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

A. N. Owen, C. Desgranges, J. Delhommelle

*Department of Chemistry, 151 Cornell Street Stop 9024, University of North Dakota,
Grand Forks, North Dakota 58202, USA*

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.

Key words: Expanded Wang-Landau, vapor-liquid equilibria, natural gas, acid gases, hydrogen sulfide, force field

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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 .

Email address: jerome.delhommelle@und.edu (J. Delhommelle)

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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, 2, 3, 4, 5, 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, 12, 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 parametrized 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, 12, 13] is a Monte Carlo (MC) simulation method that consists in determining, with great accuracy, the partition function of the grand-canonical 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, 12, 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, 16, 17, 18, 19, 20, 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, 23, 24, 26, 25, 27, 28, 29] and the grand-canonical ensemble [11, 12, 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, 31, 32, 33, 34, 35, 36, 37, 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, 41, 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, 44, 45] 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 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 parametrize 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, 48, 49, 50, 51, 52, 53, 54, 55, 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, 58, 59, 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 $H-S$ bondlength 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 'Results' section of this paper.

2.3. Simulation details

We use a Monte Carlo simulation framework to perform EWL simulations [11, 12, 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

$$u(r_{ij}) = \frac{\xi^{1/3}\epsilon_{ij}}{1-6/\alpha} \left[\frac{6}{\alpha} \exp \left(\alpha \left[1 - \frac{r_{ij}}{\xi^{1/4}r_m} \right] \right) - \left(\frac{\xi^{1/4}r_m}{r_{ij}} \right)^6 \right] + \frac{\xi^{1/3}q_iq_j}{4\pi\epsilon_0r_{ij}} \quad (2)$$

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 parametrization 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.

Once these partition functions are known, the grand-canonical partition function, as well as the resulting number distribution $p(N)$, can be calculated

Figure 1: (a) Reduced canonical partition functions $Q^*(N_{H_2S}, V, T)$ for temperatures ranging from , (b) Map of the number probability against the temperature and N_{H_2S} .

for any value of the chemical potential μ

$$\begin{aligned}\Theta(\mu, V, T) &= \sum_N Q(N, V, T) \exp(\beta\mu N) \\ p(N) &= \frac{Q(N, V, T) \exp \beta\mu N}{\Theta(\mu, V, T)}\end{aligned}\quad (3)$$

$p(N)$ provides a direct way to determine the conditions of phase coexistence, by finding numerically the value of the chemical potential corresponding to equal probabilities for the vapor phase (i.e. $\sum_{N < N_b} p(N)$) and for the liquid phase (i.e. $\sum_{N > N_b} p(N)$), with N_b being set to half the maximum number of molecules sampled during the EWL simulations. We present in Fig. 1(b) the number distributions at coexistence for all temperatures studied in this work and plot them as a function of N and T . The darker regions in this plot are associated with a very low probability, while the lighter regions (which reveal the phase envelope) are associated with a high probability at coexistence. $p(N)$ can then be used to determine all other thermodynamic properties of the system, including e.g. the pressure P , the density ρ , the internal energy U and the entropy S as

$$\begin{aligned}P &= \frac{k_B T \ln \Theta(\mu, V, T)}{V} \\ \rho &= \sum_N \frac{mN}{V} p(N) \\ U &= \sum_N (E_{pot}(N) + \frac{5}{2} N k_B T) p(N) \\ S &= k_B \ln \Theta(\mu, V, T) + \frac{(U - \mu \langle N \rangle)}{k_B T}\end{aligned}\quad (4)$$

The ability of the force field developed for H_2S to model accurately the VLE properties of hydrogen sulfide can now be assessed by comparing the EWL simulation results to the available experimental data. The first set of properties used for this assessment are the densities at coexistence, shown in Fig. 2, together with the experimental data. The EWL results for the force field developed in this work are in very good agreement with the experimental densities over the whole range of temperature. The vapor pressure for H_2S can also be determined using Eq. 4 and plotted as a Clapeyron plot as a function of the reciprocal temperature (see Fig. 3). This plot also shows the very good agreement between the EWL simulation results and the experimental data, further establishing the reliability of the new force field developed in this work.

