Adsorption/Repulsion of Single-atom Lennard-Jones Fluid Particles on/by Two Parallel Infinite Walls

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Summary

Adsorption/repulsion processes of single-atom Lennard-Jones fluid particles on/by two parallel infinite walls were simulated with Grand Canonical Monte Carlo method (GCMC). With increased strength of the particle-wall interactions, more uneven distributions of particles were observed. However, more even distributions of particles were observed at elevated temperatures.

Introduction

Heterogeneous catalysis involves solid catalysts and reactants in liquid or gas phase. Therefore, reactants are usually adsorbed on the surface of a catalyst before the reaction takes place. The adsorption process, which depends on various parameters (e.g., the reactant-surface interactions, bulk reactant concentration/pressure, etc.), can be described with adsorption isotherms (i.e., plot of an amount of material adsorbed versus pressure at a fixed temperature). This contribution is to model the adsorption/repulsion process of unspecified single-atom Lennard-Jones fluid particles on/by two parallel infinite walls.

Methods

The energy interactions between any two fluid particles with a distance, r, is given by the truncated Lennard-Jones 12-6 potential.

$$U(r) = \begin{cases} 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] & for\ r < r_c \\ 0 & for\ r \geq r_c \end{cases}$$

The cutoff distance, r_c, is assumed to be 2.5σ. Two flat adsorbing walls of infinite size are in parallel with each other at a distance of L. The interaction between a fluid particle and the wall is given by the Lennard-Jones 9-3 potential.

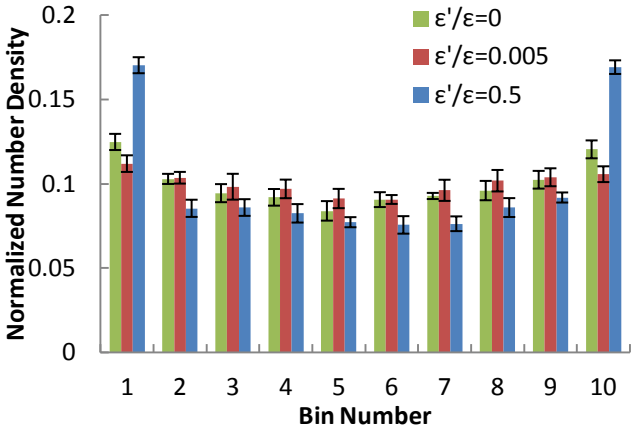
$$U'(r) = 4\epsilon'\left[\left(\frac{\sigma'}{z}\right)^{9} - \left(\frac{\sigma'}{z}\right)^{3}\right]$$

The simulation cell is a cubic box of a side length L, with periodic boundary conditions applied in the x and the y directions. The value of σ'/σ was assumed to be 1, while the value of ϵ'/ϵ varied with different strengths of particle-wall interactions. Grand Canonical Monte Carlo (GCMC) simulation was performed with specified chemical potential (μ), box volume (V) and, temperature (T). The fraction of attempted moves dedicated to additions/deletions was 50% and the acceptance ratio of displacement was 30-50%. Since the extreme proximity of a particle to the wall may result in overflow of the overall potential energy and system instability, a boundary layer of 0.9σ was defined, so that any attempted move into the boundary layer was rejected. After equilibrium was achieved between the bulk and the adsorbed particles, the space between two walls (excluding the two boundary layers) was divided into 10 bins evenly and the histogram of normalized number density (i.e., the fraction of the number of particles in each bin) was computed. Simulation was also performed with two parallel infinite walls which had repelling interactions with fluid particles.

Results

Adsorption

Without particle-wall interactions, the normalized number density is determined by thermodynamic fluctuation and an almost even distribution of particles is observed between the walls with minor wall effects (Figure 1, top). With increase in particle-wall interactions, more particles are adsorbed and higher normalized number density is observed at the proximity of the walls (Figure 1, top). Moreover, lower overall potential energies are observed with stronger particle-wall interactions at the same μVT conditions. Since thermodynamic fluctuations are suppressed at lower temperatures, the normalized number density is dominated by the particle-wall interactions. Therefore, higher normalized number density is observed at the proximity of the walls (Figure 1, bottom).



