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Chemical potentials of water, methanol, carbon dioxide and hydrogen sulphide at low temperatures using continuous fractional component Gibbs ensemble Monte Carlo

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ABSTRACT

Chemical potentials of coexisting gas and liquid phases for water, methanol, hydrogen sulphide and carbon dioxide for the temperature range $T = 220$ K to $T = 375$ K are computed using two different methodologies: (1) Widom's test particle insertion (WTPI) method in the conventional Gibbs Ensemble (GE), and (2) the Continuous Fractional Component Gibbs Ensemble Monte Carlo (CFCGE MC) method. It is shown that the WTPI method fails to accurately compute the chemical potentials of water and methanol in the liquid phase at low temperatures, while accurate chemical potentials in the liquid phase are computed using CFCGE MC method. For the CFCGE MC method, the statistical uncertainty for computed chemical potentials of water and methanol in the liquid phase are considerably smaller compared to the WTPI method. For the water models considered in this study (SPC, TIP3P-EW, TIP4P-EW, TIP5P-EW), computed excess chemical potentials based on three-site models are in better agreement with the chemical potentials computed from an empirical equation of state from the NIST database. For water, orientational biasing is applied during test particle insertion to check whether certain orientations of test particle are energetically unfavourable. A two-dimensional Overlapping Distribution Method (ODM) in the NVT ensemble is derived for this purpose. It is shown that failure of the WTPI method for systems with a strong hydrogen bonding network does not depend on orientation of the test molecule in that system. For all systems in this study, the WTPI method breaks down when the void fraction of the system drops below approximately 0.50.

1. Introduction

In the past century, different molecular simulation methods have been developed to compute equilibrium and transport properties of fluids primarily by Molecular Dynamics (MD) techniques, or by sampling phase-space using Monte Carlo (MC) simulations [1–3]. Many thermodynamic properties such as the density and pressure of a system are straightforward to compute [4–7]. The Gibbs Ensemble (GE) was introduced by Panagiotopoulos in 1987 to compute the coexistence densities and simulate VLE of pure components and mixtures of different components [4,8]. Computing the correct coexistence densities in the conventional GE depends on efficient molecule exchange between the boxes. At high densities, successful molecule insertions depend strongly on occurrence of spontaneous cavities large enough to accommodate the inserted molecule. As a result of rare occurrence of such cavities at high densities, GE simulations suffer from low acceptance probabilities for molecule insertions. For a discussion on the accuracy and efficiency of the GE, the reader is referred to studies by Siepmann and co-workers [7,9,10].

The coexistence properties of gas and liquid in the GE can be sampled when the chemical equilibrium between the phases is reached, which requires equal chemical potentials of each component, equal pressures, and equal temperatures in both phases. Hence, studying VLE of pure components or mixtures of different components requires knowledge of free energies to satisfy the condition of chemical equilibrium [6,8,11,12]. Likewise, knowledge of the chemical potential plays an important role in understanding processes such as chemical reactions, diffusion, phase transitions, mass transfer and the direction in which these processes take place[13–15]. However, the calculation of free energies has turned out to be much more difficult [16,17] compared to other properties such as density or pressure. Different methods for computing free energies such as thermodynamic integration[18], perturbation theory [19], expanded ensembles [20–22] and histogram reweighting methods have been developed and thoroughly reviewed in literature [21,23]. Widom's Test Particle Insertion (WTPI) method [24] is the most commonly used method for determining chemical potentials by sampling the interaction energy of a test molecule inserted at a randomly selected position in the system. It is well known that WTPI method breaks down at high densities because of frequent overlaps between the test molecule and the molecules within the system [25–27]. Since spontaneous cavities large enough to fit a test molecule are less likely to occur in high-density phases, it renders the WTPI method inefficient or essentially useless [3,13,24,28] for computing chemical potentials.

Coskuner et al. have used the WTPI method to compute, among other properties, the chemical potential of TIP5P water in the temperature range of $T = 300\,\text{K}$ to $T = 320\,\text{K}$ in the *NPT* ensemble [29]. However, the chemical potentials are not in agreement with the experimental Equation of State (EoS) [30,31]. This deviation may stem from either inefficiency of the WTPI method at low temperatures [25–27], or the hydrogen bonding network of water. Other reasons may include inefficiency of the simulations or a force field limitation. To identify the underlying reason and criterion for the limitations of the WTPI method, we have chosen to simulate the VLE of four different components in the GE with similar coexistence liquid densities, namely water and methanol (with a hydrogen bonding network), and hydrogen sulphide and carbon dioxide (without a hydrogen bonding network). To study the role of different models, we have used several force fields for water and methanol: SPC,[32] TIP3P-EW [33], TIP4P-EW [34] and TIP5P-EW [35]) water, OPLS and TraPPE methanol [36,37], hydrogen sulphide [38] and TraPPE carbon dioxide [39].

Number densities and void fractions of all systems in this work are compared as it may provide a criterion for limitation of the WTPI method. As an independent check, the Overlapping Distribution Method (ODM) is used in the *NVT* ensemble [3, 40] to check the reliability of the WTPI results at different system temperatures. As water has a strong hydrogen bonding network, a two-dimensional ODM in the *NVT* ensemble is used to test if certain orientations of the test molecule inside the hydrogen bonding network of water lead to inefficiency/failure of the WTPI method. In this method, different number of hydrogen bonds between the test molecule and its surrounding molecules corresponds to different orientations of the test molecule.