The critical properties of the model can be estimated by fitting the EWL results with a critical scaling law [65] to obtain the critical temperature for the model, the law of rectilinear diameters [66] to obtain the critical density

Figure 2: VLE curve for H_2S : Expanded Wang Landau results (squares) vs. experimental data (circles) [64]. Filled symbols indicate the critical point.

Figure 3: Logarithm of pressure for H_2S as a function of the reciprocal temperature: Expanded Wang Landau results (squares) vs. experimental data (circles) [64]. Filled symbols indicate the critical point.

and Antoine’s law to obtain the critical pressure. The equations used are as follows [67, 68, 69]

$$\begin{aligned}\rho_l - \rho_v &= A(T - T_c)^\beta \\ \frac{1}{2}(\rho_l + \rho_v) &= \rho_c + B(T - T_c) \\ \log P &= C - \frac{D}{(T+E)}\end{aligned}\tag{5}$$

The results obtained for the critical data are summarized in Table 1. The critical point, as predicted by the new force field, is found to be in good agreement with the experimental data. Using Antoine’s law, we are also able to provide an estimate for the boiling temperature T_b . The new force field predicts a boiling temperature of $T_b^{EWL} = 217\text{ K}$ in good agreement with the experimental data ($T_b^{exp} = 212.9\text{ K}$).

Table 1: Critical properties for H_2S .

	$T_c(K)$	$\rho_c(g/cm^3)$	$P_c(bar)$
Experiment	373.4	0.3476	89.6
This work	375	0.352	82.5

We finally show the variations of the entropies of the two coexisting phases as a function of temperature, as calculated according to the last line of Eq. 4. This plot shows the rapid increase in the entropy of the liquid phase of H_2S at coexistence (by more than 25% between 225 K and 343 K), as a result of the decrease in density of the liquid at coexistence as the temperature increases. This behavior is correlated with the decrease in the entropy of the vapor phase at coexistence as temperature increases (by 10% over the same temperature interval), which results from the increase in the vapor density at coexistence as temperature increases.

3.2. VLE results for the H_2S - CH_4 binary mixture

The next step in this work consists in extending the EWL simulations to the binary mixture of H_2S with CH_4 . In this case, the output from the EWL simulations are the canonical partition functions for the mixture $Q(N_{H_2S}, N_{CH_4}, V, T)$. We show in Fig. 5(a) the canonical partition functions, as a function of the number of molecules of H_2S and CH_4 , for a temperature of 311 K. Similarly to the case of a single component system, discussed in

Figure 4: Entropies of the coexisting phases of H_2S (top: vapor and bottom: liquid) as a function of temperature: Expanded Wang Landau results (squares).

the previous section, we can calculate the grand-canonical partition function for the binary mixture $\Theta(\mu_{H_2S}, \mu_{CH_4}, V, T)$ and the number distribution probability $p(N_{H_2S}, N_{CH_4})$, for any set of chemical potentials (μ_{H_2S}, μ_{CH_4}) , as

$$\Theta(\mu_{H_2S}, \mu_{CH_4}, V, T) = \sum Q(N_{H_2S}, N_{CH_4}, V, T) \exp(\beta(\mu_{H_2S}N_{H_2S} + \mu_{CH_4}N_{CH_4}))$$

$$p(N_{H_2S}, N_{CH_4}) = \frac{Q(N_{H_2S}, N_{CH_4}, V, T) \exp(\beta(\mu_{H_2S}N_{H_2S} + \mu_{CH_4}N_{CH_4}))}{\Theta(\mu_{H_2S}, \mu_{CH_4}, V, T)} \quad (6)$$

The conditions of phase coexistence are determined by finding numerically the set of chemical potentials giving equal probabilities for the vapor phase (left hand side of Eq. 7) and for the liquid phase (right hand side of Eq. 7), with N_{b,H_2S} and N_{b,CH_4} being set to half the maximum number of molecules sampled during the EWL simulations:

$$\sum_{N_{H_2S} < N_{b,H_2S}} \sum_{N_{CH_4} < N_{b,CH_4}} p(N_{H_2S}, N_{CH_4}) = \sum_{N > N_{b,H_2S}} \sum_{N_{CH_4} > N_{b,CH_4}} p(N_{H_2S}, N_{CH_4}) \quad (7)$$

Fig. 5(b) shows the two peaks (in bright colors) corresponding to the two coexisting phases (the vapor being the peak on the left, while the liquid is

(a)

(b)

Figure 5: (a) Reduced canonical partition function $Q^*(N_{H_2S}, N_{CH_4}, V, T)$ as a function of N_{H_2S} and N_{CH_4} , (b) Map of the number probability against N_{H_2S} and N_{CH_4} for a pressure of 59.5 bar.

