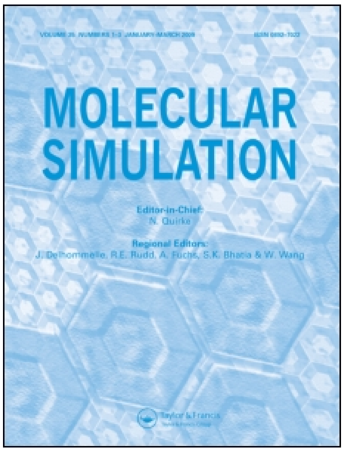

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Gibbs ensemble Monte Carlo simulations of binary vapour–liquid–liquid equilibrium: application to *n*-hexane–water and ethane–ethanol systems

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Gibbs ensemble Monte Carlo (GEMC) simulations in the isochoric–isothermal (NVT) ensemble were used to simulate vapour–liquid–liquid equilibrium (VLLE) for binary *n*-hexane–water and ethane–ethanol mixtures. The GEMC simulation of binary VLLE data proved to be extremely difficult and that is probably the reason why the open literature is so sparse with simulations for these types of systems. The results presented in this paper are to our knowledge the first successful binary three-phase GEMC simulations of non-idealised fluid systems. This paper also shows that the isobaric–isothermal (NPT) ensemble is unsuitable for the simulation of phase equilibria of binary three-phase systems.

Keywords: Monte Carlo; Gibbs ensemble; phase equilibria

1. Introduction

Phase equilibrium data for chemical systems are of vital importance in the design and optimisation of industrial chemical separation processes which comprise mass transfer unit operations, such as distillation and solvent extraction. Phase equilibrium data are usually generated using equipment and experimental techniques that have been developed and designed over generations of study [1–3]. However, experimental measurements are extremely expensive and may be limited [4], especially when one wishes to obtain data at extreme pressures and/or temperatures. An alternative, cheaper means of generating phase equilibrium data is via molecular simulation.

There is a multitude of Monte Carlo (MC) molecular simulation studies of biphasic fluid equilibrium [liquid–liquid equilibrium (LLE) and vapour–liquid equilibrium (VLE)], e.g. see [5–8], and three-phase vapour–liquid–liquid equilibrium (VLLE) of ternary mixtures have also been studied, e.g. see [9–11]. With the exception of a study by Canongia Lopes and Tildesley [12], where the Gibbs ensemble MC (GEMC) method [13] was generalised for binary, ternary and quaternary mixtures consisting of Lennard-Jones beads in the isochoric–isothermal (NVT) ensemble, there have been to our knowledge no studies which have focused on the simulation of binary three-phase fluid equilibrium. The work presented here is hence the first GEMC binary three-phase fluid simulations of realistic systems, and helps to fill a gap in this important and technologically relevant area.

This study presents details of VLLE simulations for *n*-hexane–water and ethane–ethanol systems using NVT–GEMC simulations. In addition to their technological relevance, these systems were chosen since they form highly asymmetric mixtures, with *n*-hexane–ethane solubility in the water/ethanol-rich phase being much lower than water–ethanol solubility in the *n*-hexane/ethane-rich phase. Since at least one of the components in these mixtures has low solubility in the other component, there is a large three-phase region which increases the probability that the simulations will converge within this region.

It should be noted that biphasic liquid–liquid equilibria for alkane–water and vapour–liquid equilibria for alkane–alcohol mixtures have been simulated previously [14–16], and in all studies the correct shape of the phase envelope, in comparison with experimental data, was obtained. Some of these studies [15,16] used the force fields employed in this study.

We also show that the NPT ensemble is unsuitable for the simulation of binary three-phase mixtures.

2. Model and method

The MCCCS Towhee code (http://towhee.sourceforge.net/), which utilises the GEMC method in the NPT and NVT ensembles, was used for all simulations with the coupled–decoupled configurational-bias (CB) algorithm [17]. Experimental densities, where available, were used to calculate the total system volume for the NVT simulations. As discussed below, pre-equilibrium and equilibration runs were performed before the production runs. Equilibrium was taken to be the point in the simulation when the trends

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in the densities, compositions and pressures in each simulation box did not change anymore. Sufficiently long runs also decreased the statistical uncertainties of the average values of these thermodynamic properties.