Molecule exchanges in the GE simulations can become quite inefficient at low temperatures which may result in densities far from equilibrium leading to erroneous chemical potentials. To solve the inefficiency of molecule exchange in the GE at high densities, Shi and Maginn [21,22] developed a method based on the idea of the expanded ensembles, in which molecules are inserted/removed in a gradual manner. This method is called the Continuous Fractional Component Monte Carlo [5, 21,22,41]. Using this method, the GE is expanded with two fractional molecules per component (one in each simulation box). Interactions of the fractional molecule are scaled by a coupling parameter λ. When $\lambda = 0$, the fractional molecule has no interaction with the surroundings and behaves as an ideal gas. The fractional molecule has fully scaled interactions at $\lambda = 1$ and behaves as other molecules in the system. The fractional molecule is gradually inserted or removed by slowly changing λ. Although this method has been proven to considerably improve the molecule exchange efficiency compared to the conventional GE, it does not allow computing the chemical potential of each phase directly. Poursaeidesfahani et al. have recently developed a more efficient alternative of the CFCMC technique [41] in the GE. The crucial difference between this method and the original implementation of Maginn and co-workers is that a single fractional molecule per component is used. The main advantages of our formulation of the Continuous Fractional Component Gibbs Ensemble Monte Carlo (CFCGE MC) are direct and efficient calculation of chemical potential and more efficient molecule exchange. In addition to the conventional

volume changes and thermal equilibration trial moves, three new types of trial moves specific to the fractional molecule are used in this method. These are explained briefly in Section 2.

This paper is organised as follows. In Section 2, the relevant equations used for sampling the chemical potentials using the WTPI method in the GE and the CFCGE MC method are provided, and the differences between the two methods are explained. Additionally, equations for the conventional ODM using orientational biasing and the two-dimensional ODM are presented and explained. Void fractions of every component are also defined and tabulated at different temperatures. Simulation details are provided in Section 3. Our findings are presented in Section 4. Our results show that computing chemical potential using the WTPI method becomes quite inefficient for systems with a void fraction smaller than 0.5, while the CFCGE MC method does not have this limitation and is more efficient at high densities. Our conclusions are summarised in Section 5.

2. Methodology

An expression for the average chemical potential in the GE was first derived by Smit and Frenkel [3,42]. The computation of chemical potential for a pure component in the GE is based on the original WTPI method[43], taking into account the fluctuations in the volume and the number of molecules in box i:

$$\mu_{i,\,\text{GE}} = -k_{\text{B}} T \ln \left\langle \frac{V_i/\Lambda^3}{N_i + 1} \exp\left[-\beta \Delta U_i^+\right] \right\rangle \qquad (1)$$

$\beta = 1/(k_{\text{B}} T)$ in which k_{B} is the Boltzmann constant and T is the temperature of the system. ΔU_i^+ is the interaction energy of the test molecule with the rest of the molecules in box i. Λ is the thermal wavelength, V_i and N_i are the volume and number of molecules of box i, respectively. Due to overlaps between the test molecule and the existing molecules in a system, the potential energy change (ΔU_i^+) of the trial insertion move can become infinitely large ($\Delta U_i^+ \rightarrow +\infty$), and the corresponding Boltzmann factor becomes almost equal to zero. Since the majority of trial insertions in a dense liquid phase contribute to almost zero statistical weight, the chemical potential computed using Equation (1) may be questionable and has a typically large uncertainty in high-density phases.

To circumvent the potential sampling problems of the WTPI method, Shing and Gubbins [26,44] have proposed an alternative way of obtaining chemical potential by combining particle insertions and removals. Similarly, Bennett [40] has introduced the ODM which is used in this work as an independent check to verify the validity of the WTPI method at different system densities/void fractions. In the ODM, two separate simulations in the *NVT* ensemble based on the coexistence densities from GE simulations are performed for two separate systems 0 and 1 with N and $N + 1$ particles, respectively. Here, the volumes of systems 0 and 1 are assumed to be the same, but this is not essential [3]. It is shown that the excess chemical potential of system 0 equals [3]

$$\mu^{\text{ex}} = f_1\left(\Delta U\right) - f_0\left(\Delta U\right) \qquad (2)$$

The functions $f_0(\Delta U)$ and $f_1(\Delta U)$ are defined as

$$
\begin{aligned}
f_0\left(\Delta U\right) &= RT\left[\ln p_0\left(\Delta U\right)\right] - \frac{\Delta U}{2} \\
f_1\left(\Delta U\right) &= RT\left[\ln p_1\left(\Delta U\right)\right] + \frac{\Delta U}{2}
\end{aligned}
\tag{3}
$$

Here, $1/\beta$ is written as RT since all chemical potentials and energies are reported in [kJ.mol^{-1}]. ΔU is the potential energy difference between systems 0 and 1. $p_0(\Delta U)$ is the probability distribution for the potential energy difference ΔU between system 0 and 1 while sampling configurations in system 0. The same definition applies for $p_1(\Delta U)$ in system 1. Since the ODM combines insertion and removal trial moves, it offers a better estimate of the chemical potential compared to the WTPI method [3]. For systems with a strong hydrogen bonding network like water, the interaction energies of the test molecules may not only depend on their positions, but also on the orientations with respect to the hydrogen bonding network. The number of hydrogen bonds the test molecule forms with its adjacent molecules is related to the orientation of the test molecule. A geometrical definition [45–50] was used to count the number of hydrogen bonds between water molecules as shown in the Supporting Information. Using this geometric definition, the computed average number of hydrogen bonds for the TIP4P-EW water model in the NVT ensemble was in excellent agreement with literature [50] between $T = 300\,\text{K}$ and $T = 600\,\text{K}$. The results are shown in the Supporting Information.