Figure 6: Pressure of the $H_2S - CH_4$ mixture as a function of the mole fraction in CH_4 in the coexisting phases (right: vapor and left: liquid) at 311 K: Expanded Wang Landau results (squares) vs. experimental data (circles) [70].

the peak on the right) for a pressure of 59.5 bar. Repeating this operation for different sets of chemical potentials allows us to obtain the coexistence curve for different pressures and to plot the variation of pressure as a function of the mole fractions of H_2S in the two phases (see Fig. 6). We also plot in Fig. 6 the experimental data for this mixture [70]. Overall, the EWL results are in very good agreement with the experimental data, with deviations of less than 0.5% for the H_2S mole fraction in the liquid phase and of less than 2% for the H_2S mole fraction in the vapor phase.

3.3. VLE results for the H_2S - CO_2 binary mixture

The analysis of the output of the EWL simulations is carried out exactly as for the H_2S - CH_4 mixture discussed in the previous section. However, while the H_2S and CH_4 had comparable sizes (i.e. r_m parameters), the interaction sites of the CO_2 molecule (i.e. the atoms of C and O) and the single (united atoms-like) site standing for H_2S have markedly different sizes. This means that the choice of combining rules, used to define the parameters for the interactions between C and H_2S and between O and H_2S , will have a significant effect on the thermodynamic properties of the mixture [13, 61]. In

Figure 7: Pressure of the $H_2S - CO_2$ mixture as a function of the mole fraction in CO_2 in the coexisting phases (right: vapor and left: liquid): EWL results with the LB rules (squares), EWL results with the WH rules (triangles up), EWL results with the KG rules (diamonds), EWL results with the set of parameters of Table I (triangles down) and experimental data (filled circles) [71].

previous work, Kamath and Potoff [53], as well as Ungerer *et al.* [58], have reported that using the Lorentz-Berthelot (LB) combining rules, together with force fields based on the Lennard-Jones potential form, did not accurately model the $H_2S - CO_2$ vapor-liquid equilibria (ref. [58] also showed that the Kong (KG) rules [62] improved to some degree the agreement with the experimental data). To shed light on the impact of the combining rules on the force field developed in this work for H_2S , we have performed EWL simulations with different sets of parameters.

We plot in Fig. 7 the results obtained with the LB rules, the Waldman-Hagler (WH) rules [63] and the KG rules [62]. We also show in Fig. 7 the experimental data for the mixture. The results obtained with the LB rules significantly overestimate the CO_2 mole fraction in both phases of the mixture. This results from the fact that the LB rules lead to interactions between unlike sites that are too attractive. On the other hand, the WH and KG rules yield less attractive interactions between unlike sites, which, in turn, leads to an improvement in the agreement between the EWL results and the ex-

perimental data. Fig. 7 shows, however, that the EWL results obtained with both sets of rules underestimate the experimental mole fractions for both phases. We have therefore carried out a fourth EWL simulation with a set of parameters optimized to match the experimental data on the mixture (see Table 2) to obtain a satisfactory account of the $H_2S - CO_2$ mixture. We find the optimized values for ϵ to be significantly less than those predicted by the LB rules (by 30% for the $C - H_2S$ interaction and by 7% for the $O - H_2S$ interaction) and the optimized r_m to be greater than those predicted by the LB rules (by 3% for the $C - H_2S$ interaction and by 0.4% for the $O - H_2S$ interaction). We use the optimized set of parameters in the EWL simulation of the ternary mixture (next section).

Table 2: Optimized interactions parameters for the $H_2S - CO_2$ mixture.