The transferable potentials for phase equilibria (TraPPE-UA) [18] and simple point charge/extended (SPC/E) [19] force fields for hydrocarbons and water, respectively, were used in this study. These models have successfully been used in studies of LLE of *n*-hexane–water (TraPPE-UA and SPC/E) and VLE of ethane–ethanol (TraPPE-UA only) systems [15,16]. A minimum box length of 19.0 Å was used for all simulation boxes during volume changes, Lennard-Jones non-bonded interactions were truncated spherically at 9.5 Å (half of the minimum box length) and analytical tail corrections were applied. A hard inner cut-off radius of 0.8 Å was used, so that any attempts to insert or move a molecule within this spherical region were automatically rejected, thereby improving the simulation efficiency. Care was taken to ensure that the volume of any box did not drop below that of the corresponding minimum box length via several trial simulations; thus, the total number of molecules had to be judiciously selected to ensure that the simulation was computationally efficient and produced reliable results. The Ewald summation technique ($K_{\max} = 5$, the maximum number of inverse space vectors; $\kappa \times L = 5$, the width of the Gaussian distribution, where κ is an arbitrary number and L is the length of the simulation box) [4], with tin-foil boundaries, was used to calculate the contribution of the long-range electrostatic interactions to the total potential energy.

A total of $N = 600$ molecules was used for the *n*-hexane–water system, comprising 369 *n*-hexane and 231 water molecules. This is a reasonable system size since in a recent study of the solubility of water in alkanes and polyethylene based on the same force field that is used here, Johansson et al. [15] performed successful simulations with 500 water and 100 alkane molecules. It has been shown that the structure of pure water vapour is similar in systems containing 200 and 500 SPC/E molecules [20], and also that the structural difference between water in its pure vapour phase and liquid alkane-rich phases is very small [15]. Thus, the use of 231 water molecules in this study is justified.

The total volume of the *n*-hexane–water system was estimated using the density of a reported experimental liquid mixture at 482 K ($\rho_{\text{exp}} = 312.50\,\text{kg}\,\text{m}^{-3}$ and $z_{n\text{-hexane}} = 0.614$) [21], along with temperature-dependent liquid density correlations [22]. Initially, the pure phases were equilibrated in separate simulation boxes (for the *n*-hexane–water system, this was 231 water molecules in one box and 309 and 60 *n*-hexane molecules in two boxes with different densities corresponding to experimental values). At this stage, only volume, translation and rotation moves (selected at random) were allowed, along with CB regrowths with the following fixed probabilities: {volume; translation; rotation; CB regrowth} = {0.01; 0.33; 0.33; 0.33}. These probabilities have been used previously for similar mixtures [16]. Equilibrating the pure components in their respective simulation boxes increased the efficiency of the subsequent equilibration period since, for these type of mixtures that exhibit high degrees of mutual insolubility, there are very few alkane molecules that dissolve in the liquid water-rich phase at equilibrium, and hence very few alkane molecules are transferred to the liquid water-rich simulation box when swap moves were enabled after the initial pure components' equilibration.

Similar initial conditions were used for the ethane–ethanol system, with 200 ethanol molecules in one box and 700 and 100 ethane molecules in the other two boxes. The temperature (311.15 K) selected for the simulations was chosen to allow for comparison with experimental work done by Kato et al. [23].

The pre-equilibration runs consisted of at least 2.5×10^4 MC cycles, where each cycle consists of N attempted moves, and N is the total number of molecules in the simulation. Thereafter, swap moves were allowed with equal probabilities between each pair of simulation boxes and with the total probability of this move type set to 10%. The remaining probabilities were equally distributed among translation, rotation and CBMC regrowths (the volume-change probability remained at 1%). Equilibration runs consisted of at least 1.5×10^5 MC cycles during which the densities, potential energies, pressures and compositions were monitored for convergence. It is worth mentioning that during the pre-equilibration runs, the maximum allowable centre-of-mass translations, rotations and volume displacements were updated every 10 cycles for the first 2000 cycles, to yield acceptance rates of approximately 50% for each move type. The equilibrations were followed by production runs, consisting of at least 1.4×10^5 MC cycles, in which the final thermodynamic averages were calculated.