To study the hydrogen bonding network of water and its effect on the performance of the WTPI method, a two-dimensional ODM is derived by introducing the number of hydrogen bonds (H) as a second (integer) variable. The two-dimensional ODM can check the validity of the WTPI method for different numbers of formed hydrogen bonds between test molecule and its surrounding water molecules. If orientational biasing is included as part of the test molecule insertion and removal, the energy difference $-\beta \Delta U$ in Equations (2) and (3) should be replaced by the logarithm of the Rosenbluth weight of the test molecule [51–55]. The functions f_1 and f_0 in the two-dimensional ODM including orientational biasing become [51,52]

$$
\begin{aligned}
f_0\left(W, H\right) &= RT\left[\ln p_0\left(\ln W\right) + \frac{\ln W}{2}\right] \\
f_1\left(W, H\right) &= RT\left[\ln p_1\left(\ln W\right) - \frac{\ln W}{2}\right]
\end{aligned}
\tag{4}
$$

H is the number of hydrogen bonds between the test molecule (in the trial insertions or trial removals) and its surrounding water molecules. The derivation of Equation (4) is provided in the Supporting Information. The excess chemical potential for a given number of hydrogen bonds H equals

$$
\mu^{\text{ex}}\left(H\right) = f_1\left(W, H\right) - f_0\left(W, H\right)
\tag{5}
$$

In an attempt to quantify the limit at which the WTPI method breaks down, the number density and void fraction of all systems in this work are compared and shown in Table 1. The number density is defined as

$$
\rho_N = \frac{N}{V}
\tag{6}
$$

The void fraction (ϕ) is defined as

$$
\phi = 1 - \rho_N \cdot V_{\text{mol}}
\tag{7}
$$

V_{mol} is the volume of the molecular model. To compute the volume, each interaction site in the molecule is considered to be a sphere with diameter σ. Therefore, the volume of a molecule with k interaction sites equals the sum of the volumes of all spheres minus the intersection volume between the spheres

$$
V_{\text{mol}} = \sum_{i=1}^{k} \frac{4}{3}\pi\left(\sigma/2\right)^3 - V_{\text{intersection}}
\tag{8}
$$

$V_{\text{intersection}}$ is the total intersection volume between the spheres. The value of σ of each molecule type can be found in the force field data in the Supporting Information.

To make sure that the VLE is reached in GE simulations, independent simulations are also performed using our formulation of the CFCGE MC method which has a more efficient molecule exchange [41] and allows for direct computation of the chemical potential. The molecule swap trial move in the GE is replaced by three types of trial moves to facilitate molecule exchange between the simulation boxes in the CFCGE MC method. (1): swapping the fractional molecule to a randomly selected position in the other simulation box; (2): changing the value of scaling parameter λ while the fractional molecule stays at the same position; (3): changing the identity of the fractional molecule with a whole molecule in the other box while keeping the scaling parameter and positions fixed. Figure 1 shows a schematic representation of these types of trial moves. The acceptance rules of these moves are derived in detail in the original paper [41]. It is shown there that by sampling the probability of λ approaching zero and one in each simulation box, one can compute the chemical potential as an ensemble average without any additional post processing. The chemical potentials obtained in the CFCGE MC are identical to those in the conventional GE [41]. The chemical potential for a single component in box i in the CFCGE MC equals

$$
\mu_{i,\,\text{CFCGE MC}} = -k_\text{B}T \ln\left\langle \frac{V_i/\Lambda^3}{N_i + 1}\right\rangle - k_\text{B}T \ln\left\langle \frac{p_i\left(\lambda \uparrow 1\right)}{p_i\left(\lambda \downarrow 0\right)}\right\rangle
\tag{9}
$$

$p_i(\lambda \uparrow 1)$ and $p_i(\lambda \downarrow 0)$ are the probability of λ approaching one and zero in box i.

3. Simulation details

To compute the chemical potential of liquid and gas phases of water, methanol, and carbon dioxide, at equilibrium, MC simulations in the temperature range of $T = 210\,\text{K}$ to $T = 375\,\text{K}$ are performed in the CFCGE MC and GE.

All simulations are performed using the RASPA software package[56,57]. The chemical potentials are computed directly in the CFCGE MC simulations (Equation (9)). In the conventional GE, the WTPI method is used to compute the chemical potential of both phases (Equation (1)). Using the coexistence density of the liquid phase from GE simulations, the ODM in the NVT ensemble is performed to check independently at which densities the WTPI method breaks down. Four different rigid water models (SPC [32,58], TIP3P-EW [33], TIP4P-EW[34] and TIP5P-EW [35]) were used for this study. Rigid methanol OPLS-UA [36] and flexible TraPPE force fields were selected for

Table 1. Number densities and void fractions of carbon dioxide, hydrogen sulphide, methanol and water in the coexisting liquid phase at different temperatures.

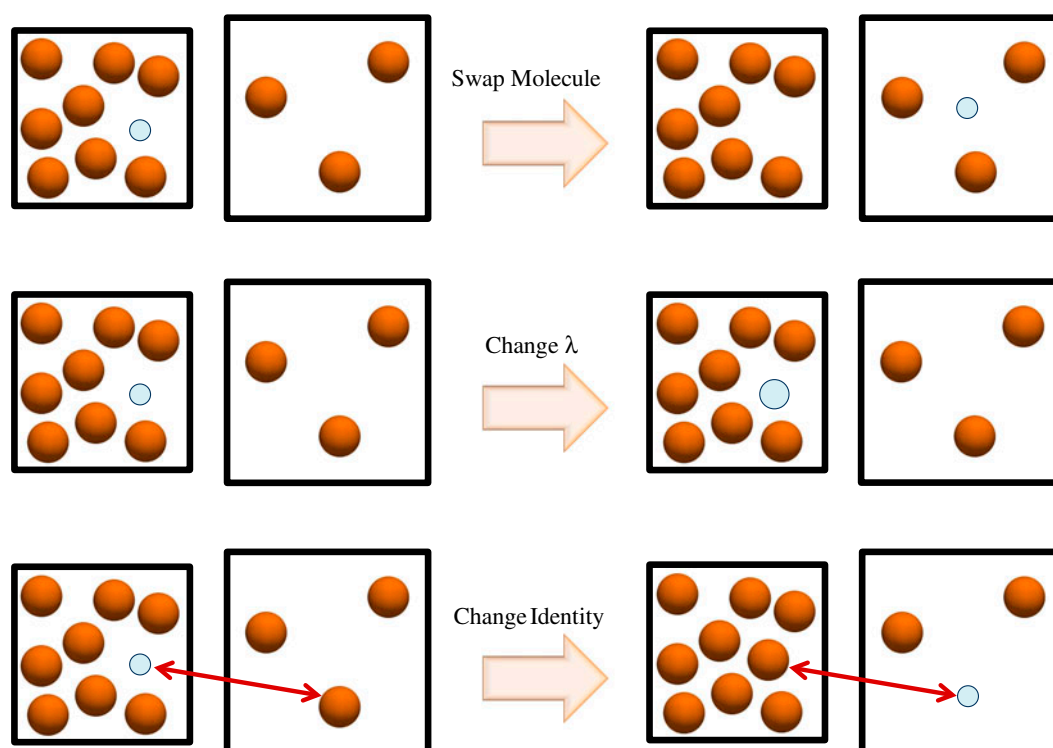| T/[K]	ρ_n/[n·Å^{-3}]	ϕ/[-]
	CO$_2$	
220	0.0160	0.51
230	0.0153	0.52
240	0.0150	0.54
250	0.0143	0.55
	H$_2$S	
210	0.0167	0.54
230	0.0160	0.56
250	0.0155	0.57
	CH$_3$OH	
240	0.0158	0.44
270	0.0152	0.46
300	0.0147	0.48
350	0.0138	0.51
	H$_2$O	
300	0.0332	0.44
325	0.0327	0.45
350	0.0322	0.46

