

Molecular simulation of Phase Equilibria: CO₂+N₂ and CO₂+O₂

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Abstract: The Monte Carlo method and the Gibbs ensemble technique were used for determining vapor and liquid phases in equilibrium for binary mixtures containing CO₂+O₂ and CO₂+N₂ of Lennard-Jones fluids at various temperatures. The simulated and Peng-Robinson EOS vapor-liquid equilibria are compared with experimental data. The results are in good agreement with experiment

Keywords: Gibbs ensemble, Monte Carlo, Peng-Robinson EOS, CO₂+N₂ and CO₂+O₂, Vapor-liquid Equilibrium.

Introduction

The most important part in modeling a process involving fluids is vapor-liquid phase behavior. This importance creates a need for accurate equilibria data for Binary systems, which can be applied to various chemical processes. For instance, to successfully design any type of separation apparatus, system has to know how a Binary mixture is equilibrating. Over the years, various modeling techniques have been designed to describe Binary systems. The equation of state method is useful for simple fluids, but it has its drawbacks. It begins to run into problems for more complicated systems, such as aqueous systems at high pressures or ionic systems. Another limitation is that it relies on experimental data. Lastly, one can not extrapolate with confidence outside the range of experimental data. These problems create a need for a different methodology to find equilibrium data. Hopefully, this need can be filled by the technique of molecular simulations. It was not until recent developments that this method became practical to run on computers. A widely-used method for two-phase molecular simulations is the Gibbs ensemble Monte Carlo method¹. The focus of the present work is the assessment of the available experimental VLE data with the development thermodynamic models and simulation results. In the following, a subset of the experimental data was used to adjust and validate the simulated and thermodynamic models developed in this work, CO₂+N₂ and CO₂+O₂.

Molecular Simulation Method

Setting up a Model

The first step in running a molecular simulation is making a model of the molecule or molecules are used. In these simulations, the Lennard-Jones potential is used to calculate the energy of the interactions by Equation (1).

$$U_{ij}(r) = 4 \times \epsilon_{ij} [(\sigma_{ij}/r)^{12} - (\sigma_{ij}/r)^6] \quad (1)$$

Where U is the configurational energy of interaction between the centers of two beads i and j a distance r apart. ϵ_{ij} and σ_{ij} are energy and size parameters for the ij interaction. σ has units of length which represents the diameter of the bead. ϵ has units of energy, and represents the depth of the potential well. For interactions between different types of beads, the Lorentz-Berthelot combining rules are used by Equations (2) and (3).

$$\sigma_{ij} = (\sigma_{ii} + \sigma_{jj}) / 2 \quad (2)$$

$$\epsilon_{ij} = (\epsilon_{ii} \times \epsilon_{jj})^{1/2} \quad (3)$$

This procedure can be expanded to describe a system made up of hundreds of diatomics. Although there are other models that describe actual intermolecular potential better, the Lennard-Jones model is much simpler and there is a lot of literature on its properties to use for comparison to simulations.

Running a Simulation

Before discussing the algorithm for doing the Gibbs ensemble calculation, let us look at the principle behind it. Figure 1 show a macroscopic two-phase region which is in equilibrium. The procedure is to be performed on a microscopic section in each of the regions. Thermodynamics gives the following requirements for equilibrium: each region is in internal equilibrium and the temperature, pressure, and chemical potential of all components in both phases are equal. First, we deal with the pure system case and then we move on to multi-component mixtures.

Phase I is the gas phase and Phase II is the liquid phase. The pure system have constant temperature T , total volume $V (= V_I + V_{II})$, and total number of particles $N (= N_I + N_{II})$. For this reason it is referred to as a constant NVT system. In the pure component case, temperature is set before the simulation is performed. The other three thermodynamic requirements are satisfied by three types of moves (Figure 2): displacement of molecules within each region, volume changes of the two regions, and particle transfers between the regions. These moves satisfy internal equilibrium, equality of pressure and equality of chemical potentials respectively.