It should be noted that, prior to conducting the three-phase simulations, the TraPPE-UA and SPC/E force fields as well as GEMC methods as implemented in the Towhee code were validated by obtaining two-phase LLE solubilities and densities that were in agreement with those reported by Johansson [24] (who used the GEMC programme of Errington and Panagiotopoulos; http://paros.princeton.edu/jerring/gibbs/index.html).

3. Results and discussion

The simulations resulted in three distinct coexisting phases (seen by the different densities shown in Table 1) at equilibrium. The equilibrium mole fractions obtained for the *n*-hexane–water mixture, which are presented in Table 1, are in reasonable agreement with experimental

Table 1. Final results for n-hexane–water NVT–GEMC simulation at 482 K, using 369 n-hexane and 231 water molecules.

	Mole fractions		
Phase	n-Hexane	Water	Specific density (kg m^{-3})
Vapour	0.76 ± 1	0.24 ± 1	97 ± 4
n-Hexane-rich liquid	0.958 ± 1 (0.8666)	0.042 ± 1 (0.1334)	413 ± 4
Water-rich liquid	0.00012 ± 4 (0.00027)	0.99988 ± 4 (0.99973)	821 ± 3

Note: The uncertainties in the final digit(s) are shown after the ± symbol, while experimental mole fractions [25] are listed in parentheses.

data (also shown in the table). The vapour-phase mole composition, $y_{n\text{-hexane}} = 0.75$, could not be compared with the literature data, since, to the best of our knowledge, vapour-phase experimental mole fractions for n-hexane–water mixtures have not been reported. Any computation to predict the vapour-phase composition using equation of states would have involved numerous assumptions having to be made, and hence would have very large uncertainties in the result, due to the high non-ideality of the system. However, comparisons were possible for the liquid phases. At 482 K, a correlation of the form $\ln x_{n\text{-hexane}} = A + (B/T) + C \ln T$ [25] for the solubility of n-hexane in the water-rich phase predicts $x_{n\text{-hexane}} = 2.749 \times 10^{-4}$. This is in very good agreement with the simulation value, $x^{\text{sim}}_{n\text{-hexane}} = 1.194 \times 10^{-4}$. Such limited mutual solubilities are usually observed for mixtures of non-polar and polar chemical species. A similar correlation for the solubility of water in the n-hexane-rich liquid gives $x_{\text{water}} = 0.1334$, while the simulation solubility is $x^{\text{sim}}_{\text{water}} = 0.0417$. The simulations in this work slightly under-predict the mutual solubilities. The results obtained here are also consistent with simulations done at lower temperatures, using the same force field. For example, at 450 K, Johansson [24] obtained a water in n-hexane solubility of $x^{\text{sim}}_{\text{water}} = 0.0132$ which, due to the lower temperature used in that simulation, is lower than the value obtained in our simulations. Similarly, the densities 488.9 and 877.9 kg m^{-3} for the n-hexane- and water-rich phases, respectively, obtained in the previous studies are larger than the values of 412.9 and 821.2 kg m^{-3} obtained in this study. Hence, the NVT simulation based on the force field used here yielded three distinct and stable phases, as well as giving equilibrium mole fractions in semi-quantitative agreement with correlation-based solubility data. Improved agreement can be obtained by fine-tuning the combining rules that are used to calculate the unlike-pair non-bonded interactions. Initial steps towards this have been taken by Johansson and Ahlström [26], who have introduced a correction parameter in the Lorentz–Berthelot energy parameter (ε) for unlike pseudoatoms (between methylene and oxygen pseudoatoms) to obtain better agreement with experimental water solubilities in alkanes. Best agreement for water in hexane solubility at this temperature is obtained when the Lennard-Jones energy parameter between the unlike components is multiplied by 1.3. A factor of 1.0 yields good solubilities in the water-rich phase, as is also shown in this study. Note that correction parameters have not been used in this work. The pressure obtained for the water–n-hexane system was 3663 kPa, while the experimental pressure was 4116.6 kPa.

The densities for the ethane–ethanol system shown in Table 2 show that three distinct phases are obtained using the NVT method, and comparison of the simulated mole fractions with experiment, also given in Table 2, shows that the force field, once again, yields data that are in semi-quantitative agreement with the experiment. The vapour pressure obtained from the NVT simulation (5721 kPa) is in fair agreement with the experimental pressure (5619 kPa).