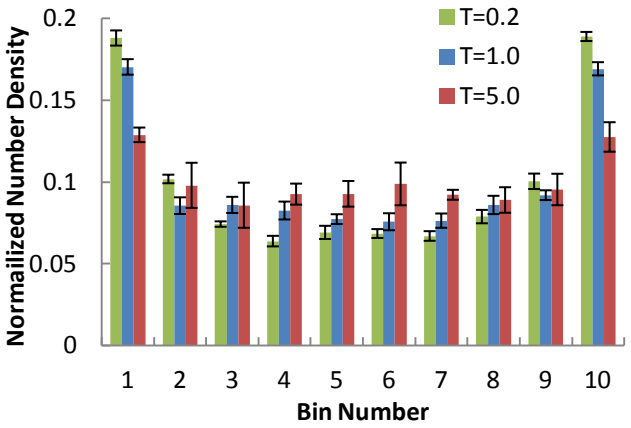
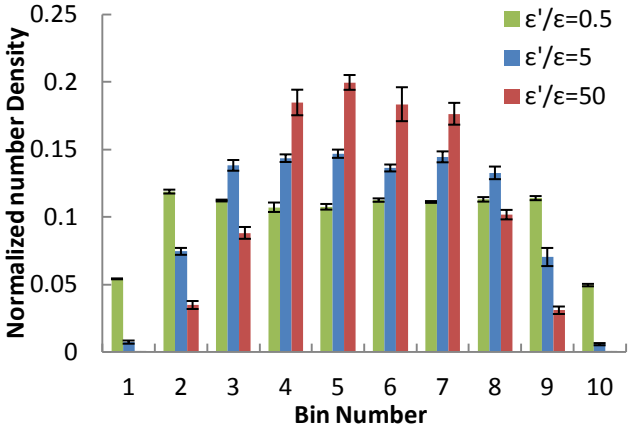


Figure 1. Adsorption of single-atom Lennard-Jones fluid particles on two parallel infinite walls: (top) histograms of normalized number densities with different strengths of particle-wall interaction; (bottom) histogram of normalized number densities at different temperatures.

Repulsion

With weak particle-wall interactions, the normalized number density is strongly affected by thermodynamic fluctuation and more even distribution of particles is observed between the walls (Figure 2, top). With increase in particle-wall interactions, more particles are repelled from the wall and higher normalized number density is observed at the center of the space between the two walls (Figure 1, top). Moreover, higher overall potential energies are observed with stronger particle-wall interactions at the same μVT conditions. Since thermodynamic fluctuations are suppressed at lower temperatures, the normalized number density is dominated by the particle-wall interactions. Therefore, higher normalized number density is observed at the center of the space between the two walls (Figure 2, bottom).



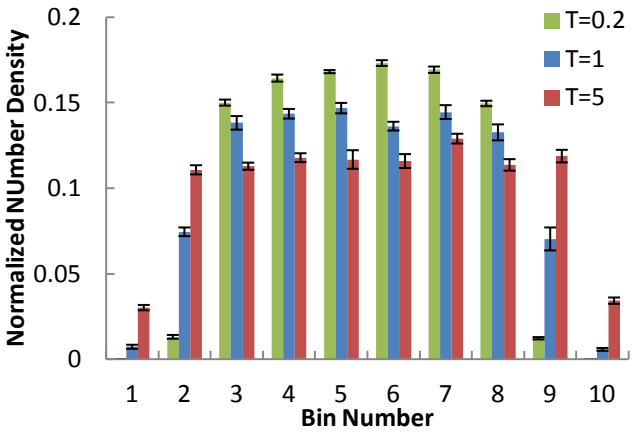


Figure 2. Repulsion of single-atom Lennard-Jones fluid particles by two parallel infinite walls: (top) histograms of normalized number densities with different strengths of particle-wall interaction; (bottom) histogram of normalized number densities at different temperatures.

References

1. Hill CG. *An Introduction to Chemical Engineering Kinetics & Reactor Design*. New York, NY: John Wiley & Sons; 1977: 167-173.
2. Errington JR. Prewetting Transitions for a Model Argon on Solid Carbon Dioxide System. *Langmuir.* 1999; 20: 3798-3804.