Figure 1. (Colour online) MC trial moves facilitating molecule exchange in the CFCGE MC simulations [41]. The coupling parameter λ scales the interactions of the fractional molecule with its surroundings. In this figure, the fractional molecule is marked with a line. These types of trial moves are: (Swap Move): the fractional molecule is randomly moved from one box to a randomly selected position in the other box, while keeping the value of λ constant. (Change λ): random change of the coupling parameter λ keeping the position of the fractional molecule constant. Trial moves that result in $\lambda < 0$ or $\lambda > 1$ are automatically rejected. (Change Identity): trial move to change the fractional molecule into a whole molecule and changing a randomly selected whole molecule in the other box into the fractional molecule, while keeping all positions fixed. For more details about the CFCGE MC method and the acceptance rules the reader is referred to the original publication [41].

methanol [37]. For carbon dioxide, TraPPE force field parameters were used [38]. Details about the force field parameters, truncation of intermolecular potentials, and tail corrections are provided in the Supporting Information. For all water models 10^5 equilibration cycles were carried out followed by $2.3 \cdot 10^6$ MC cycles. For methanol, carbon dioxide models $2 \cdot 10^5$ equilibration cycles were carried out followed by $1.2 \cdot 10^6$ MC cycles. Each MC cycle in RASPA consists of N Monte Carlo trial moves, where N equals the number of molecules. The Wang-Landau algorithm

[59,60] was used to compute the weight function in the CFCGE MC simulations.

For CFCGE MC, trial moves were selected with the following probabilities: probability of volume exchange between the boxes: 1.0%. The rest of the trial moves were selected with an equal probability of 19.8% including: translation, rotation, swap molecules, change value of lambda and change identity trial move. No biasing was used for molecule insertions or deletions using CFCGE MC. However, it is possible to combine orien-
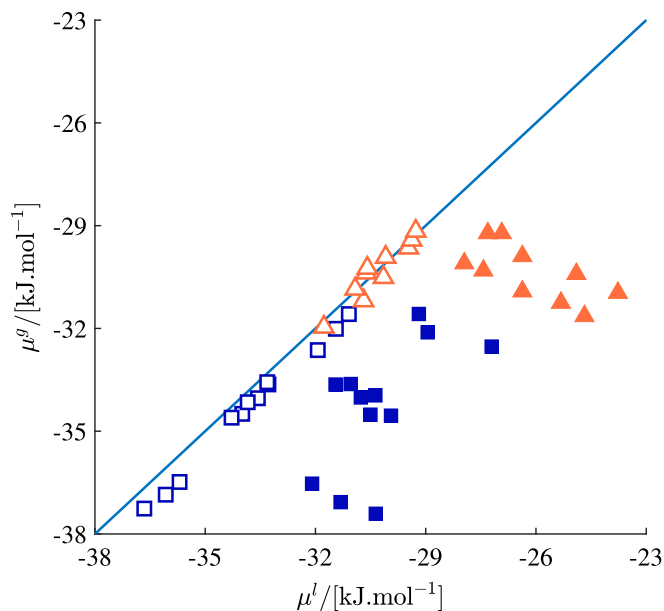
Figure 2. (Colour online) Comparison of chemical potentials of gas and liquid phases using the CFCGE MC method and the WTPI method in GE. □: computed chemical potentials of water SPC, TIP3P-EW and TIP4P-EW models using the CFCMC GE method, △: computed chemicals potential of methanol models OPLS-UA and TraPPE using CFCGE MC method, ■: computed chemical potentials of water SPC, TIP3P-EW and TIP4P-EW models using the WTPI method, and ▲: computed chemical potentials of the methanol models OPLS-UA and TraPPE using the WTPI method. The line is a guide to the eye to indicate the equal chemical potentials between the gas and liquid phase at coexistence. Error bars are smaller than symbol sizes. The raw data are listed in tables S1, S2 and S5 in the Supporting Information.
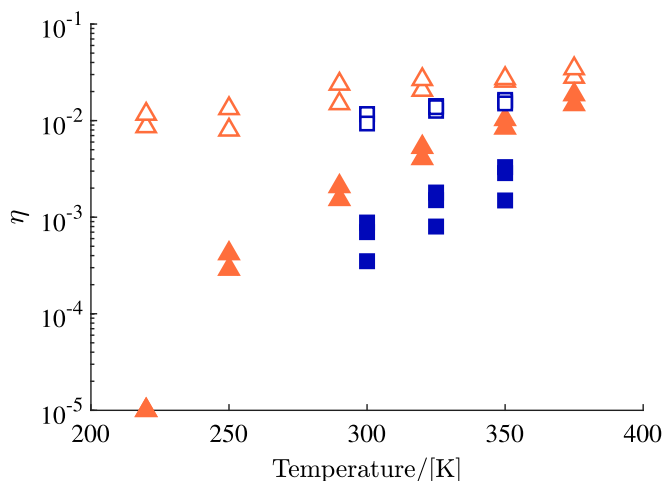