	$\epsilon/k_B(K)$	α	$r_m (\text{\AA})$
$O - H_2S$	132.70	13.167	3.842
$C - H_2S$	63.92	13.167	3.791

3.4. VLE results for the $H_2S-CH_4-CO_2$ ternary mixture

We now turn to the prediction of the properties of the ternary mixture $H_2S-CH_4-CO_2$. Studying a ternary mixture means that an extra dimension is added in the EWL simulations, resulting in an output which becomes the canonical partition functions $Q(N_{H_2S}, N_{CO_2}, N_{CH_4}, V, T)$. The analysis of the results is similar to that of a binary mixture, with sums extending over the numbers of molecules of H_2S , CO_2 and CH_4 in e.g. Eq. 7. The key quantity to determine the conditions of phase coexistence and the mole fractions of each component in the two coexisting phases becomes $p(N_{H_2S}, N_{CO_2}, N_{CH_4})$.

We plot in Fig. 8 the projection of $p(N_{H_2S}, N_{CO_2}, N_{CH_4})$ for the liquid phase in the $N_{H_2S}-N_{CH_4}$ plane and in the $N_{H_2S}-N_{CO_2}$ (the temperature is 310.47 K and the pressure is 49 bar). The two bright regions, shown in Fig. 8(a) and Fig. 8(b), provide a direct access to the ratios of $N_{H_2S}:N_{CH_4}$ and of $N_{H_2S}:N_{CO_2}$, and hence to the mole fractions of each component in the liquid phase. A similar analysis is applied to determine the mole fractions in the corresponding vapor phase.

We finally compare the predictions of the EWL simulation to the experimental data [72]. Following Robinson and Bailey’s analysis [72], we first

Figure 8: Map of the number probability for the liquid phase of the ternary mixture $H_2S - CH_4 - CO_2$ at a pressure of 49 bar: (a) in the N_{H_2S} - N_{CH_4} plane, and (b) in the N_{H_2S} - N_{CO_2} plane.

Figure 9: Variation of $K_{H_2S} = y_{H_2S}/x_{H_2S}$ as a function of the C parameter at 41.3 bar. EWL results are shown as a line, while experimental data [72] are shown as filled circles.

define the parameter C as the ratio of the mole fraction CO_2 to the sum of the mole fraction CO_2 plus CH_4 in the vapor phase). We then calculate the ratio of the mole fractions in H_2S in the two coexisting phases, i.e. $K_{H_2S} = y_{H_2S}/x_{H_2S}$, and plot this ratio as a function of the C parameter in Fig. 9 (we also provide a comparison between the experimental data and the EWL results for the mole fractions at coexistence in Table 3). This plot shows that the results obtained in the EWL simulations for the ternary mixture are in good agreement with the experimental data (within 0.02 for the K_{H_2S} ratio).

4. Conclusions

In this work, we have developed a new force field for H_2S , based on an exp-6 functional form for the dispersion-repulsion. Taking advantage of the EWL simulation method which allows to calculate a wide range of properties from a single simulation run, we have tested this force field against the available experimental data and shown that the force field models accurately the properties of single component systems of H_2S . We have then used this force field, together with existing, exp-6 based, force fields for CH_4 and CO_2 , to

Table 3: $H_2S - CH_4 - CO_2$ ternary mixture: vapor (y_{H_2S} , y_{CO_2} and y_{CH_4}) and liquid (x_{H_2S} , x_{CO_2} and x_{CH_4}) compositions for different values for the parameter C .

	C	y_{H_2S}	y_{CO_2}	y_{CH_4}	x_{H_2S}	x_{CO_2}	x_{CH_4}
Experiment ⁷²	0	0.710	0.000	0.290	0.966	0.000	0.034
This work	0.04	0.73	0.01	0.26	0.98	0.00	0.02
Experiment ⁷²	0.2	0.690	0.063	0.247	0.952	0.020	0.028
This work	0.21	0.72	0.06	0.22	0.97	0.01	0.02
Experiment ⁷²	0.4	0.680	0.128	0.192	0.930	0.050	0.020
This work	0.37	0.72	0.10	0.18	0.96	0.03	0.01
Experiment ⁷²	0.8	0.640	0.288	0.072	0.876	0.116	0.008
This work	0.83	0.65	0.29	0.06	0.91	0.09	0.00

model the vapor-liquid equilibria of binary and ternary mixtures. While the $H_2S - CH_4$ mixture was accurately modeled with the standard LB rules, no combining rules were found to perform well for the $H_2S - CO_2$ mixture and an optimization of the parameters for the unlike interactions was also carried out. Finally, the resulting force field gave results in good agreement with the experiment when applied to the ternary mixture $H_2S - CH_4 - CO_2$.