4. NPT GEMC simulations

In this study, we have also tested the ability of the NPT ensemble to reproduce the results reported above when the NVT ensemble was used. Since similar results were obtained for both systems, only the results of the n-hexane–water system are presented in detail.

A test was performed where the initial conditions were identical to the equilibrated n-hexane–water system reported above. Analysis of the simulation results revealed

Table 2. Final results for ethane–ethanol NVT–GEMC simulation at 311 K, using 800 ethane and 200 ethanol molecules.

	Mole fractions		
Phase	Ethane	Ethanol	Specific density (kg m^{-3})
Vapour	0.9903 ± 52 (0.990)	0.0097 ± 52 (0.010)	168 ± 2
Ethane-rich liquid	0.963 ± 15 (0.921)	0.037 ± 15 (0.079)	273 ± 2
Ethanol-rich liquid	0.609 ± 54 (0.677)	0.391 ± 54 (0.323)	513 ± 19

Note: The uncertainties in the final digit(s) are shown after the ± symbol, while experimental mole fractions [23] are listed in parentheses.

that these simulations reverted to two liquid phases, i.e. a water-rich liquid phase in one box ($\rho = 826 \pm 6\,\mathrm{kg\,m^{-3}}$) and *n*-hexane-rich liquid phases in the other two boxes ($\rho = 424 \pm 3\,\mathrm{kg\,m^{-3}}$). A second test of the NPT ensemble was done using the pressure of 3663 kPa obtained from the NVT simulations ($T = 482\,\mathrm{K}$). This is the pressure that is relevant for the force field used here. However, even when this three-phase pressure, temperature and composition were specified, the NPT method did not produce a stable vapour phase – the density and composition of this phase fluctuated between those of the vapour and *n*-hexane-rich liquid phases.

The underlying reason why the NPT ensemble fails to reproduce three-phase equilibrium is to be found in the relevance of the Gibbs phase rule. We first consider a single-component system with two coexisting phases, where the Gibbs phase rule states that there is only one intensive degree of freedom. That is, the two-phase region is a line in the P–T (P-composition and T-composition) planes and hence, to obtain equilibrium between the two phases [27] using an NPT ensemble, one needs to initially (*a priori*) know the equilibrium pressure and temperature (for the force field used in the simulations). Since this is not the case for NVT simulations, where the pressure can change during the simulations, this ensemble is preferred for single-component systems with two coexisting phases [28]. The same reasoning applies to a two-component, two-phase system where there is, once again, only one intensive degree of freedom. In this case, the three-phase region is a line in the P–T planes. Hence, one needs to initially (*a priori*) know the equilibrium values of two of these variables (e.g. pressure and temperature) and one needs to initially choose the value of the third variable (e.g. composition) within the interval allowed in the phase diagram. That is, two simulations that are initiated with different values of the total composition will yield the same three-phase system if both of the simulations yield the correct compositions in each of the three phases (this is possible since the total number of molecules in each phase can differ between the two simulations). However, the interval from which the initial composition can be selected is limited, and the probability that any initial choice of P, T and composition will converge to the phase transition is extremely small [24]. Even when the initial pressure, temperature and compositions of the three phases are specified at their equilibrium values, every perturbation to these conditions, i.e. an accepted swap move, will cause the system to move off its three-phase trajectory and onto a two-phase path in Gibbs phase space. Thus, the probability that the system will return to its original three-phase path is extremely small. This is why the NVT–Gibbs ensemble is preferred over its constant pressure counterpart, since changes in pressure during the simulations, as well as compositions in each box, increase the probability of obtaining three stable phases – fixing two extensive variables (N and V) adds flexibility to the simulation compared to one extensive variable (N, in NPT simulations).

5. Conclusions

In summary, we report the first successful GEMC simulations of binary VLLE of realistic systems. Binary three-phase fluid equilibrium for complex chemical systems can be studied using the NVT–GEMC method. Equilibrium mole fractions, obtained from the NVT simulations, are in semi-quantitative agreement with experiment, for both the *n*-hexane–water and ethane–ethanol systems under the conditions studied here. NPT simulations are incapable of producing stable binary three-phase equilibria.

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