Simulation of Xe Adsorption into UiO-66 Crystal by Grand Canonical Monte Carlo Method

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1. Introduction

Metal Organic Frameworks (MOFs) are concerned as adsorption materials due to their high surface area and controllable characteristics such as pore sizes. In nuclear engineer those characteristics can be used to selective separation and adsorption of radioactive fission gases such as Xe, Kr, I. Those noble gases have high values in many industrial fields. However as the low chemical interactions of noble gases, efforts to raise selectivity of those gases are consisting these days.

Since those noble gases have high values, dealing with computer simulation can raise efficiency of the study such as experimental budget or time.

In this study, we focused on Xe adsorption to UiO-66 crystal model using Grand Canonical Monte Carlo (GCMC) simulation. And observed adsorption result according to temperature and particle numbers.

2. Background

2. 1. Grand Canonical Monte Carlo simulation

Grand Canonical Monte Carlo simulation is monte carlo simulation with Grand Canonical Ensemble. Grand Canonical Ensembles are Ensembles that particles and energy can interact with outer systems. Therefore, it often used to modify adsorption system. GCE has constant volume, chemical potential and one of temperature or pressure is fixed. Using partition function ratio between insertion and deletion particles makes an acceptation probabilities of particle insertion and deletion.

Therefore, monte carlo simulation makes insertion and deletion determine and event acceptance by using calculated acceptation probabilities.

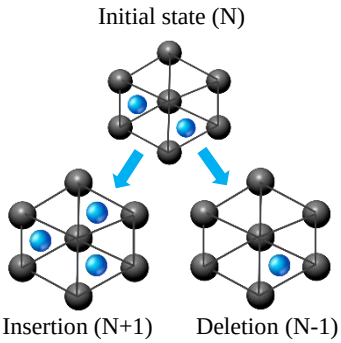

Fig 1. Possible states can lead from N particles state

The acceptation probability of an insertion at N particles, volume V , chemical potential μ is known as[1]

$$P_{accept}(N \to N+1) = min\left[1, \frac{V}{N\Lambda^3} e^{\beta(\mu - \Delta U)}\right] \quad (1)$$

Where de Broglie wavelength $\Lambda = h/\sqrt{2\pi m_p k_B T}$, $\beta = \frac{1}{k_B T}$, T is temperature. And the ΔU can be calculated by sum of Lennard jones potential by addition of Xe particle.

2.2 Lennard-Jones Potential.

The change of energy by insertion or deletion of particle can be calculated by Lennard-Jones potential. Sum of Lennard Jones potential of add particle and every existing particle will be calculated at every addition. The Lennard-Jones potential between 2 particle i, j is known as

$$\mathbf{U = 4\sqrt{\varepsilon_i \varepsilon_j}\left[\left(\frac{\sigma_{ij}}{r}\right)^{12} - \left(\frac{\sigma_{ij}}{r}\right)^{6}\right]} \quad (2)$$

Where $\boldsymbol{\varepsilon_i}$ is potential depth of particle i, $\boldsymbol{\sigma_{ij}}$ is minimum distance between two particle i and j, r is distance of two particles.

3. Methods

First, from the MOF coordinate file, extract information of existing particles' coordination, particle types. In this study will use UiO-66 crystal built by $(2 \times \mathbf{2} \times \mathbf{2})$ of unit structure.

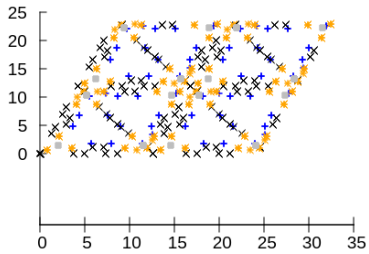

Fig 2. X-Z axis of Plotted UiO-66 $(2 \times \mathbf{2} \times \mathbf{2})$ crystal with Gnuplot

According to the normal Monte Carlo tequnique, after generating random numbers, actions such as particle insertion, deletion , and move are performed according to the range of random numbers, and each probability range is determined by thermodynamic variables. If insertion occurs, save Xe particle position and this position also will be used to calculation of Lennard-Jones

potential with other Xe. If deletion selected, delete one of saved Xe position. And Repeat simulation with difference temperature and steps.

