the thermodynamic properties so obtained [11]. We finally add that this approach has been tested for single component systems [11,39], fluids adsorbed in nanoconfined systems [12,40–42] as well as for binary mixtures [13].

2.2. Force fields

The force fields used in this work are based on the functional form of Errington et al. [43–46] for the repulsion–dispersion interactions and given by the following expression:

$$\begin{aligned} u(r) &= \frac{\epsilon}{1-6/\alpha}\left[\frac{6}{\alpha}\exp\left(\alpha\left[1-\frac{r}{r_m}\right]\right)-\left(\frac{r_m}{r}\right)^6\right] && (r > r_{\max}) \\ &= \infty && (r < r_{\max}) \end{aligned} \tag{1}$$

In Eq. (1), r_m is the distance for which the potential reaches a minimum, r_{max} is the smallest positive distance for which $du(r)/dr = 0$ and ϵ and α are two potential parameters. As discussed by Errington et al., it is convenient to discuss the potential parameters in terms of σ (i.e. the distance for which $u(r) = 0$, obtained numerically by solving the equation $u(\sigma) = 0$) rather than in terms of r_m. In addition to the repulsion–dispersion interaction, a Coloumbic term is added to account for the interactions between partial charges. The parameters used in this work for CH_4 and CO_2 are given in Errington et al. [43] and in Liu et al. [8], respectively.

For H_2S, we parameterize a force field for using the functional form of Eq. (1) for the repulsion–dispersion interactions. In line with the force fields developed previously for this molecule [47–56], we add to the repulsion–dispersion interaction terms a distribution of point charges to model the polar nature of hydrogen sulfide. Building on the ability of the force field proposed by Kristof and Liszi to model mixtures of H_2S with short alkanes [57–60], we retain the same distribution of 4 point charges [47] to model the polar nature of H_2S, with 1 charge $q_S = 0.4e$ on the S atom, 1 charge $q_H = 0.25e$ on each H atom and 1 charge $q_a = -0.9e$ on the bisector of the H–S–H angle, at a distance $\delta = 0.1933$ Å from the S atom. The geometry of the molecule is also taken to be the same as in Ref. [47], with the H—S bond length fixed to $d_{H-S} = 1.34$ Å and the H–S–H angle fixed to 92°. Once the distribution of point charges has been chosen, we then optimize the dispersion–repulsion parameters to obtain an accurate picture of the properties of pure H_2S. We choose to have a single interaction site, located on the S atom, for the dispersion–repulsion interactions. We find the following set of parameters for the dispersion–repulsion interaction site: $\epsilon/k_B = 240$ K, $r_m = 4.25$ Å and $\alpha = 12.4$. We discuss the performance of the model, as tested against the available experimental data, in the Section 3 of this paper.

2.3. Simulation details

We use a Monte Carlo simulation framework to perform EWL simulations [11–13]. The MC steps applied to the molecules considered in this work are either the translation of a single molecule (37.5% of the MC steps), the rotation of a single molecule (37.5% of the MC steps) or in a change in (N, l) (25% of the MC steps).

During the EWL simulations, the interaction between an interaction site of type i of the fractional molecule and an interaction site j of a full molecule is given by

$$\begin{aligned} u(r_{ij}) = {} & \frac{\xi^{1/3}\epsilon_{ij}}{1-6/\alpha}\left[\frac{6}{\alpha}\exp\left(\alpha\left[1-\frac{r_{ij}}{\xi^{1/4}r_m}\right]\right)-\left(\frac{\xi^{1/4}r_m}{r_{ij}}\right)^6\right] \\ & +\frac{\xi^{1/3}q_iq_j}{4\pi\epsilon_0 r_{ij}} \end{aligned} \tag{2}$$

with the coupling parameter ξ defined as the ratio l/M for the fractional molecule. In addition to the coupling of Eq. (2), we also apply a homothetic transformation for the skeleton of the fractional molecule. This means that, for a given stage l, the actual H—S bondlength of the fractional molecule is equal to $(l/M)^{1/4}d_{H-S}$.

The final value of the convergence factor for the EWL process is set to $f = 10^{-8}$ and the number of intermediate stages is chosen as $M = 100$. A spherical truncation was applied to the calculations of LJ interactions, with tail corrections applied beyond the cutoff set to half the boxlength L. The Ewald summation technique was applied to calculate the long-range Coulombic interactions, with the screening parameter for the charge Gaussian distribution set to $5.6/L$ and the reciprocal cutoff vector set to $k_{max} = 6(2\pi)/L$.

Interactions between unlike parameters were calculated using the Lorentz–Berthelot combining rules for the H_2S–CH_4 and CO_2–CH_4 interactions. However, these rules tend to overestimate the attraction between dispersion–repulsion site when sites are of very dissimilar sizes [13,61], such as e.g. between the C atom of CO_2 and the H_2S site. In particular, previous work has shown that the H_2S–CO_2 interaction is not accurately modeled if the Lorentz–Berthelot rules are used [53,58] and that the Kong rules [62] yielded results that were closer to the experimental data. In this work, we test several combining rules (Lorentz–Berthelot, Kong and Waldman-Hagler [63]) and propose an optimal set of parameters for the interaction between H_2S and CO_2.

3. Results and discussion

3.1. VLE results for pure H_2S

We start by assessing the performance of the parameterization developed in this work for H_2S. The output from the EWL simulations are the values taken by the canonical partition function $Q(N, V, T)$ (here, the volume of the system in the EWL simulations is that of a cubic box, with a boxlength of 25 Å). We show in Fig. 1(a) the variations of the canonical partition function as a function of the temperature for 8 different temperatures, ranging from 225 K to 333.6 K.