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From Ideal Order to Real Disorder: Research Progress in Molecular Simulation of Porous Materials for CO_2 Adsorption

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Abstract

This review investigated different methods with different simulations for gas adsorption simultaneously to display different mechanisms of gas adsorption in different material systems: gas adsorption, the influences of different morphologies and sizes in ZIF-8/PVDF are investigated with CG (Coarse-Grained) Model; CG (Coarse-Grained) Model, the adsorption and diffusion behavior of CO2, CH4, N2 in interfacial systems composed of a polymer of intrinsic microporosity (PIM-1) and amorphous silica with GCMC (grand Canonical Monte Carlo) and MD (molecular dynamics) simulation is introduced systemically. The gas permeation behavior in the single crystal of syndiotactic polystyrene (s-PS) S-I form using the Amber force field is reported. Meanwhile, each system for gas separation with its properties is displayed in detail; furthermore, the similarities and differences among these methods are shown, and the results of each method are exhibited. For each system, the experimental process and data are shown together. Furthermore, the similarities and differences among these methods were shown. For each system, the experimental process and data were shown together. The results of each method are presented and discussed by comparing across different experimental systems, and further research perspectives are outlined to elucidate the various mechanisms governing gas behavior under different conditions.

Keywords

gas behavior MOF composites, s-PS, PIM-1

1. Introduction

Global warming is a worldwide concern that impacts the environment, leading to many problems, such as sea-level rise and ocean acidification due to rising atmospheric CO2. Suitable methods for CO2 are vital for addressing environmental issues [1]. Meanwhile, the CO_2 captured from the atmosphere can be utilized as a raw material to produce valuable chemicals, materials, and fuels for transportation [2]. the researches and reviews of gas separation and carbon capture methods are necessary to find an effective and realistic approach to lower CO_2, in this study, different approaches for gas adsorption combining with different simulations within different material systems were exhibited clearly and precisely: the MOF(ZIF-8/PVDF)composite with different nanoparticle morphology and sizes combined with hybrid MARTINI/FM force field(Fully Crystalline Ordered Porous System); The gas permeation behavior in the single crystal of syndiotactic polystyrene (s-PS)

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S-I form combined with amber force field(Semi-Ordered system), and composed of a polymer of intrinsic microporosity (PIM-1) and amorphous silica with GCMC and MD simulation(Fully Amorphous system)

Finally, by comparison of the ideal system to the orderless system, based on the merits and demerits of each method. The realization of the mutual complementarity of different systems was achieved to obtain more detailed information on gas adsorption, which can be meaningful for reaching a multidimensional and realistic conclusion that better fits real situations.

2. Theoretical Background

2.1 Hybrid MARTINI/FM Force Field

It is a specific combination of the MARTINI force field and force matching (FM), as for the MARTINI component, it can be seen as a mapping rule, which means several atoms are seen as a bead for later simulations to get a balance of accuracy of simulations and computational efficiency; however, the details of interaction among atoms are neglected [3]. As for the FM component, it is a CG parametrization approach that derives effective CG interaction potentials directly from reference all-atom MD trajectories. Which means, MARTINI provides a universal, general, read-to-use CG resolution, while FM is used to improve the accuracy of application-specific CG models, especially at the atomic level [4-5].

2.2 CG Resolution

Coarse-grained (CG) is a mapping approach used to improve computational efficiency by representing several atoms as a single bead with a specified ratio. In the hybrid MARTINI/FM force field, this ratio is 4:1.

2.3 Grand Canonical Monte Carlo (GCMC)

It is a statistical mechanical simulation method with a Monte Carlo (MC) molecular modeling framework. It works with the μVT (grand canonical) ensemble, where the chemical potential (μ), system volume (V), and temperature (T) are variables. The particles inside are free to locate. This is used for modeling gas adsorption in porous materials. In this simulation, the Boltzmann distribution at a given temperature is followed; rather than using fixed-particle simulations, the system includes four types of movement: translation, rotation, insertion, and deletion. With this simulation, thermodynamic properties that correspond to experimental results can be obtained; meanwhile, it is well-suited to most intermolecular force fields for porous materials, but it does not capture dynamic information such as diffusion coefficients and mass transport. And, the accuracy is associated with the underlying force field [6].