The simulation runs as follows. After entering in all the necessary parameters (temperature, number of particles initially in each phase, initial densities, epsilon, sigma, the bond lengths), the program starts by generating an initial configuration. Next, it picks a type of move to perform. The percentage of how often a move is picked is set by the user (example: 30% displacement, 1% volume change, 69% transfer). Then, the computer attempts to make that move. The probability of the move being accepted is calculated by one of the following formulas, where p_{transfer} is the formula for a transfer from region II to region I.

$$p_{\text{displacement}} = \min [1, \exp(-\beta \times \Delta U)] \quad (4)$$

$$p_{\text{volume}} = \min [1, \exp(-\beta \times \Delta U_I - \beta \times \Delta U_{II} + N_I \ln(V_I + \Delta V) + N_{II} \ln(V_{II} - \Delta V))] \quad (5)$$

$$p_{\text{transfer}} = \min [1, N_{II} \times V_I / ((N_I + 1) \times V_{II}) \times \exp(-\beta \times \Delta U_I - \beta \times \Delta U_{II})] \quad (6)$$

The computer generates a random number between zero and one. If this number is greater than the probability, then the move is rejected and the system retains the old configuration and a new move is attempted. If it is less than or equal to the number than the move is accepted and the system moves to the new configuration. This cycle is repeated on the order of 10^6 times. There are two periods of the simulation - the equilibration and production periods. The simulation records certain properties of the system (pressure, density, internal energy)

and averages them over the production period to use for the equilibrium data at that temperature. There is an upper and lower temperature limit that can be used for each system when the temperature is too low, the liquid phase begins to get very dense and the chemical potential equilibration is difficult to satisfy because most of the transfer moves are rejected. A particle has trouble moving from gas to liquid because most of the attempted transfers place it in a position overlapping another particle. Moving a particle from liquid to gas is difficult because it involves a large cost in energy. The upper limit is the critical point. Once the temperature of the run gets too close to the critical point, the length of interaction between molecules approaches infinity.

Peng-Robinson Equation of State

Cubic EOS offer a compromise between generality and simplicity that is suitable for numerous purposes. They are excellent tools to correlate experimental data and are therefore often used for many technical applications. In the present work, the Peng- Robinson EOS with the Van der Waals one-fluid mixing rule was adjusted to binary experimental².

Results and Discussion

The molecular interaction parameter are given in Table-1³. The results section is divided into two parts – CO₂+N₂ and CO₂+O₂ mixtures.

Carbon Dioxide + Nitrogen

Figure-3 depicts the VLE of CO₂+N₂ at 232.7K including experimental data⁴, molecular simulation results, Peng-Robinson EOS. The experimental data shows some scatter, the simulation results are within this error bound. This also holds for the Peng-Robinson EOS.

Carbon Dioxide + Oxygen

Figure-4 presents the VLE data of CO₂+O₂ at 232.7 K from experiment⁵, molecular

simulation, Peng-Robinson EOS. As before, the experimental data shows some scatter, particularly on the dew line. Again, it can be seen that the Peng- Robinson EOS overshoots in the critical region of the mixture. The molecular model shows reliable results.

Concluding Remarks

The Gibbs Ensemble Monte Carlo is used to study the vapor-liquid equilibria properties of methane and ethane. Simulation results and Peng- Robinson EOS for the pressure-composition diagrams of the system CO₂+N₂ and CO₂+O₂ at 232.7K temperature is compared to experimental data. Comparison of the simulated and Peng-Robinson EOS results with experimental data demonstrated that Gibbs Ensemble Monte Carlo simulations can be used to predict vapor-liquid equilibria with accuracy close to experiments.

Table-1: Interaction parameters are used for simulation.

