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# Phase-coexistence simulations of fluid mixtures by the Markov Chain Monte Carlo method using single-particle models

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ABSTRACT

We present a single-particle Lennard–Jones (L-J) model for $CO_2$ and $N_2$. Simplified L-J models for other small polyatomic molecules can be obtained following the methodology described herein. The phase-coexistence diagrams of single-component systems computed using the proposed single-particle models for $CO_2$ and $N_2$ agree well with experimental data over a wide range of temperatures. These diagrams are computed using the Markov Chain Monte Carlo method based on the Gibbs-*NVT* ensemble. This good agreement validates the proposed simplified models. That is, with properly selected parameters, the single-particle models have similar accuracy in predicting gas-phase properties as more complex, state-of-the-art molecular models. To further test these single-particle models, three binary mixtures of $CH_4$, $CO_2$ and $N_2$ are studied using a Gibbs-*NPT* ensemble. These results are compared against experimental data over a wide range of pressures. The single-particle model has similar accuracy in the gas phase as traditional models although its deviation in the liquid phase is greater. Since the single-particle model reduces the particle number and avoids the time-consuming Ewald summation used to evaluate Coulomb interactions, the proposed model improves the computational efficiency significantly, particularly in the case of high liquid density where the acceptance rate of the particle-swap trial move increases. We compare, at constant temperature and pressure, the Gibbs-*NPT* and Gibbs-*NVT* ensembles to analyze their performance differences and results consistency. As theoretically predicted, the agreement between the simulations implies that Gibbs-*NVT* can be used to validate Gibbs-*NPT* predictions when experimental data is not available.



## 1. Introduction

The properties of phase coexistence are important for many industrial and engineering applications such as the mixture separation through distillation column [1], the transport instability due to blockage by natural gas hydrates [2] or sulfur deposition [3], $CO_2$ sequestration [4], and enhanced oil recovery [5]. To obtain the necessary data through experimental observations is time consuming and expensive. Thus, molecular simulations based on the Monte Carlo method are auxiliary tools commonly used to understand phase-coexistence properties.

The Markov Chain Monte Carlo (MC) method proposed by Metropolis et al. [6] is successful in simulating problems at equilibrium state. The MC method uses the importance sampling idea to generate configurations $\vec{X}$, which is a high-dimen-

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sional vector made up of many molecular positions, according to the probability distribution function $f(\vec{X})$. The consecutive configurations constitute a Markov Chain. The MC method estimates the expected values of the quantities of interest by averaging over the sampled configurations. The use of Markov Chain makes the algorithm simple and universal but also leads to high correlation of the consecutive samples, which significantly increases the stochastic error in the MC results. Recently, the relationship of the stochastic error with the sample size and sampling interval was analyzed [7] to minimize the computational requirements (memory usage and computational time).

In MC simulations, hundreds or thousands of molecules are distributed inside a cubical box. Periodic boundary conditions are used to analytically enlarge the computational domain as we study the behavior of a bulk fluid far away from the interface. For problems where the quantities of interest (e.g., pressure, density, mole fraction of each component) depend on molecular positions but are independent of the molecular velocities, the MC method records and updates only these positions. The MC method based on the Gibbs-*NVT* ensemble was proposed in [8]. It uses two simulation boxes, one for the liquid phase and one for the gas phase. The temperature, $T$, the total number of molecules in the two boxes, $N$, and the total volume of the two boxes, $V$, are fixed. The algorithm allows molecules to swap from one phase to the other and volume exchange between the two phases, by changing one box's volume and correspondingly modifying the other's volume keeping the total volume constant. The Gibbs-*NVT* ensemble MC method effectively simulates phase-coexistence of single component systems but becomes inconvenient for simulating multi-component systems as the pressure is an output of the simulation rather than an input parameter. For the multi-component systems, we use the Gibbs-*NPT* ensemble MC method [9] where the pressure, $p$, of the two boxes is freely selected and fixed during the simulation. The total volume is not conserved as the volume of each simulation box is changed independently. Many successful applications of the MC method based on Gibbs-*NVT* and Gibbs-*NPT* ensembles have been reported in the literature [7,10–19].

In this paper, the phase-coexistences of binary mixtures of $CH_4 + CO_2$, $CH_4 + N_2$ and $CO_2 + N_2$ are simulated using a Gibbs-*NPT* ensemble method. We study the variation with pressure of the mole fraction of each component in the two phases. In order to improve the efficiency of the MC simulation, we neglect the intramolecular structure and model $CO_2$ and $N_2$ by a single particle as in the traditional model for $CH_4$, as originally proposed in [20]. The Lennard–Jones parameters for $CO_2$ and $N_2$ are determined by matching the experimental data in [21,22] at a temperature far away from the critical temperature and then used in the whole temperature range of interest. The single-particle modeling idea is based on the fact that the reduced equations of state of small molecules are similar to each other. The single-particle model and the selected parameters for $CO_2$ and $N_2$ are verified first in the simulations of phase-coexistence of single-component systems by comparison with experimental data [21,22] over a wide range of temperatures. This comparison shows that the single-particle model of $CO_2$ with properly selected parameters has similar accuracy in predicting the gas-phase properties as the traditional three-particle model used in [23]. To further verify the predictive capabilities of the single-particle model we simulate binary mixtures. As in the single-component case, the MC results using the simplified model agree well with experimental data [24–26] over a wide range of pressures. We compare the accuracy of the single-particle model against a three-particle model used in [27] for $CO_2$ in the case of the binary mixture of $CH_4 + CO_2$. Again, the accuracy of the single-particle model is similar to that of the more complex model in the gas phase. The aim of our work is to develop highly efficient models with acceptable accuracy. In addition, we present the comparison between the Gibbs-*NPT* and Gibbs-*NVT* ensemble MC methods in simulating fluid mixture at the same temperature and pressure. This comparison shows differences in the performance between the two algorithms. While comparing the average results of each ensemble method shows that they are consistent with each other under appropriately selected conditions.

## 2. MC algorithm based on the Gibbs-*NVT* and Gibbs-*NPT* ensembles

For problems of equilibrium state, the partition function of statistical mechanics provides the formula of $f(\vec{X})$ and the probability density distribution of the system's configuration $\vec{X}$ is $f(\vec{X})/\int_\Omega f(\vec{X})d\vec{X}$ where $\vec{X}$ is a high-dimensional vector containing the positions of all molecules. The pressure, density, and mole fraction, which depend explicitly on the molecular positions, are expressed as the corresponding expected values defined by the following integral:

$$\langle A\rangle = \frac{\int_\Omega f(\vec{X})A(\vec{X})d\vec{X}}{\int_\Omega f(\vec{X})d\vec{X}}, \tag{2.1}$$

where $A(\vec{X})$ is the transient value of the quantity of interest at a particular configuration $\vec{X}$ of the system. It is convenient to use the Markov Chain Mote Carlo (MC) method [6] to generate consecutive configurations $\vec{X}_i$ according to $f(\vec{X})$. Then, the expected value $\langle A\rangle$ is estimated by the average value $\frac{1}{n}\sum_{j=1}^{n}A(\vec{X}_j)$ over the $n$ sampled configurations $\vec{X}_j$. Detailed introduction to the MC method is given in [17,28] among others.

### 2.1. Gibbs-NVT ensemble

As mentioned above, each molecule is modeled as a single particle and we refer to them simply as particles. For the description with intramolecular structure, the algorithms and formulas described here should be modified accordingly [28]. A box is employed to represent the gas phase and a second one represents the liquid phase while different components can be found in a single box. Two-component systems are discussed here and the notations $a, b$ are used to represent