2.4 Molecular Dynamics (MD) Simulation

This is a physics-driven computational method for modeling movement particles over time. It deals with Newton's classical laws of motion for every particle, which determine the position and velocity of each particle and yield a continuous, time-ordered trajectory of the system's evolution [7]. Meanwhile, instead of random configurations of MC, inside MD simulation, each configuration follows classical mechanics, so the exact position and diffusion, rotation, collision, or other information can be observed [7]. Finally, MD is just an algorithm for the motion of particles; it is not a force-field theory, and it can be used alongside other force fields or simulations.

2.5 Assisted Model Building with Energy Refinement (AMBER) Force Field

The AMBER is an all-atom representation system of classical-atom, fixed-charge additive molecular mechanics force fields. It consists of a standardized set of analytical potential-energy functions and empirically derived atomic parameters that can be used to quantify interatomic interactions in systems [8-10]. The AMBER force field is built on the Born-Oppenheimer approximation and the molecular mechanics approximation. According to different types of connections between atoms, different molecular interactions can be simulated by a certain method. The structure and dynamics of molecular interactions can be obtained with high accuracy; however, electronic polarization, charge transfer, or many-body effects can not be described by the fixed-charge model [9].

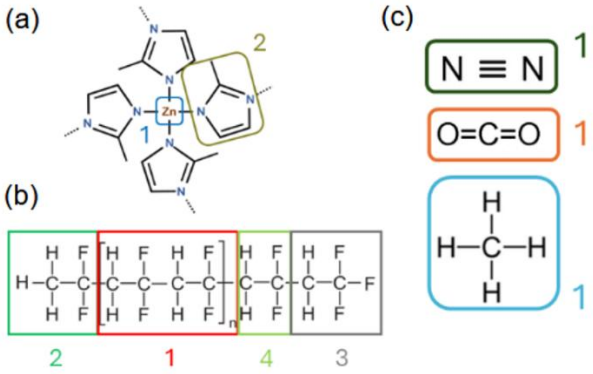
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3. Literature Review

3.1 MOFs Composites with the Hybrid MARTINI/FM Force Field

CG simulations are used to study the impact of nanoparticle morphology and size for gas adsorption in ZIF-8/PVDF [10].

Figure 1: Molecular modeling



In Figure 1, (a) models ZIF-8, (b) models PVDF, and (c) models N2, CO2, and CH4. The entire modeling process is carried out under single-gas loading. As shown in Figure 1(a), atoms are replaced by a bead in this simulation domain. Three different ZIF-8 nanoparticles were considered to study the influence of filler morphology and size in the gas adsorption and structuring within the composite: a cube of radius ≈69 Å(CB), two rhombic dodecahedra of radius ≈62 and 48 Å (RD), and two small rhombic dodecahedra with radius ≈ 24 and 28 Å (SRD), each system only comprises one of these [11]. The morphology of the nanoparticle is shown in Figure 2. Beads in blue and dark yellow are bead types 1 and 2, respectively.

Figure 2: Configuration of the empty CB, RD, and SRD

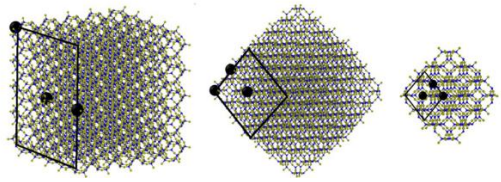
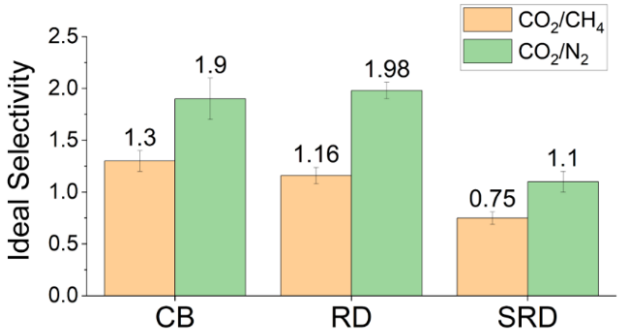


