

## The Effect of Framework Flexibility on Diffusion of Small Molecules in the Metal-Organic Framework IRMOF-1

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### Abstract

Many efforts have been made to model adsorption and diffusion processes in metal-organic frameworks (MOFs) in the past several years. In most of these studies, the framework has been kept rigid. In this study, we examine the effect of using a flexible framework model on the self-diffusion coefficients and activation energies calculated for several short n-alkanes and benzene in IRMOF-1 from molecular dynamics simulations. We find only minor differences between flexible and rigid framework results. The self-diffusion coefficients calculated in the flexible framework are 20-50% larger than the ones calculated in the rigid framework, and the activation energies differ by only 10-20%.

**Key words:** diffusion, molecular dynamics simulation, metal-organic framework, framework flexibility, alkane, benzene

### 1. Introduction

Metal-organic frameworks (MOFs) are a new class of micro- and mesoporous, crystalline materials with potential applications in gas storage, separations, sensing, and catalysis [1]. MOF structures are formed from the coordination of metal corner units with organic linking struts and are prime examples of reticular chemistry, which is defined as the linking of molecular building blocks by strong bonds [2].

Structural flexibility is a well-known property of MOFs [3]. For example, IRMOFs exhibit negative thermal expansion [4] and MILs exhibit breathing [5]. Nevertheless, most Monte Carlo (MC) and molecular dynamics (MD) simulations of adsorption and diffusion processes in MOFs have constrained the MOF framework atoms to their crystallographically determined positions [6-8]. In many cases, this assumption has given results that are in good agreement with experiment for both adsorption and diffusion [6-14]. Additionally, Greathouse et al. [13] recently studied the adsorption of noble gases in IRMOF-1 using MC simulations in flexible and rigid frameworks and reported only minor differences between the results. However, MD simulations by

Amirjalayer et al. [15] have suggested that sorbent flexibility may have a significant effect on the diffusion of guest species in MOFs. Tafipolsky et al. [16] developed a force field that allows for IRMOF-1 framework flexibility, and Amirjalayer et al. [15] used this force field to calculate the self-diffusivity and activation energy for benzene at a low loading in IRMOF-1 with and without framework flexibility. The diffusion coefficient that they determined for benzene in the flexible framework was in good agreement with the intracrystalline self-diffusivity measured by Stallmach et al. [17] from PFG NMR experiments; however, the diffusivity calculated while holding the framework rigid was nearly an order of magnitude higher. Amirjalayer et al. also found a substantially lower activation energy for the rigid framework simulation compared to the flexible framework simulation. Greathouse and Allendorf [18] performed a similar study and found that the self-diffusivity of benzene at the same low loading in IRMOF-1 was higher when calculated with their flexible framework model compared to their rigid model. This is a change in the opposite direction of the results of Amirjalayer et al., and the magnitude of the change was a factor of two as opposed to the factor of eight found by Amirjalayer.

In this study, we examine the effect of framework flexibility on self-diffusion coefficients and activation energies calculated from molecular dynamics simulations for methane, propane, n-butane, n-hexane, and benzene diffusion in IRMOF-1.

## 2. Methods

The self-diffusion coefficients ( $D_s$ ) and activation energies for diffusion ( $E_a$ ) of methane, propane, n-butane, n-hexane, and benzene in IRMOF-1 were calculated from molecular dynamics simulations. The NVT ensemble was used with the Nose-Hoover chain thermostat [19]. A 0.5 fs time step was used for the alkane simulations and a 2 fs time step was used for the benzene simulations. The self-diffusion coefficients were obtained from the mean-squared displacement (MSD) using an order-n method [20, 21]. In equilibrium, the diffusivities are computed by taking the slope of the MSD vs. time at long times using an Einstein relation:

$$D_s = \frac{1}{6N} \lim_{t \rightarrow \infty} \frac{d}{dt} \left\langle \sum_{i=1}^N \left( r_i(t) - r_i(0) \right)^2 \right\rangle \quad (1)$$

where  $r_i(t)$  is the position of molecule  $i$  at time  $t$ ,  $r_i(0)$  is the initial position, and  $\langle \dots \rangle$  denotes an ensemble average. Note that the simulations need to be sufficiently long in order to obtain reliable results.