Figure 3. (Colour online) Molecule exchange efficiencies in the GE and CFCGE MC. Efficiency of the swap trial move in the GE, defined as the ratio between accepted molecule insertions and the total attempted swap trial moves (closed symbols). Efficiency of the identity change move in the CFCMC, defined as ratio between accepted change identity trial moves and total number of trial moves to facilitate molecule transfers [41]. (open symbols). □: SPC, TIP3P-EW and TIP4P-EW water (CFCMC) △: OPLS-UA and TraPPE methanol (CFCMC), ■: SPC, TIP3P-EW and TIP4P-EW water (GE), ▲: OPLS-UA and TraPPE methanol (GE).

tational biasing with CFCGE MC for a higher computational efficiency [61]. For conventional GE simulations, trial moves were selected with the following probabilities: probability of volume exchange between the boxes: 1.2%. The rest of the trial moves were selected with an equal probability of 24.7% including: translation, rotation, swap. For insertion of molecules in the

conventional GE, orientational biasing was used with 10 trial directions. For flexible methanol in CFCGE MC simulations, the probability of volume exchange was 0.8%. The probabilities of selecting other moves were evenly distributed between the aforementioned trial moves above and an additional molecule reinsertion trial move. For flexible methanol in GE simulations, probabilities of selecting volume exchange was 1.0%. The probabilities of selecting other moves were evenly distributed between the aforementioned moves above and an additional molecule reinsertion trial move.

4. Results

Simulation results show that computed chemical potentials of hydrogen sulphide and carbon dioxide using the WTPI method are in excellent agreement in the gas and liquid phases at coexistence. However, this is not the case for water and methanol. Figure 2 compares the computed chemical potentials of water and methanol at coexistence using both methods. It is clearly shown that computed chemical potentials of water and methanol in the gas phase and the liquid phase at coexistence are only in excellent agreement when using the CFCGE MC method. The inability to accurately compute the chemical potentials of the liquid phase at coexistence can be either due to inefficiency of the GE simulations to reach equilibrium, or the inefficiency of the WTPI for the chemical potential in the dense liquid phase. The molecule exchange efficiency in the conventional GE simulations is up to orders of magnitude lower than for the CFCGE MC simulations as shown in Figure 3 (efficiencies defined in the caption). Despite the lower efficiency of molecule exchanges in the GE, the coexistence densities obtained from CFCGE MC and GE simulations are in excellent agreement for all components (coexistence liquid densities are listed in the Supporting Information). Hence, both methods have converged to the same equilibrium densities. Since identical equilibrium densities are obtained using both methods, any difference between in computed chemical potentials can only be attributed to inefficient computation of excess part of the chemical potential. The contribution of excess chemical potential in the dense liquid phase is significant due to strong interactions of the test molecule with its surroundings, while in the gas phase, the inserted test molecule has limited interactions with its surroundings which means that the chemical potential of the gas phase is mainly determined by the ideal part. Since chemical potentials in the liquid and gas phases are equal in CFCGE MC simulations, it can be concluded that the CFCGE MC method computes the excess part of the chemical potential correctly for water and methanol in the liquid phase, and the WTPI method does not. Computed chemical potentials of coexisting phases of all systems using both methods are shown in Figures 4 and 5 as a function of temperature.

The inability of the WTPI method to compute the excess chemical potentials of water and methanol accurately may be due to the existence of a strong hydrogen bonding network. A two-dimensional overlapping distribution method in the *NVT* ensemble at the coexisting liquid densities was used to verify whether certain orientations of the test molecule can be energetically unfavourable such that the performance of the WTPI method is affected. The number of hydrogen bonds that test
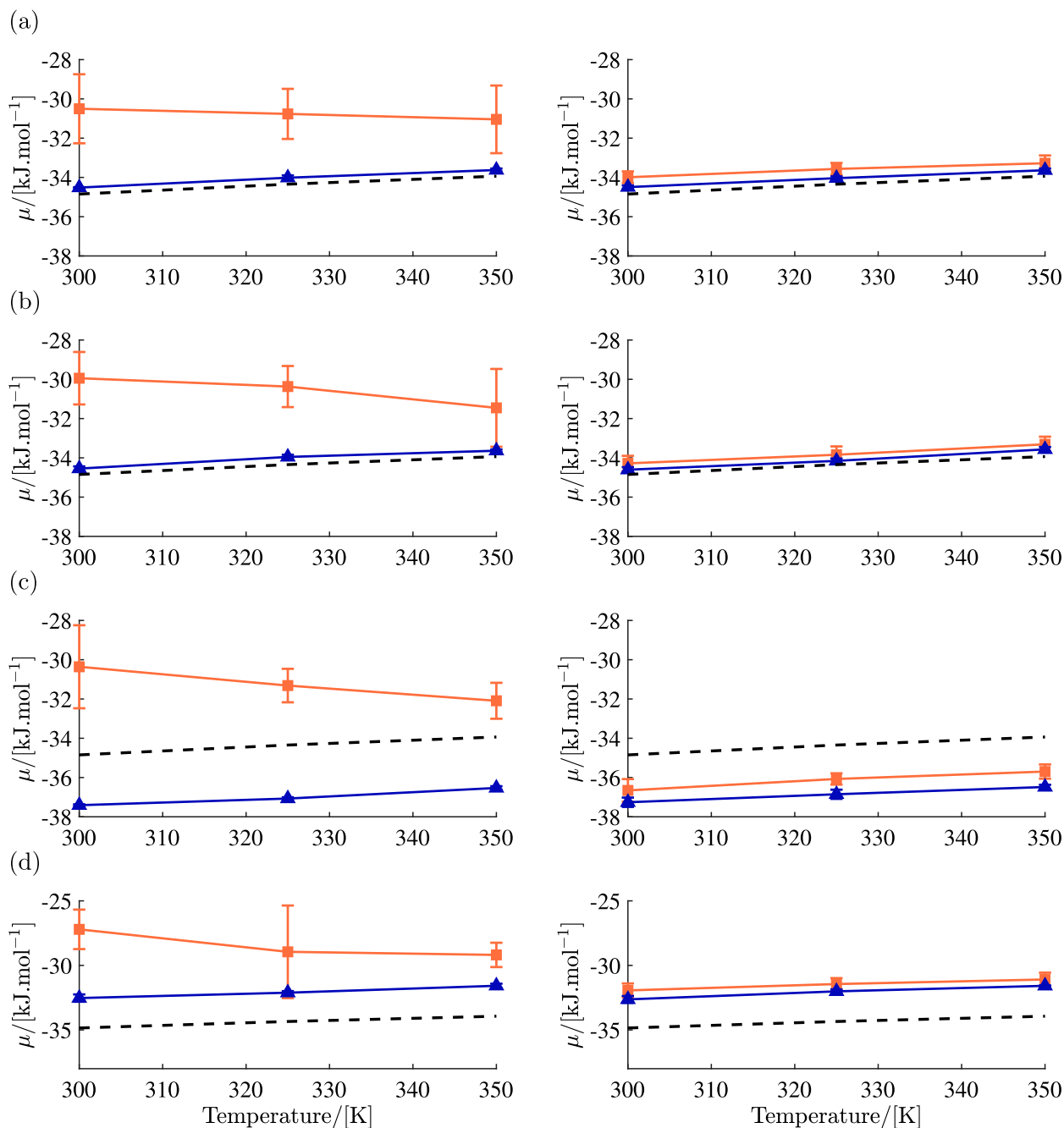
(a)