Figure 3: Ideal selectivity (S) for (CO2/CH4) and (CO2/N2)

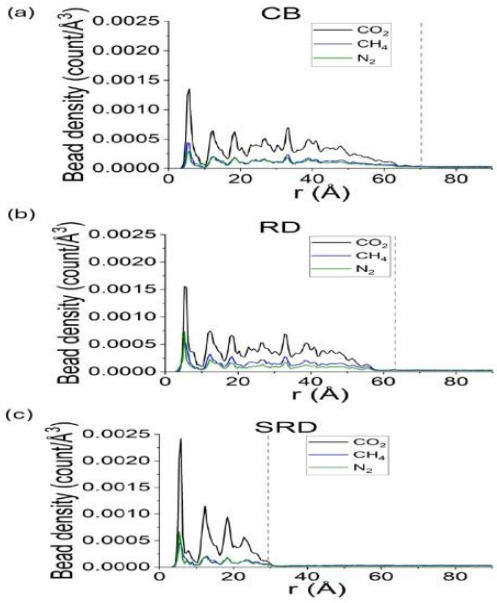


As the figure 3 shown, the ideal CO2/CH4 and CO2/N2 are regarded as S, which are got from the data of gas adsorption ability obtained by GCMC/MD simulations, the process of calculations follows the equation: $Sgas1/gas2 = Agas1/Agas2$ [10, 12], where A is the equilibrium number of molecules of each gas under the experimental thermodynamic conditions. he larger the ratio, the more preferentially the material adsorbs gas1 which is CO_2. It is easy to observe that three MOF systems have priority for CO_2 which is expected, meanwhile,

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the MOF with CB and RD nanoparticle shows better CO_2 adsorption priority than SRD, even, as for the material system with SRD particle, the CH_4 adsorption is better than CO_2, however, the total mass (loading amount) of MOF in the three simulated systems varies, the system with SRD has the smallest particles the lowest proportion of ZIF-8 and the highest proportion of the PVDF polymer phase in the system.

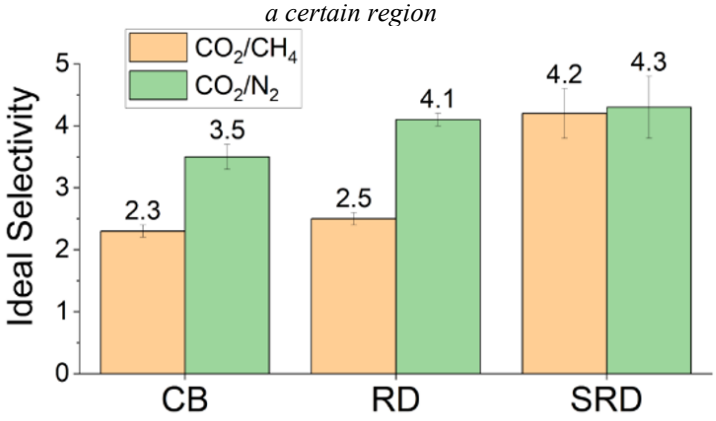
Figure 4: CO2, CH4, and N2 bead density for different morphologies with single gas loading (a) CB, (b) RD, and(c) SRD



In Figure 4, the gray dashed line represents the physical boundary of ZIF-8 particles — the left side of the dashed line is the interior of MOF nanoparticles, and the right side is the external PVDF polymer matrix. It is easy to find that MOF is the key point for gas adsorption, instead of polymer, which means the former figure is meaningless for the ability for gas adsorption due to the different amount of MOF.

The influence of the MOF's weight difference needs to be eliminated. As shown in Figure 5, the masses and numbers of gas molecules were counted only within the nanoparticle domain, rather than for the whole material.