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References

- [1] Y. Belmabkhout, G. De Weireld and A. Sayari, *Amine-bearing mesoporous silica for CO_2 and H_2S removal from natural gas and biogas*, Langmuir 25, 13275-13278 (2009).
- [2] H. Lin, E. Van Wagner, R. Raharjo, B. D. Freeman and I. Roman, *High-Performance Polymer Membranes for Natural-Gas Sweetening*, Advanced Materials 18, 39-44 (2006).
- [3] J. Vaughn and W. J. Koros, *Effect of the Amide Bond Diamine Structure on the CO_2 , H_2S , and CH_4 Transport Properties of a Series of Novel*

- 6FDA-Based Polyamide-Imides for Natural Gas Purification*, *Macromolecules* 17, 7036-7049 (2012).
- [4] R. Cheng, W. Zhou, L. Lin, T. Xie and Y. Zhang, *Removal of high concentrations of H_2S from simulated natural gas by *Acidithiobacillus ferrooxidans* immobilized on polyurethane foam*, *Journal of Chemical Technology and Biotechnology* 88, 975-978 (2013).
  - [5] C. Ratnasamy, J. P. Wagner, S. Spivey and E. Weston, *Removal of sulfur compounds from natural gas for fuel cell applications using a sequential bed system*, *Catalysis Today* 198, 233-238 (2012).
  - [6] S. Kumar, W. Lim, K. Choi and I. Moon, *Removal of CO_2 and H_2S from natural gas: an amine solution and ionic liquids approach*, *Theory and Applications of Chemical Engineering* 17, 141 (2011).
  - [7] A. Chapoy, C. Coquelet, H. Liu, A. Valtz and B. Tohidi, *Vapour-liquid equilibrium data for the hydrogen sulphide (H_2S) + carbon dioxide (CO_2) system at temperatures from 258 to 313K*, *Fluid Phase Eq.* 356, 223-228 (2013).
  - [8] Y. Liu, A.Z. Panagiotopoulos and P. G. Debenedetti, *Monte Carlo Simulations of High-Pressure Phase Equilibria of CO_2 - H_2O Mixtures*, *J. Phys. Chem. B* 115, 6629-6635 (2011).
  - [9] R. H. Socolow, *Can we bury global warming?*, *Scientific American* 293, 49-55 (2005).
  - [10] D. J. Depaolo and F. M. Orr Jr, *Geoscience research for our energy future*, *Physics Today* 61, 46-51 (2008).
  - [11] C. Desgranges and J. Delhommelle, *Evaluation of the grand-canonical partition function using expanded Wang-Landau simulations. I. Thermodynamic properties in the bulk and at the liquid-vapor phase boundary*, *J. Chem. Phys.* 136, 184107 (2012).
  - [12] C. Desgranges and J. Delhommelle, *Evaluation of the grand-canonical partition function using expanded Wang-Landau simulations. II. Adsorption of atomic and molecular fluids in a porous material*, *J. Chem. Phys.* 136, 184108 (2012).

