ABSOLUTE AND EXCESS ADSORPTION DISTINGUISH FROM THE MOLECULE DYNAMICS

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ABSTRACT

Absolute and excess adsorption are important concepts in gas capture and storage. Current measurement is based on the Gibbs excess adsorption theory, without directly distinguishing method. In this study, we use molecular dynamics to simulate the adsorption process of methane and Cu-BTC, finding that the energy distribution of methane molecules can reflect that property. Furthermore, we compared the experiment data and simulation result with the pair of methane and MOF-5, clarifying the feasibility of absolute and excess distinguish from the energy distribution perspective.

KEY WORDS

Excess adsorption, MOF, Molecular dynamics.

1. INTRODUCTION

The study of absolute and excess adsorption is significant in optimizing adsorption processes such as gas capture, storage, and separation. Understanding the difference between absolute and excess adsorption gives insight into improving selectivity or adsorption capacity for porous materials. Up to now, the Gibbs excess adsorption theory has been used to distinguish absolute and excess adsorption:

$$q_{excess} = q_{absolute} - V_{pore}\rho_{bulk} \qquad (1)$$

The uptake of excess adsorption is determined by the uptake of absolute adsorption minus the amount of free gas, where the amount of free gas is considered as the bulk phase gas occupied the pore volume of material. However, it is not sure if the free gas exists inside the pore of the material, since in a narrow space, the interaction from the material surface is unneglectable compared with bulk space. The adsorption phase is not clearly understood as well. Therefore this theory cannot explain the concept precisely. Molecular dynamic is a method that can analyze the behavior of each molecule in microscope scale. In this study, we simulated the adsorption of methane and Cu-BTC with 3 bulk phase: 115K liquid, 115K gas, and 298K gas, to observe the action of adsorbates. And simulated the adsorption of methane with MOF-5 in 200K and 300K to meet the experiment conditions. The result shows that the absolute and excess adsorption distinguish form energy distribution has better feasibility then traditional Gibbs excess adsorption theory.

2. METHOD

2.1 Configuration and force fields

The metal-organic framework Cu-BTC is a 2 2 2 supercell with a cubic length of 52.882 Å, and the methane is considered a boll model. The interaction is described with 12-6 Lennar-Jones (LJ) potential, and the parameters are referred from UFF and DREIDING, listed in Table 1. All the verification was done in our previous work [1].

Table 1: LJ parameter for interaction force of methane and Cu-BTC.

Atom	**ε (kcal/mol)**	**σ (Å)**
CH_4-C1	0.1672	3.60
CH_4-C2	0.1672	3.60
CH_4-C3	0.1672	3.60
CH_4-Cu	0.0383	3.42
CH_4-O	0.1678	3.38
CH_4-H	0.0669	3.28
CH_4-CH_4	**0.2941**	**3.72**

2.2 Simulation details

All the simulations are developed in LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator). A methane gas region, which is utilized as a bulk phase was created first, where it was a cubic box in the dimension of 400 Å for gaseous and 250 Å for liquid adsorption. The timestep is 1 fs. For gaseous methane, 1ns NVT for relaxation and another 1 ns for production. For liquid methane, 200 ps NVT for relaxation and 200 ps for production.

After the bulk phase is created, the Cu-BTC supercell is inserted into the center of the methane box. The methane molecules in the region of Cu-BTC supercell are deleted to make the initial uptake become zero. Then NVT simulation stars. The simulation time is 1 ns, 10 ns, and 5 ns, for 115K liquid, 115K gas, and 298K gas methane, respectively. The trajectory and energy of methane molecules are recorded.