Fluid	ϵ/k_B (k)	σ (Å)
CO ₂	201.71	4.444
N ₂	91.85	3.919
O ₂	113.27	3.654

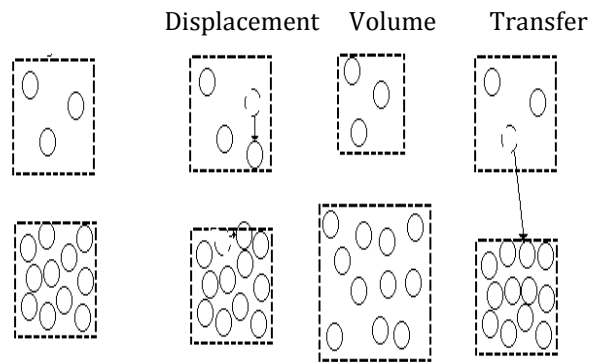
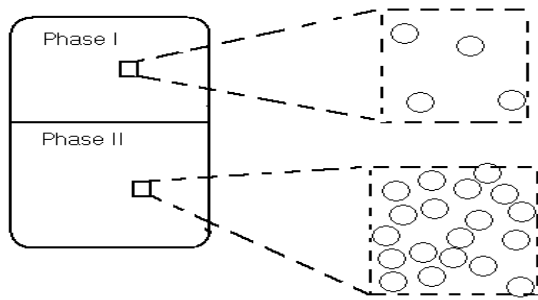


Figure 1: The Gibbs ensemble takes a microscopic section of a macroscopic system which is in equilibrium.

Figure 2: Types of moves.

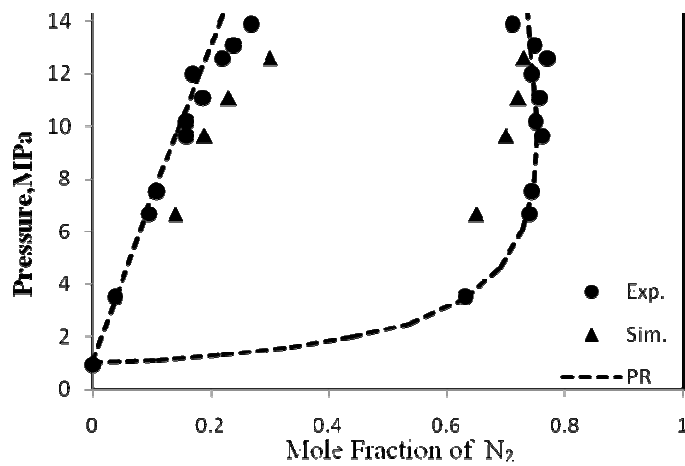


Figure 3: Vapor-liquid equilibrium of the binary mixture CO₂+N₂ at 232.7K

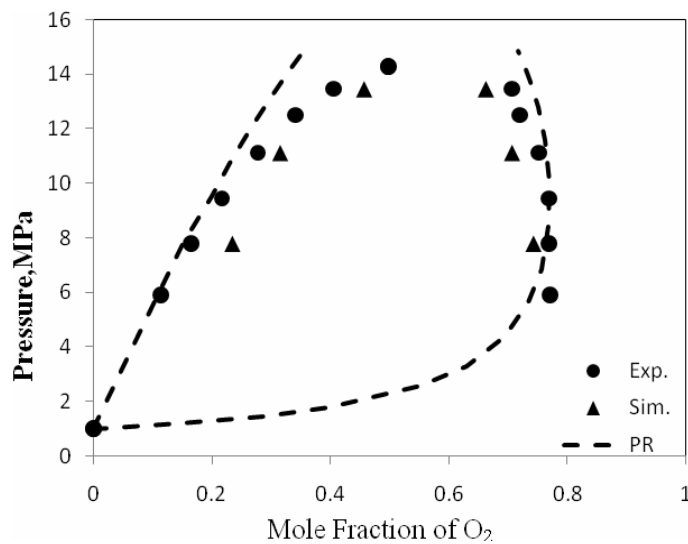


Figure 4: Vapor-liquid equilibrium of the binary mixture CO₂+O₂ at 232.7K

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