- [13] C. Desgranges and J. Delhommelle, *Evaluation of the grand-canonical partition function using expanded Wang-Landau simulations. III. Impact of combining rules on mixtures properties*, J. Chem. Phys. 136, 104109 (2014).
- [14] D. A. McQuarrie, *Statistical Mechanics*, Harper & Row, New York (1976).
- [15] F.G. Wang and D.P. Landau, *Determining the density of states for classical statistical models: A random walk algorithm to produce a flat histogram*, Phys. Rev. E 64, 056101 (2001).
- [16] F.G. Wang and D.P. Landau, *Efficient Multiple Range Random Walk Algorithm to Calculate Density of States*, Phys. Rev. Lett. 86, 2050 (2001).
- [17] J.J. de Pablo, Q. Yan, and R. Faller, *Density-of-states Monte Carlo method for simulation of fluids*, J. Chem. Phys. 116, 8649 (2002).
- [18] M.S. Shell, P.G. Debenedetti, and A.Z. Panagiotopoulos, *An improved Monte Carlo method for direct calculation of the density of states*, J. Chem. Phys. 119, 9406 (2003).
- [19] M.S. Shell, P.G. Debenedetti, and A.Z. Panagiotopoulos, *Generalization of the Wang-Landau method for off-lattice simulations*, Phys. Rev. E 66, 056703 (2002).
- [20] M.S. Shell, P.G. Debenedetti, and A.Z. Panagiotopoulos, *Flat-histogram dynamics and optimization in density of states simulations of fluids*, J. Phys. Chem. B 108, 19748-19755 (2004).
- [21] J. Luettmmer-Strathmann, F. Rampf, W. Paul, and K. Binder, *Transitions of tethered polymer chains: A simulation study with the bond fluctuation lattice model*, J. Chem. Phys. 128, 064903 (2008).
- [22] G. Gazenmuller and P.J. Camp, *Applications of Wang-Landau sampling to determine phase equilibria in complex fluids*, J. Chem. Phys. 127, 154104 (2007).
- [23] C. Desgranges and J. Delhommelle, *Phase equilibria of molecular fluids via hybrid Monte Carlo Wang-Landau simulations: Applications to benzene and n-alkanes*, J. Chem. Phys. 130, 244109 (2009).

- [24] T. Aleksandrov, C. Desgranges, and J. Delhommelle, *Vapor-liquid equilibria of Copper using Hybrid Monte Carlo Wang-Landau Simulations*, Fluid Phase Eq. 287, 79 (2010).
- [25] C. Desgranges, E.A. Kastl, T. Aleksandrov, and J. Delhommelle, *Optimisation of multiple time-step hybrid Monte Carlo Wang-Landau simulations in the isobaric-isothermal ensemble for the determination of phase equilibria*, Molec. Simul. 36, 544-551(2010).
- [26] C. Desgranges, J.M. Hicks, A. Magness, and J. Delhommelle, *Phase equilibria of polycyclic aromatic hydrocarbons by hybrid Monte Carlo Wang-Landau simulations*, Mol. Phys. 108, 151-158 (2010).
- [27] C. Desgranges, K. Ngale, and J. Delhommelle, *Prediction of critical properties for Naphthalene, Triphenylene and Chrysene by Wang-Landau simulations*, Fluid Phase Eq. 322-323, 92-96 (2012).
- [28] K.N. Ngale, C. Desgranges, and J. Delhommelle, *Wang-Landau configurational bias Monte Carlo simulations: vapour-liquid equilibria of alkenes*, Molec. Simul. 38, 653-658 (2012).
- [29] T. Aleksandrov, C. Desgranges, and J. Delhommelle, *Numerical estimate for boiling points via Wang-Landau simulations*, Molec. Simul. 38, 1265-1270 (2012).
- [30] A.P. Lyubartsev, A.A. Martsinovski, S.V. Shevkunov, and P.N. Vorontsov-Velyaminov, *New approach to Monte Carlo calculation of the free energy: Method of expanded ensembles*, J. Chem. Phys. 96, 1776-1783 (1992).
- [31] F. Escobedo and J.J. de Pablo, *Expanded grand canonical and Gibbs ensemble Monte Carlo simulation of polymers*, J. Chem. Phys. 105, 4391 (1996).
- [32] C.R.A. Abreu and F.A. Escobedo, *A general framework for non-Boltzmann Monte Carlo sampling*, J. Chem. Phys. 124, 054116 (2006).
- [33] F.A. Escobedo and F.J. Martinez-Veracoechea, *Optimization of expanded ensemble methods*, J. Chem. Phys. 129, 154107 (2008).