Figure 5: Values of CO2/CH4 and CO2/N2 ideal selectivity for the ZIF-8 nanoparticle, counting only molecules inside a certain region



The realistic trend can be observed from Figure 5 that the CO2 priority is SRD>RD>CB. Because the SRD has the smallest volume, it has the biggest surface area. The influence of the filler in materials on the ability for gas adsorption may be mainly about the interaction area, which is validated in the fully crystalline material in this experiment.

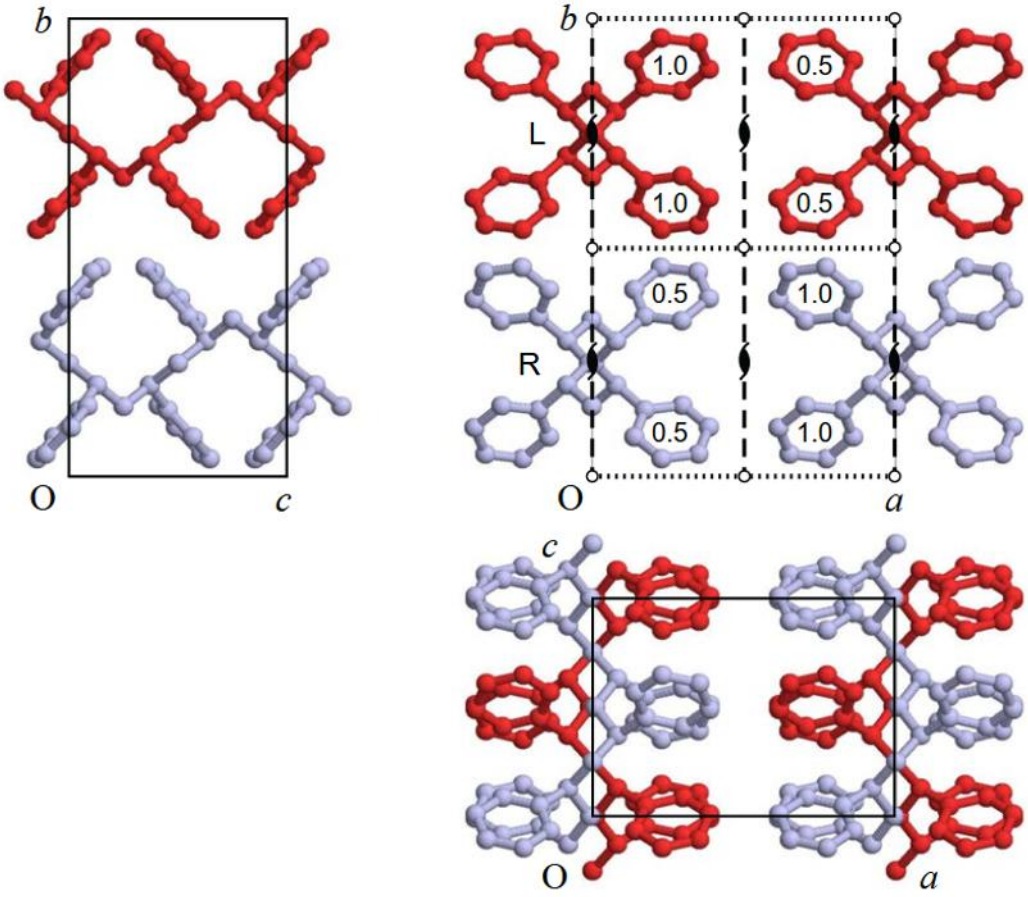
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3.2 s-PS (Syndiotactic Polystyrene) with MD (Semi-ordered Structure)

MOF composites with a fully ordered structure were discussed. Then, more varied material systems need to be investigated to draw more general conclusions. In section B, the s-PS with semi-ordered structure is investigated due to its Crystalline system with one-dimensional channels, which is less ordered [13].

