



Gibbs Ensemble Simulation of Phase Equilibria of Binary Mixture Containing Methane and Ethane

KEYWORDS

Gibbs ensemble, Monte Carlo, Methane and Ethane, Vapor-liquid Equilibrium

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ABSTRACT *The Monte Carlo method and the Gibbs ensemble technique were used for determining composition and densities of vapor and liquid phases in equilibrium for binary mixtures containing methane-ethane of Lennard-Jones fluids at various temperatures. The simulated vapor-liquid equilibria are compared with experimental data and the simulated results are in good agreement with experiment*

I. 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 method [1]. This technique is used to find vapor-liquid equilibria data first for pure Methane, and then for mixtures of Methane-Ethane components. Then, the results are compared to experimental data. Finally, after finding the best parameters to fit the experimental data, runs are done to see how accurately the parameters predict the behavior of these systems at high density and pressure in the single phase.

II. MOLECULAR SIMULATION METHOD

A. Setting Up a Model

The first step in running a molecular simulation is making a model of the molecule or molecules is to be used. In these simulations,

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.

B. 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 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.

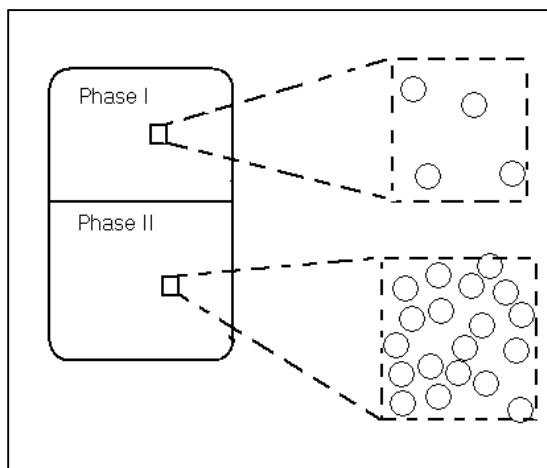


Figure 1: The Gibbs ensemble takes a microscopic section of a macroscopic system which is in equilibrium.

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).

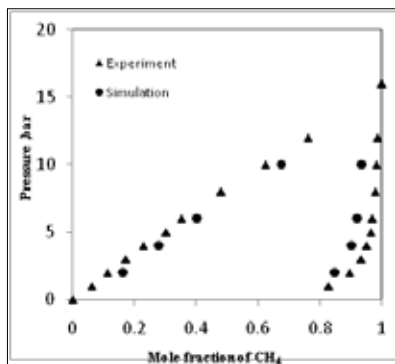
III. RESULTS AND DISCUSSION

Molecular simulation Phase equilibrium data is obtained from [2]. The molecular interaction parameter are given.

METHANE-ETHANE MIXTURE

Four NPT runs of different mixtures of Methane and Ethane are performed.

Figure-2: Phase diagram for Methane-Ethane mixture at 160 K.



Mole fraction data of vapor and liquid for CH₄ obtain from molecular simulation are match with experimental VLE data [5] of CH₄ + C₂H₆ at 160 K. By simulation, an equimolar composition in the liquid phase was regarded, where the mixing effect is strongest.

IV. CONCLUDING REMARKS

The Gibbs Ensemble Monte Carlo is used to study the vapor-liquid equilibria properties of methane and ethane. Simulation results for the temperature-density coexistence curve of pure methane as well as the pressure-composition diagrams of the system methane-ethane at 160 K temperature is compared to experimental data. Comparison of the simulated results with experimental data demonstrated that Gibbs Ensemble Monte Carlo simulations can be used to predict vapor-liquid equilibria with accuracy close to experiments.

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