(b)

(c)

(d)

Figure 4. (Colour online) Chemical potentials of coexisting phases of water models for temperature range $T = 300$ K to $T = 350$ K: (a) SPC; (b) TIP3P-EW; (c) TIP4P-EW and; (d) TIP5P-EW (left: WTPI method in the conventional GE, right: CFCGE MC method). In all subfigures: ▲: computed chemical potentials in the gas phase, ■: computed chemical potentials in the liquid phase, (▬ ▬ ▬): computed chemical potentials from the Helmholtz EoS based on empirical data [31]. The raw data are listed in table S5 in the Supporting Information.

molecule forms with its adjacent molecules follows from the orientation of the test molecule in the hydrogen bonding network. Figure 6 shows results of implementing the two-dimensional ODM for TIP4P-EW water model at 300 K as a function of number of formed hydrogen bonds between the test molecule and its surrounding molecules. For $H \geqslant 4$, the overlap between functions $f_0(W, H)$ and $f_1(W, H)$ becomes smaller which results in poor statistics and therefore these are not shown in Figure 6. It is shown in Figure 6 that excess chemical potentials computed using the two-dimensional ODM and the WTPI method are not equal for any value of H. This observation does not depend on the number of hydrogen bonds the test molecule forms with its

surrounding molecules in the present system at $T = 300$ K. The two-dimensional ODM method was also used to show that the chemical potential of water at $T = 500$ K was computed accurately using the WTPI method, for all values of H. Simulation results of the two-dimensional ODM for TIP4P-EW water at $T = 500$ K are provided in the Supporting Information.

Table 1 shows number densities and void fractions of all systems in the liquid phase at coexistence in the temperature range of $T = 250$ K to $T = 350$ K. It can be seen that water has the largest number density (around 0.03) between $T = 300$ K to $T = 350$ K, while number densities of other systems are much smaller (around 0.015) in the temperature range of $T = 220$ K
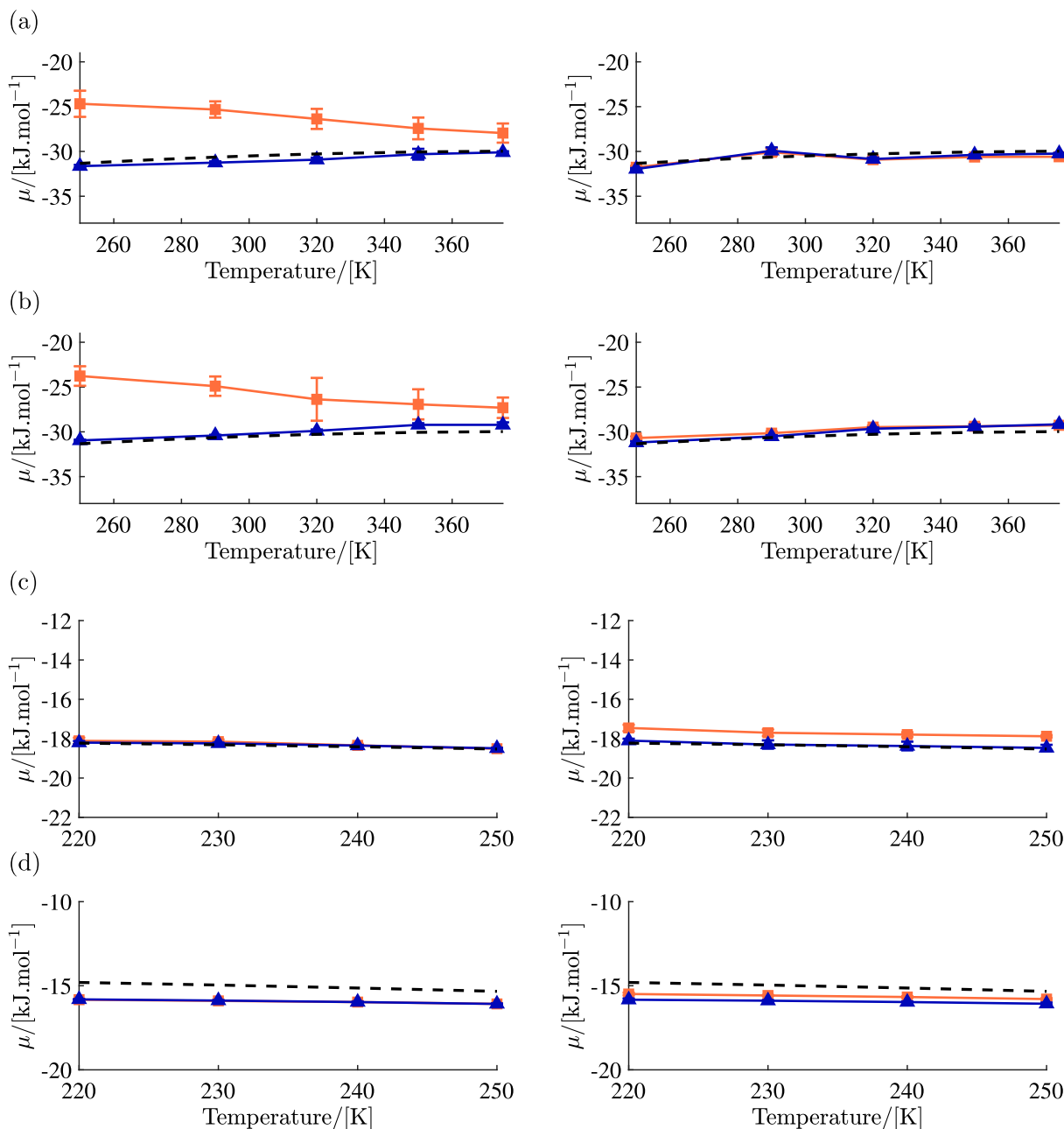
(a)