The AMBER force field is used for s-PS; the entire simulation process is the same as in previous studies [14,15]. In this system, the gases are modeled as a rigid body. S-PS with S-I form is constructed by stress treatment for the initial ε form crystal [16]. Finally, as for the gas behaviors, the chemical potential of gas molecules in materials is calculated by the Wisdom particle insertion [17]. Compared with GCMC, because the pore channel size of the S-I phase is highly matched with gas molecules, the interactions among gases can be ignored, and the accuracy and computational efficiency of its particle insertion method are better than GCMC. Then, the whole system is run to simulate the gas behaviors in materials.

Figure 6: Structure of s-PS with S-I form crystal



As shown in Figure 6, compared with MOF composites, the S-I crystalline phase is a result of single-crystal s-PS with stress along a single axis. Thus, the s-PS with S-I form crystal is closer to real materials in life due to its more voids and free space. As shown in Figure 6, there are three subgraphs showing projection along the a-c-b axis. The key information is from the c-axis. It is evident that only along the c-axis can the cavity be formed, resulting in a single channel for gas adsorption.

Meanwhile, the cavity matches the shape of CO_2, which leads to higher CO2 selectivity. The major axis length of the ellipsoidal cavity precisely matches the total molecular length of CO_2, which means that it is tough for CO2 to rotate inside the cavity. The energy from molecular thermal motion is converted into motion rather than rotation. By this experiment, even though the total amount of CO2 adsorption is lower in MOF

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composites in section A, the s-PS with S-I form provides a new perspective for gas adsorption in materials that are less ordered.

3.3 PIM-1 and amorphous silica with GCMC/MD simulations

As for the system that is less ordered, the performance of gas adsorption of materials is greatly different from that of the ordered system, which means different dimensions and perspectives are needed for us to do more research about gas adsorption in materials. In section C, the amorphous structure that is closest to realistic conditions is investigated. In this section, as for PIM-1 with amorphous silica, which is a gully amorphous, GCMC is responsible for quantitatively calculating the gas adsorption equilibrium (solubility S), while MD is used to compute gas diffusion behavior (diffusion coefficient D). Together, they provide a complete description of membrane separation performance (permeability P=S×D) [18].

The PIM-1 chain is uncoiled in the z-direction and inserted into the Vacuum layer of the silica slab system, as shown in Figure 7.

Figure 7: The structure of MMM-1 and MMM-2

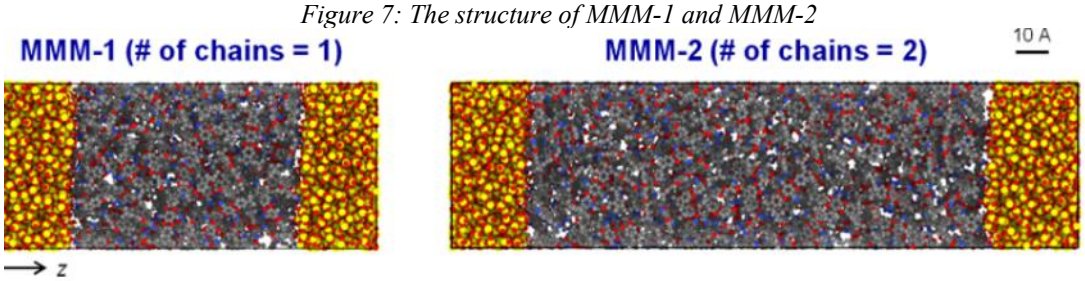
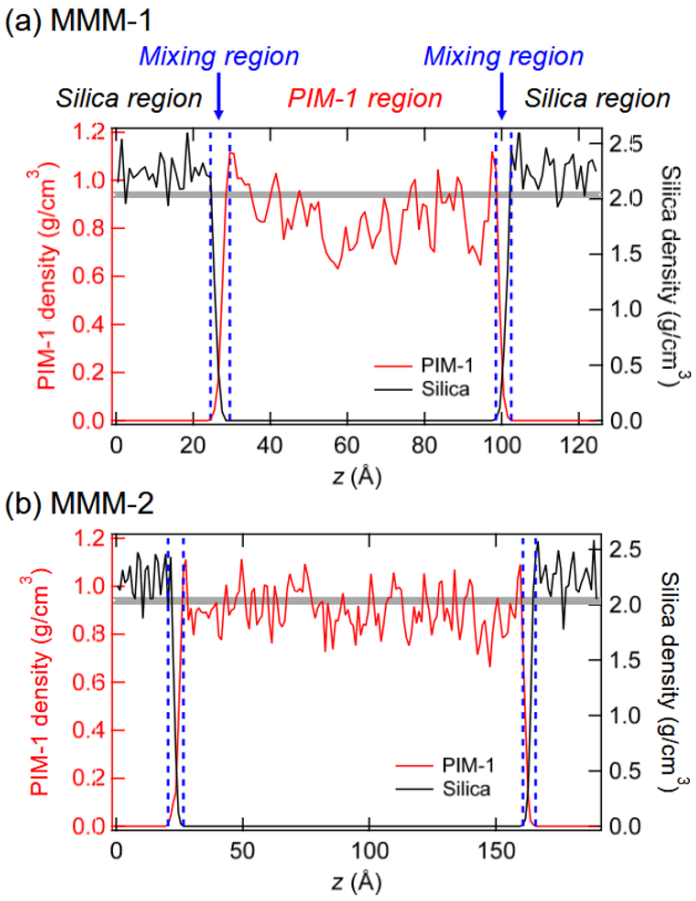