- [34] W. Shi and E.J. Maginn, *Continuous fractional component Monte Carlo: An adaptive biasing method for open system atomistic simulations*, J. Chem. Theory Comp. 3, 1451-1463 (2007).
- [35] M. Muller and W. Paul, *Measuring the chemical potential of polymer solutions and melts in computer simulations*, J. Chem. Phys. 100, 719 (1994).
- [36] J.K. Singh and J.R. Errington, *Calculation of Phase Coexistence Properties and Surface Tensions of n-Alkanes with Grand-Canonical Transition-Matrix Monte Carlo Simulation and Finite-Size Scaling*, J. Phys. Chem. B 110, 1369 (2006).
- [37] A.S. Paluch, V.K. Shen, and J.R. Errington, *Comparing the use of Gibbs ensemble and grand-canonical transition-matrix Monte Carlo methods to determine phase equilibria*, Industrial & Engineering Chemistry Research 47, 4533-4541(2008).
- [38] K.S. Rane, S. Murali, and J.R. Errington, *Monte Carlo simulation methods for computing liquid-vapor saturation properties of model systems*, J. Chem. Theory Comp. 9, 2552-2566 (2013).
- [39] C. Desgranges and J. Delhommelle, *Thermodynamics of Phase Coexistence and Metal-Nonmetal Transition in Mercury: Assessment of Effective Potentials via Expanded Wang-Landau Simulations*, J. Phys. Chem. B 118, 3175-3182 (2014).
- [40] J.M. Hicks, C. Desgranges, and J. Delhommelle, *Characterization and Comparison of the Performance of IRMOF-1, IRMOF-8 and IRMOF-10 for CO₂ Adsorption in the Subcritical and Supercritical Regimes*, J. Phys. Chem. C. 116, 22938-22946 (2012).
- [41] A. R. V. Koenig, C. Desgranges and J. Delhommelle, *Adsorption of hydrogen in covalent organic frameworks using expanded Wang-Landau simulations*, Molec. Simul. 40, 71-79 (2014).
- [42] E. Hicks, C. Desgranges and J. Delhommelle, *Adsorption and diffusion of the antiparkinsonian drug amantadine in carbon nanotubes*, Molec. Simul. 40, 656-663 (2014).

- [43] J. R. Errington, G. C. Boulougouris, I. G. Economou, A. Z. Panagiotopoulos and D. N. Theodorou, *Molecular simulation of phase equilibria for water-methane and water-ethane mixtures*, J. Phys. Chem. B 102, 8865-8873 (1998).
- [44] J. R. Errington and A. Z. Panagiotopoulos, *A fixed point charge model for water optimized to the vapor-liquid coexistence properties*, J. Phys. Chem. B 102, 7470-7475 (1998).
- [45] J. R. Errington and A. Z. Panagiotopoulos, *A new intermolecular potential model for the n-alkane homologous series*, J. Phys. Chem. B 103, 6314-6322 (1999).
- [46] T. R. Forester and I. R. McDonald, *Intermolecular Potentials and the Properties of Liquid and Solid Hydrogen Sulphide*, Chem. Phys. 129, 225-234 (1989).
- [47] T. Kristóf and J. Liszi, *Effective intermolecular potential for fluid hydrogen sulfide*, J. Phys. Chem. B 101, 5480-5483 (1997).
- [48] J. Delhommelle, P. Millie and A. H. Fuchs, *On the role of the definition of potential models in Gibbs ensemble phase equilibria simulations of the H₂S-pentane mixture*, Mol. Phys. 98, 1895-1905 (2000).
- [49] J. Vorholz, B. Rumpf and G. Maurer, *Prediction of the vapor-liquid phase equilibrium of hydrogen sulfide and the binary system water-hydrogen sulfide by molecular simulation*, Phys. Chem. Chem. Phys. 4, 4449-4457 (2002).
- [50] S. K. Nath, *Molecular simulation of vapor-liquid phase equilibria of hydrogen sulfide and its mixtures with alkanes*, J. Phys. Chem. B 107, 9498-9504 (2003).
- [51] W. Lin, Q. Yang and C. Zhong, *Molecular simulation of vapor-liquid equilibria of toxic gases*, Fluid Phase Eq. 220, 1-6 (2004).
- [52] G. Kamath, N. Lubna and J. J. Potoff, *Effect of partial charge parametrization on the fluid phase behavior of hydrogen sulfide*, J. Chem. Phys. 123, 124505 (2005).