The simulation box contained 1 unit cell, which is  $25.8320 \text{ \AA} \times 25.8320 \text{ \AA} \times 25.8320 \text{ \AA}$  and contains 8 IRMOF-1 cages. The loading for each type of guest species is provided in Table 1. The IRMOF-1 parameters from the force field of Dubbeldam et al. [4] were used with minor modifications to better represent the carboxylate group. These are: 1) minor changes to the equilibrium bond lengths, Cc-Cc and Cb-Cc  $1.36 \text{ \AA}$ , Ca-Cb  $1.42 \text{ \AA}$ , and Ob-Ca  $1.25 \text{ \AA}$ , 2) minor changes to the equilibrium bend-angles, Ob-Ca-Ob  $130^\circ$  and Ob-Ca-Cb  $115^\circ$ . The atom types are defined in Ref. [4]. This evolution of the force field predicts the proper unit cell size at zero Kelvin and will be published in detail elsewhere.

**Table 1.** Guest loading in IRMOF-1.

Species	Loading (molecules/unit cell)	Loading (carbon/unit cell)
Methane	48	48
Propane	16	48
n-Butane	12	48
n-Hexane	7	42
Benzene	10	60

The alkanes were described by a united atom model. The Lennard-Jones parameters for the alkane interactions ( $\sigma_{\text{CH}_4} = 3.72 \text{ \AA}$ ,  $\sigma_{\text{CH}_3} = 3.76 \text{ \AA}$ ,  $\sigma_{\text{CH}_2} = 3.96 \text{ \AA}$ ,  $\epsilon_{\text{CH}_4}/k_B = 158.5 \text{ K}$ ,  $\epsilon_{\text{CH}_3}/k_B = 108.0 \text{ K}$ ,  $\epsilon_{\text{CH}_2}/k_B = 56.0 \text{ K}$ ) were taken from the TraPPE force field [22-24]. The bonds between the  $\text{CH}_2$  and  $\text{CH}_3$  groups were allowed flexibility in length, angle, and torsion angle. The bend and torsion potentials were taken from TraPPE and the bond stretching potential was taken from Nath et al. [25].

Benzene was modeled with explicit carbon and hydrogen atoms joined together by rigid bonds. Each carbon atom was assigned a  $-0.095$  charge and each hydrogen atom was assigned a  $+0.095$  charge. The charges and Lennard-Jones parameters ( $\sigma_C = 3.60 \text{ \AA}$ ,  $\sigma_H = 2.36 \text{ \AA}$ ,  $\epsilon_C/k_B = 30.7 \text{ K}$ ,  $\epsilon_H/k_B = 25.5 \text{ K}$ ) were also taken from the TraPPE force field [26]. The carbon-hydrogen cross-species Lennard-Jones parameters of the benzene molecules were calculated from Lorentz–Berthelot mixing rules, and the electrostatic interactions were calculated by Ewald summation [20]. A cutoff of  $12.0 \text{ \AA}$  was used, and the Lennard-Jones potentials were shifted to zero at the cutoff.