Figure 8: The material distributions along the z-direction



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As shown in Figure 8, the mixed phase is influenced by surface interference, and the density is decreased. The MMM-1 is decreased more than the MMM-2. Under lower pressure (1 atm), Gases are significantly enriched in the interfacial region, indicating that microcavities at the interface serve as adsorption sites with superior energy performance. Then, with the increase in pressure, the gases are enriched in the PIM-1 phase, which means the free volume inside the amorphous polymer is more attractive to gases.

4. Cross-systematic Discussion

In this study, the factors on gas adsorption ability in three independent materials systems with different degrees of order were investigated and displayed clearly. When it comes to fully ordered structure, the superficial area of filler contributes to gas adsorption mainly, in section A, extra experiment for gas adsorption of composite, was carried to validate the difference between the gas adsorption ability of MOF and PVDF, however, the experiments with single gas was not carried, the interaction among different gases can not be neglected, and the contribution of matrix was not validated. Then, to demonstrate improved gas adsorption performance across different structures, s-PS was investigated in this study. The AMBER force field was used in this section; the behavior of the CO2 and N2 in the molecular channel was investigated simultaneously. The volume of N2 is smaller, and CO2 is moving faster, which offers a new perspective on the influence of cavity shape on molecular motion; however, s-PS with P-I is a special phase, so the general trend has yet to be validated. Finally, this study focused on a fully amorphous structure, which is a common material system in real life. GCMC with MD was used in section C to provide a whole perspective for gas behavior. Under different air pressures, this material system exhibits markedly different gas behaviors; distinct mechanisms of gas adsorption in fully amorphous materials were observed. However, in this experiment, only the different air pressure of a single gas was considered, which is so different from the air mixture in real life. [

5. Conclusion

By investigating and displaying three materials system, as for different ordered structure, various mechanism behind gas adsorption and diffusion can be validated, as for fully-ordered structure, the superficial area of filler can be the key point of gas adsorption, when the degree of order decreases, the contributions of free volume are needed to be paid attention, meanwhile, it is necessary to focus on air pressure as well, because air pressure also has impact on mechanism of gas behavior, in real life, materials are mixture of different phases normally, thus, different mechanisms of gas adsorption are needed to be considered and combined to modified materials. In further experiments, depending on the particle scale, different simulation methods need to be considered. In real life, the materials are a mixture of different phases; typically, combining various gas-adsorption mechanisms is key to improving performance.

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Conflicts of Interest

The authors declare no conflict of interest.

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