- [53] G. Kamath and J. J. Potoff, *Monte Carlo predictions for the phase behavior of $H_2S + n$ -alkane, $H_2S + CO_2$, $CO_2 + CH_4$ and $H_2S + CO_2 + CH_4$ mixtures*, Fluid Phase Eq. 246, 71-78 (2006).
- [54] R. Hellmann, E. Bich, E. Vogel and V. Vesovic, *Ab initio intermolecular potential energy surface and thermophysical properties of hydrogen sulfide*, Phys. Chem. Chem. Phys. 13, 13749-13758 (2011).
- [55] S. Riahi and C. N. Rowley, *A Drude polarizable model for liquid hydrogen sulfide*, J. Phys. Chem. B 117, 5222-5229 (2013).
- [56] Gutiérrez-Sevillano, Juan José and Martín-Calvo, Ana and Dubbeldam, David and Calero, Sofía and Hamad, Said, *Adsorption of hydrogen sulphide on Metal-Organic Frameworks*, RSC Advances 3, 14737-14749 (2013).
- [57] J. Delhommelle, A. Boutin and A. H. Fuchs, *Molecular simulation of vapour-liquid coexistence curves for hydrogen sulfide-alkane and carbon dioxide-alkane mixtures*, Molec. Simul. 22, 351-368 (1999).
- [58] P. Ungerer, A. Wender, G. Demoulin, E. Bourasseau and P. Mougin, *Application of Gibbs ensemble and NPT Monte Carlo simulation to the development of improved processes for H_2S -rich gases*, Molec. Simul. 30, 631-648 (2004).
- [59] G. Galliero, C. Nieto-Draghi, C. Boned, J. B. Avalos, A. D. Mackie, A. Baylaucq and F. Montel, *Molecular dynamics simulation of acid gas mixtures: A comparison between several approximations*, Industrial & engineering chemistry research 46, 5238-5244 (2007).
- [60] J.-C. Neyt, A. Wender, V. Lachet and P. Malfreyt, *Modeling the Pressure Dependence of Acid Gas+ n -Alkane Interfacial Tensions Using Atomistic Monte Carlo Simulations*, J. Phys. Chem. C 116, 10563-10572 (2012).
- [61] J. Delhommelle and P. Millie, *Inadequacy of the Lorentz-Berthelot combining rules for accurate predictions of equilibrium properties by molecular simulation*, Mol. Phys. 99, 619-625 (2001).

- [62] C. L. Kong, *Combining Rules for Intermolecular Potential Parameters. II. Rules for the Lennard-Jones (12-6) potential and the Morse Potential*, J. Chem. Phys. 59, 2464-2467 (1973).
- [63] M. Waldman and A. T. Hagler, *New Combining Rules for rare gas van der Waals parameters*, J. Comput. Chem. 14, 1077-1084 (1993).
- [64] R. Goodwin, *NBS Report No. NBSIR 83-1694*, p. 175 (1983).
- [65] H. E. Stanley, *Introduction to phase transitions and critical phenomena*, Oxford University Press: New York (1971).
- [66] J. S. Rowlinson and F. L. Swinton, *Liquids and liquid mixtures*, Butterworths: London (1982).
- [67] J. Delhommelle, A. Boutin, B. Tavitian, A. D. Mackie and A. H. Fuchs, *Vapour-liquid coexistence curves of the united-atom and anisotropic united-atom force fields for alkane mixtures*, Mol. Phys. 96, 1517-1524 (1999).
- [68] P. Ungerer, C. Beauvais, J. Delhommelle, A. Boutin, B. Rousseau and A. H. Fuchs, *Optimization of the anisotropic united atoms intermolecular potential for n-alkanes*, J. Chem. Phys. 112, 5499 (2000).
- [69] J. Delhommelle, C. Tschirwitz, P. Ungerer, G. Granucci, P. Millie, D. Pattou and A. H. Fuchs, *Derivation of an optimized potential model for phase equilibria (OPPE) for sulfides and thiols*, J. Phys. Chem. B 104, 4745 (2000).
- [70] H. H. Reamer, B. H. Sage, W. N. Lacey, *Phase Equilibria in Hydrocarbon Systems-Volumetric and Phase Behavior of the Methane-Hydrogen Sulfide System*, Industrial & Engineering Chemistry 43, 976-981 (1951)
- [71] J. A. Bierlein and W. B. Kay, *Phase-Equilibrium Properties of System Carbon Dioxide+Hydrogen Sulfide*, Industrial & Engineering Chemistry 45, 618-624 (1953)
- [72] D. B. Robinson and J. A. Bailey, *The Carbon Dioxide-Hydrogen Sulphide-Methane System. Part I: Phase Behavior at 100°F*, Industrial & Engineering Chemistry 45, 618-624 (1953)