4. Results

After several steps of simulation, The Xe particles are highly found at away from MOF particles and Xe particles each other.

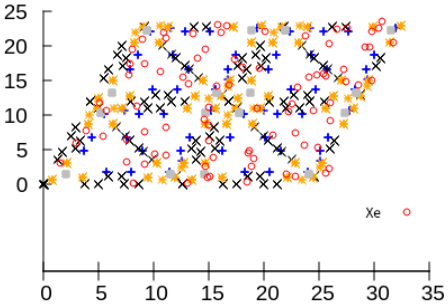

Fig 3. X-Z axis of Plotted UiO-66 (2 × **2** × **2**) crystal after Xe insertion 10000 step in 300K

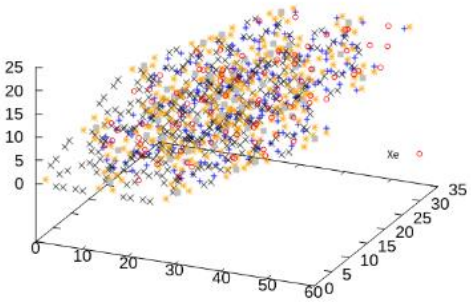

Fig 4. Plotted UiO-66 (2 × **2** × **2**) crystal after Xe insertion 10000 step in 300K

At the beginning of the simulation, the Xe content in the MOF increases, but after a certain time, the insertion and deletion of Xe become similar, and a region in which the Xe concentration no longer increases with time appears.

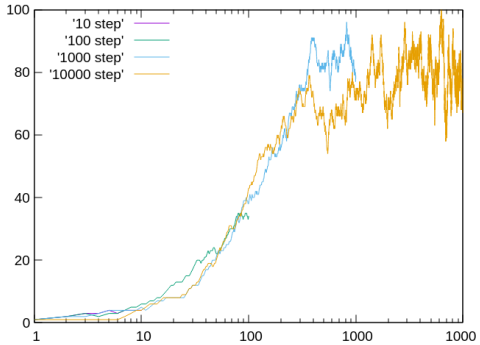

Fig 5. Inserted Xe particle numbers by simulation steps with different maximum steps

When difference temperature condition, the higher temperature condition shows more higher peak than low temperature .

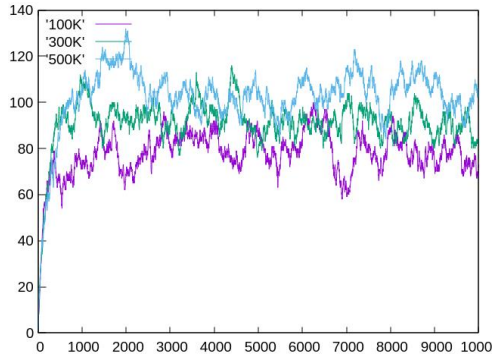

Fig 6. Inserted Xe particle numbers by simulation steps with different temperature condition

5. Conclusion

In this study, the Xe adsorption performance of UiO-66 MOF was evaluated on the basis of Grand Canonical Monte Carlo using an in-house code, and the tendency for the amount of Xe adsorption to increase with increasing temperature was observed, which is consistent with the theoretical prediction.

Currently, the cooperative group is evaluating the adsorption performance according to the pressure of Xe, and is conducting a study to interpret the experimental results using the code developed in this experimental study.

REFERENCES

[1] René Pool, Jaap Heringa, Martin Hoefling, Roland Schulz, Jeremy C. Smith and K. Anton Feenstra. Enabling Grand-Canonical Monte Carlo: Extending the
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