(b)

(c)

(d)

Figure 5. (Colour online) Chemical potentials of coexisting phases of methanol, hydrogen sulphide and carbon dioxide (liquid and gas) in the temperature range $T = 220$ K to $T = 375$ K: (a) methanol TraPPE; (b) methanol OPLS-UA; (c) H_2S TraPPE; (d) CO_2 TraPPE force field (left: WTPI method in the conventional GE, right: CFCGE MC method). In all subfigures: ▲: computed chemical potential in the gas phase, ■: computed chemical potentials in the liquid phase, (▬ ▬ ▬): computed chemical potentials from the Helmholtz EoS based on empirical data [63–65]. The raw data are listed in tables S1, S2, S3 and S4 in the Supporting Information.

and $T = 350$ K. Therefore, the number density cannot consistently offer a criterion for limitation of the WTPI method for water and methanol. For systems studied in this work, efficiency of the WTPI method appears to be correlated with the void fraction of the system. There is a clear distinction between void fractions of water and methanol systems (where WTPI method fails) compared to void fractions of carbon dioxide and hydrogen sulphide systems (where WTPI method works). It seems that for all systems in this study, the WTPI method fails when the void fraction of the system drops approximately below 0.50. This has also been independently tested using the ODM in the *NVT* ensemble as can be seen in the Supporting Information. Figure 7 shows the relative difference between the

chemical potentials in the coexisting gas and liquid phases as a function of void fraction of the liquid system. It can be seen in Figure 7 that as the void fraction drops below 0.5, the relative difference increases rapidly. A similar conclusion can be drawn for a LJ liquid, which is shown in the Supporting Information. Providing a more accurate criterion on the limitations of the WTPI method requires studying several other components.

Although the failure of the WTPI method is explained for all systems based on the void fraction, the computed chemical potentials of water using the CFCGE MC method deviate from the empirical EoS in case of four-site and five-site models. This is most probably a limitation of the force field since chemical potentials of the two phases are equal using the CFCGE MC
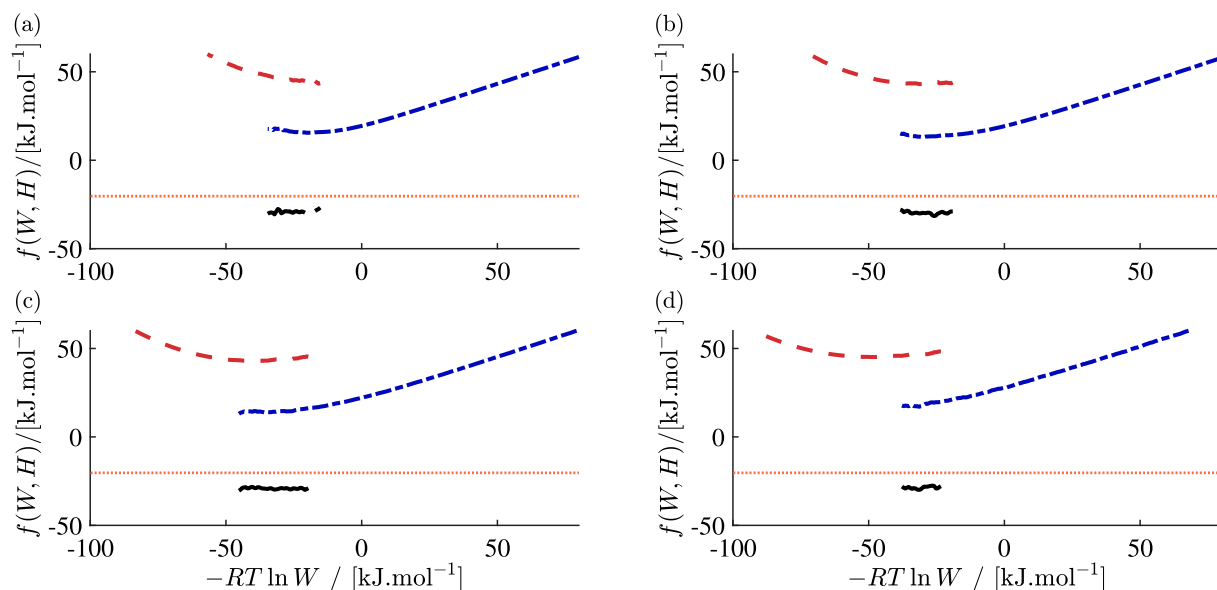
Figure 6. (Colour online) Two-dimensional overlapping distribution method (Equation (5)) applied to the TIP4P-EW liquid water model in the *NVT* ensemble with a void fraction of $\phi = 0.45$, based on the computed coexistence densities at $T = 300$ K. The sampled hydrogen bond count in each subfigure equals: (a) $H = 0$; (b) $H = 1$; (c) $H = 2$; (d) $H = 3$. In all sub-figures: (— — —): $f_1(W, H)$, (— · — ·): $f_0(W, H)$, (·····): μ^{ex}_{WTPI}, (———): $f_0(W, H) - f_1(W, H)$.
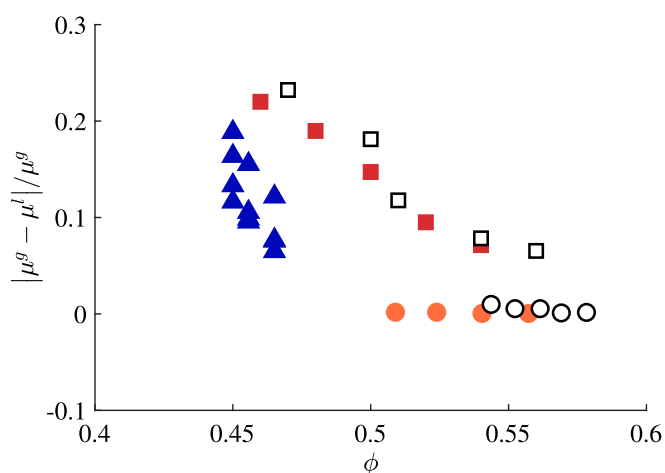