3. RESULT

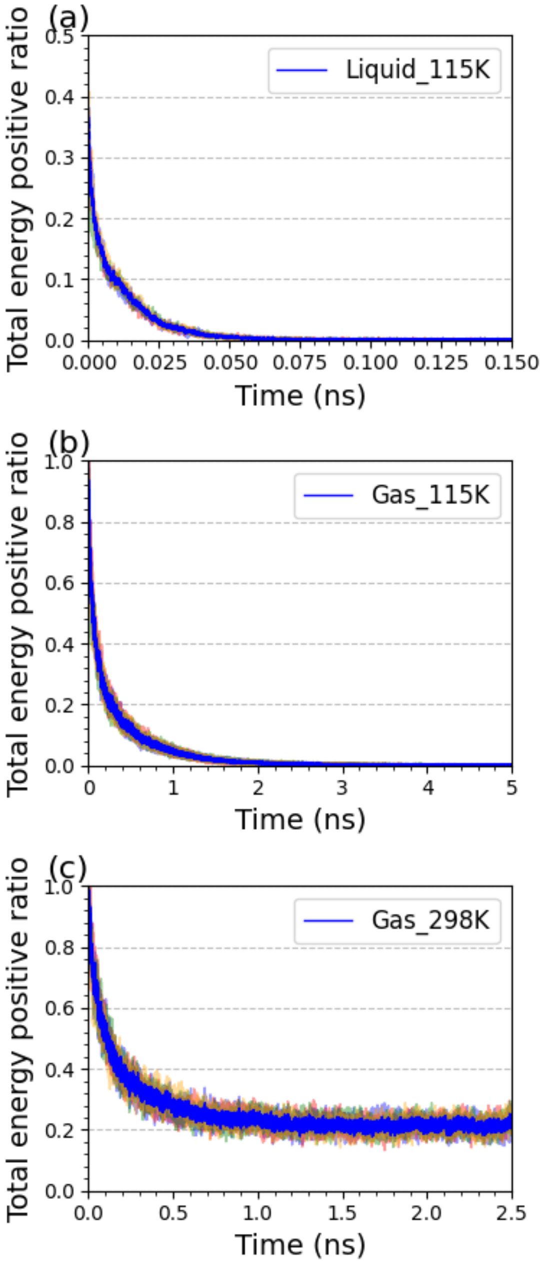

Fig.1: The total energy positive ratio development during the adsorption process of methane with Cu-BTC under the bulk phase of (a) 115K liquid, (b) 115K gas, and (c) 298K gas.

In Gibbs excess adsorption theory, the vital point is to recognize the “free gas”. In this simulation, the free gas is considered as the molecule that is equipped with enough energy and is able to escape from the the surface of the adsorbent. Here, it is described as the methane molecule having enough kinetic energy to overcome the potential energy from the Cu-BTC pore surface. Therefore, the total energy of methane molecules should be positive. Fig.1 shows the total energy positive ratio changes during the adsorption process. From Fig.1 (a) and (b), it can be seen that in 115K, there are almost no positive energy molecule when the adsorption approaching saturation. That is because in low temperature, the adsorption phase is a kind of liquid phase, where the connection between molecules is strong. So there is no free gas in those two bulk condition adsorption. That indicated why Gibbs excess adsorption theory cannot be applied in low temperature because there is no free gas. In the beginning, the positive ration is different between liquid and gas is due to the bulk phase.

From Fig.1 (c), the positive ratio become stable until the saturation period, indicating that the ratio of free gas is about 23%. And at the beginning, similar to 115K gas, the positive ratio starts from around 100%. It is a kind of gas adsorption feature. To further confirm this phenomenon, we simulate the methane with MOF-5, and compare the results by the equation of Gibbs theory (Bulk) and the energy distribution (Energy).

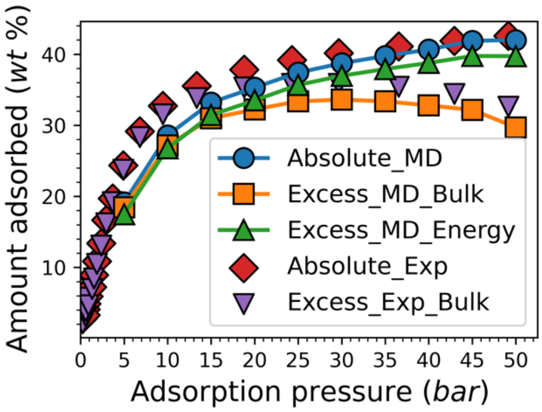

Fig.2: Absolute and excess adsorption of methane with MOF-5 at 200K.

In Fig.2, the excess adsorption calculated from Gibbs theory from the MD can match the experiment data. While for the excess adsorption calculated from the energy, the trend is different, more like the absolute adsorption. The energy perspective can explain the ratio of free gas changing with the temperature. With the temperature decreasing, the free gas ratio also decreases, which is continuous. But in Gibbs’s theory, at low temperature and high pressure condition, it should contain an unneglectable free gas, which is against the real situation.

4. CONCLUSION

The absolute and excess adsorption distinguish from the energy distribution of molecules provides a brand-new insight into understanding this concept. It has better feasibility than Gibbs excess adsorption theory but needs more verification in further study.

REFERENCES

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