### 3. Results and Discussion

The benzene self-diffusion coefficients and activation energies from Amirjalayer et al. [15], Greathouse and Allendorf [18], our study, and the experimental data of Stallmach et al. [17] are shown in Table 2. All of the simulations used a loading of 10 molecules/unit cell and the experiments used a loading of 6 molecules/unit cell. We find only a small difference between the self-diffusion coefficients calculated in rigid and flexible IRMOF-1 frameworks using the force field of Dubbeldam et al., and both values are similar to the experimental value measured by Stallmach et al. They also agree well with the value calculated by Amirjalayer et al. in a flexible framework. Greathouse and Allendorf found that diffusion is a factor of 2 faster in a flexible framework than in a rigid one, but both of their diffusivities are an order of magnitude lower than the other values in the table. The reason for this is unclear but may be related to the relatively short duration of their simulations ( $0.5 \text{ ns}$ ). We found that  $20 \text{ ns}$  simulations were needed to achieve reliable results for benzene in IRMOF-1 [21]. For the activation energies, we again find only a small difference between the flexible and rigid framework models. The large  $D_s$  and the small  $E_a$  found by Amirjalayer et al. for simulations in the rigid framework seem out of line with the other results in the table, but the reason for this is not clear.

**Table 2.** Comparison of self-diffusion coefficients and activation energies for benzene in IRMOF-1 determined from MD simulations with and without framework flexibility and the PFG NMR result of Stallmach et al. All of the  $D_s$  values shown were determined at 298 K and a low loading.

	This study	Amirjalayer et al. [15]	Greathouse Allendorf [18]	Stallmach et al. [17]
$D_s$ ( $10^{-9}$ m <sup>2</sup> /s) flexible	2.8	2.5	0.2	1.9
$D_s$ ( $10^{-9}$ m <sup>2</sup> /s) rigid	1.9	19.5	0.1	
$E_a$ (kJ/mol) flexible	10.4	13.8	14.3	
$E_a$ (kJ/mol) rigid	11.4	4.0	9.8	-

The self-diffusion coefficients calculated for the alkanes and benzene from flexible and rigid framework models are shown in Figure 1. The differences between the results obtained from the two sets of simulations are minor. The diffusivities obtained from the model with framework flexibility are slightly higher (ca. 20-50%) than when the framework is kept rigid. The results for benzene and hexane are in good agreement with the experiments of Stallmach et al. [17], but the calculated self-diffusion coefficient for methane is nearly an order of magnitude lower in all simulations. This discrepancy cannot be explained by framework flexibility and will be discussed in a future publication.

Self-diffusivities were computed over a range of temperatures to obtain activation energies for methane, n-butane, n-hexane and benzene. Figure 2 shows the Arrhenius plot used for this analysis. There is relatively little scatter in the data, and the data can be accurately fit using straight lines. The activation energies are plotted in Figure 3. The activation energies determined from the flexible model are 10-20% different from the activation energies obtained from the rigid model. For methane, n-butane, and benzene, the activation energies calculated in the flexible framework are lower than those calculated in the rigid framework, and the opposite is true for n-hexane. Since the self-diffusion coefficient is most difficult to calculate at 298 K, and this point appears to strongly influence the calculated activation energies, we also calculated the activation energies without this point to test the relationship between the flexible and rigid results. We found that the activation energies are always lower when the 298 K data are excluded, but the trends in Figure 3 are not changed.

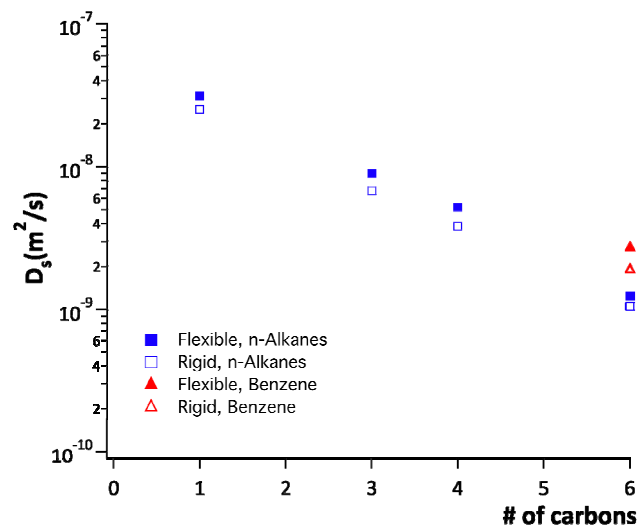


Fig. 1: Self-diffusion coefficients calculated with rigid and flexible IRMOF-1 force fields.