Figure 7. (Colour online) Relative difference between the chemical potentials in the coexisting gas and liquid phases using the WTPI method as a function of the void fraction. ▲: Water (SPC, TIP3P-EW, TIP4P-EW, TIP4P-EW, TIP5P-EW); ■: Methanol TraPPE; □: Methanol OPLS-UA; ●: carbon dioxide TraPPE; ○: hydrogen sulphide.

Figure 8. (Colour online) Comparison of computed excess chemical potentials of different water models for different methods at VL coexistence. Chemical potentials of water computed by Coskuner and Deiters [29] at different temperatures with a modified TIP5P model with different methods are shown with closed symbols: ●: Widom's test particle insertion method, ▲: Widom's test particle deletion method, ■: Theodorou deletion method [17]. Excess chemical potentials of different water models using CFCGE MC simulations are shown with open symbols: ▽: TIP5P-EW water model, ○: SPC water model, △: TIP3P-EW water model, □: TIP4P-EW, (— — —): based on empirical Helmholtz equation of state [31] provided by NIST, REFPROP [30].

method. Figure 8 shows computed excess chemical potentials of the aforementioned water models in the CFCGE MC together with those reported by Coskuner and Deiters [29] who used a five-site water model. Moreover, the excess chemical potential of water at different temperatures was computed using IAPWS empirical EoS [31] and shown in Figure 8. Similar to the EoS, the excess chemical potentials of water obtained from CFCGE MC method increase linearly in the temperature range of $T = 300$ K and $T = 350$ K. Since the water models were not fitted to experimental chemical potential data, some deviation from the empirical data is expected depending on the model. It is shown in Figure 8 that other test particle methods (Theodorou deletion method [17], Widom's test particle deletion method [62]) fails to compute the chemical potentials of water accurately as
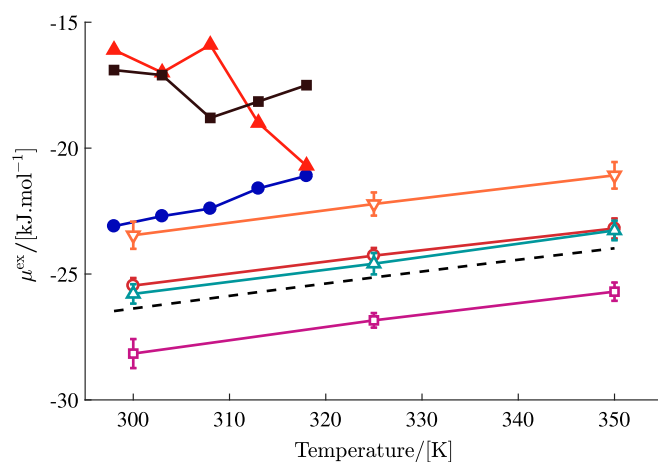
well. Excess chemical potentials of methanol, hydrogen sulphide and carbon dioxide are also listed and compared to data using an empirical equation of state in the Supporting Information [63–65].

5. Conclusions

Despite the lower molecule exchange efficiency of the GE simulations, equal densities from CFCGE MC and GE simulations were obtained for all systems in this study. Computed chemical potentials using CFCGE MC for all systems in study are equal

in both phases at coexistence. This is not the case for computed chemical potentials of water and methanol in the two phases using the WTPI method. However, for all cases the chemical potential of the gas phase using the WTPI method agrees well with the chemical potentials computed using the CFCGE MC method. Therefore, it is concluded that WTPI method is unable to compute the chemical potential of water and methanol accurately in the liquid phase. Since all densities computed in CFCGE MC are in very good agreement with the GE simulations in this study, any inefficiency of the WTPI method comes from sampling the excess part of the chemical potential. By gradual molecule insertion and removal during the MC simulations, the CFCGE MC method has resolved the sampling issue of the WTPI method. Using the CFCGE MC method, one would be able to compute the chemical potentials of the two phases directly without any further calculations which provides an independent check for the condition of chemical equilibrium. Computed chemical potentials of water using three-site models are in better agreement with IAPWS empirical EoS [31,64]. Chemical potentials of methanol computed using both TraPPE and OPLS-UA force fields and hydrogen sulphide force fields are in excellent agreement with the empirical EoS [63,64]. Slight deviations in the chemical potential of carbon dioxide relative to the experimental EoS [65] are observed. Inefficiency of the WTPI method in water with a strong hydrogen bonding network is independent on the number of hydrogen bonds the test molecule forms with its surrounding molecules. For all systems in this study, it is shown consistently that efficiency of the WTPI method strongly depends on the void fraction of the system and reduces significantly for void fractions smaller than 0.50. More data will be needed to determine a more accurate limit for void fraction where the WTPI works.

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