

Investigation on vapor-liquid equilibrium of Argon atoms by a Gibbs ensemble Monte Carlo simulation

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Abstract

Vapor-liquid coexistence properties are studied using a Gibbs ensemble Monte Carlo simulation. Two simulation boxes with a fixed total number of Argon atoms and a constant total volume are coupled to each other (i.e., the two boxes can exchange volumes and particles), so that the phase coexistence between liquid and vapor can be achieved. Then, a series of simulations were run varying the reduced temperature. The simulation results (phase diagram) and the literature values are reasonably matched.¹ The more realistic and complete model of a potential to describe interactions between particles may improve the quality of a simulation result in the future.

Background

A pure substance exists in one of three distinct states (solid, liquid, and gas). However, at specific combinations of state conditions (e.g., temperature, pressure, and density) the substance can exist in more than one form such that multiple phases are in equilibrium.²

Simulation Methods

The vapor-liquid coexistence of Argon atoms was studied using the Gibbs ensemble Monte Carlo simulation. The Lennard-Jones potential is used to describe the interaction between the particles, and the potential is cut and shifted at a distance of $r_c = 2.5$. The phase equilibrium of two simulation boxes with a fixed total number of Argon atoms ($N = 240$), total density ($\rho = 0.3$), and reduced temperature (varying from 0.75 to 1.2) was achieved by allowing the boxes to exchange their volume and particles. Each simulation condition is run five times to minimize the error. There are three possible moves that can happen in the simulation (particle displacement moves, volume exchange moves, and particle exchange moves). The parameters of the simulation are given below:

N (total number of atoms) = 240

ρ (total density) = 0.3

T (reduced temperature) = 0.75 – 1.2

dx (maximum displacement) = 0.001

r_c (cutting distance) = 2.5

Equilibrium steps = $1000 * N$ (1000 Monte Carlo sweeps)

Production steps = $500 * N$ (500 Monte Carlo sweeps)

dv (maximum volume exchange) = $(N/2 / \rho) / 5$

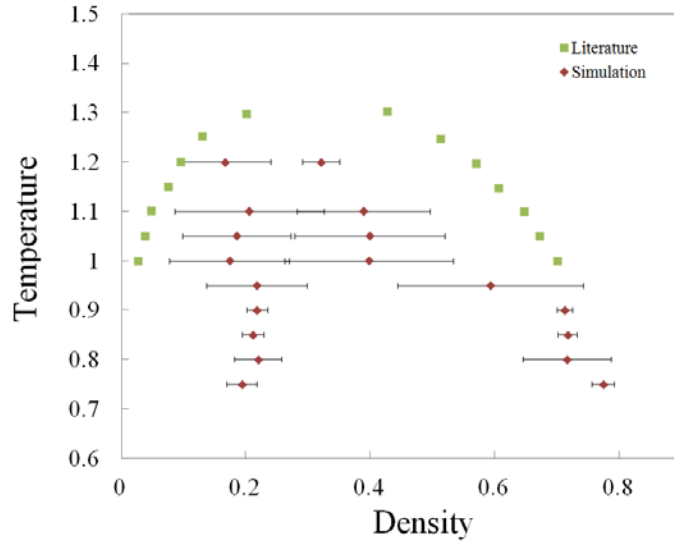


Figure 1. Vapor-liquid reduced temperatures versus densities graph. Green squares represent literature values from Rodrigues and Fernandes, and red diamonds represent the simulation results.¹ The black lines represent the standard deviation of the simulation result.

	ρ box 1	ρ box 2
Run 1	0.72	0.23
Run 2	0.59	0.28
Run 3	0.74	0.20
Run 4	0.76	0.20
Run 5	0.76	0.19
Average	0.72	0.22
Standard deviation	0.07	0.04

Table 1. Representative example of simulation result. The reduced temperature was at 0.8.

Results and interpretation

For all simulation runs, after 1000 Monte Carlo sweeps, one box contains significantly fewer particles (lower density) compared to the other box. This indicates that the two phases, vapor (less dense) and liquid (more dense), coexist at the specific condition. The densities of the two boxes and reduced temperature were recorded (e.g., table 1) and plotted in figure 1. The phase equilibrium curve from the simulation results shows a smaller parabolic shape (i.e., a higher density of vapor phase and a lower density of liquid phase at a specific temperature) compared to literature values from Rodrigues and Fernandes. This difference between the literature value and the simulation result is most likely due to the different potential that was used in the simulation. In the literature, Rodrigues and Fernandes utilized EHFACE realistic pair potential of Dias da Silva et al plus the ATM three-body potential.¹ However, the Lennard-Jones potential with cutting distance of 2.5 was used for this simulation study. Thus, the difference in the model may have caused the difference in the phase diagram shape.

In order to achieve simulation results matching the literature value better, the more realistic and complete model of potential should be used to study the phase coexistence properties of a substance. Also, the longer simulation time with a larger number of particles may result in a better match with literature values.

Movie

The set of particles on the left side of screen represents the box with a vapor phase, and the set of particles on the right side of the screen represents the box with a liquid phase.

[1] Sergio P. J. Rodrigues and Fernando M. S. Silva Fernandes, *J. Phy. Chem.*, **98**, 3917-3920, 1994

[2] M.Scott Shell, *CHE 210A phase equilibrium lecture note*, 2008