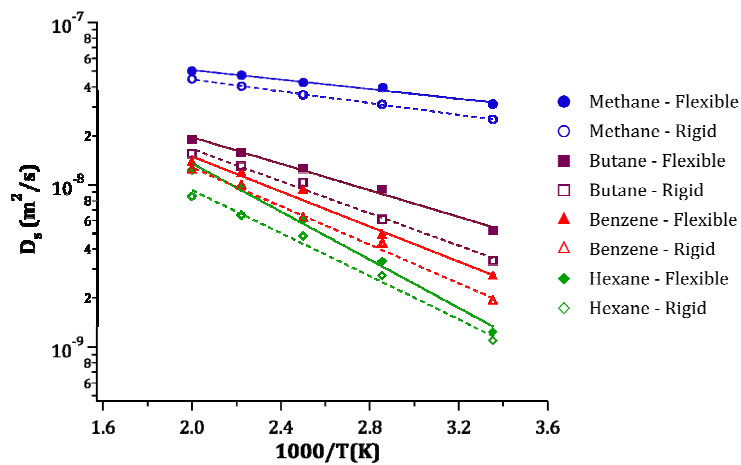


Fig. 2: Arrhenius plots used to determine activation energies.

Consistency between diffusion coefficients and activation energies calculated with rigid and flexible IRMOF frameworks, in fact, should be expected when the guest size is small compared to the window size. The positions of the vibrating IRMOF framework atoms remain relatively close to their crystallographic positions, and the residence times of the species we studied (ca. 10-150 ps in a single cage) are sufficiently long for them to experience an averaged framework that is roughly the same for the rigid and flexible structures. Therefore the activation energies, which are related to how difficult it is to

move through the connecting windows, should not be greatly affected by the framework flexibility. The pre-exponential factor in the Arrhenius relationship should also not be greatly affected, as this is related to how often a molecule is “pushed” towards the window attempting to diffuse through it and is driven by vibrations inside of the cage.

Framework flexibility will be more important for structures that can change conformation under thermal conditions such as IRMOF-7 [27], breathing structures such as MILs, and structures with small pores or tight channels. Seehamart et al. [28] found that framework flexibility has qualitative as well as quantitative effects on the diffusivity of ethane in the MOF Zn(tbip), which has relatively tight channels. Generally, little effect of framework flexibility has been found for zeolites (See Refs. [29, 30] and references therein) unless the guest size approaches the zeolite pore size.

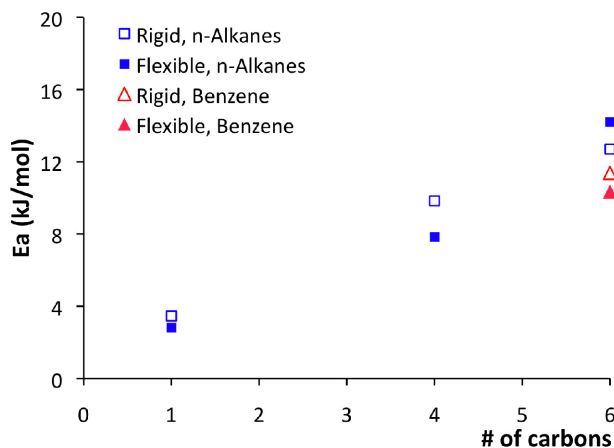


Fig. 3: Activation energies calculated with rigid and flexible IRMOF-1 models.

#### 4. Conclusion

In this study, we examined the effect of using a flexible framework model for the diffusion of several short n-alkanes and benzene in IRMOF-1. We found only minor differences between the results from the rigid and flexible framework models. The self-diffusion coefficients from the flexible framework simulations were slightly larger than those from the rigid simulations and the activation energies did not show a clear trend.

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