



N₂ in ZIF-8: Sorbate induced structural changes and self-diffusion



T. Chokbunpiam^{a,b,c}, R. Chanajaree^d, T. Remsungnen^e, O. Saengsawang^{b,f}, S. Fritzsche^{c,*}, C. Chmelik^g, J. Caro^h, W. Janke^c, S. Hannongbua^{b,*}

^a Petrochemical Science Program, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand

^b Chulalongkorn University, Computational Chemistry Unit Cell (CCUC), Department of Chemistry, Faculty of Science, Bangkok 10330, Thailand

^c University of Leipzig, Institute of Theoretical Physics, Faculty of Physics and Geosciences, Postfach 100920, Leipzig 04009, Germany

^d Chulalongkorn University, Metallurgy and Materials Science Research Institute (MMRI), Bangkok 10330, Thailand

^e Faculty of Applied Science and Engineering, Nong Khai Campus, Khon Kaen University, Nong Khai 43000, Thailand

^f Office of Corporate R&D, IRPC Public Company Limited, Rayong, Thailand

^g University of Leipzig, Institute of Experimental Physics I, Faculty of Physics and Geosciences, Postfach 100920, Leipzig 04009, Germany

^h Leibniz University Hannover, Institute of Physical Chemistry and Electrochemistry, Callinstr. 3-3A, D-30167 Hannover, Germany

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ABSTRACT

In the field of nanoporous materials, guest-induced structural changes in metal–organic frameworks (MOFs) attracted great attention over the last years. One example concerns a gate-opening effect in MOF ZIF-8 which was found to occur upon sorption of N₂. To mirror these structural changes in molecular simulations, suitable force fields for the proper description of framework flexibility are required.

We demonstrate that our previously published force field is able to reproduce these structural changes in classical MD simulations. In particular, with our parameter set the diameter of the windows connecting adjacent cavities is found to match the X-ray values almost perfectly. We focus on investigating the impact of the structural changes on the mobility of N₂ molecules in ZIF-8 framework and compare the results with those of another parameter set, which was published recently by Zhang and coworkers.

The size of the windows increases notably, when the critical “gate-opening” loading is surpassed. Most surprisingly, this pronounced increase does not result in a speed-up of the N₂ self-diffusivity. It appears, that a complex interplay of host–host and host–guest interactions increases the mutual hindrance of the N₂ molecules and counter balance the acceleration of the mobility due to the larger window size.

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1. Introduction

Among the promising new porous materials which have been synthesized during the last few decades, metal–organic frameworks (MOF's), or porous coordination polymers (PCP's), play an important role as they can be tailored easily in order to fit the needs of industrial applications [1–8]. A distinctive property of many MOF systems which cannot be found among the classical microporous materials is their dynamic and flexible structure changing in response to external stimuli in a reversible manner – these are so called 3rd generation MOFs [9]). The structural changes of these MOF's might be distinguished in those which involve substantial changes of the unit cell size (often referred to as “breathing”) [1,10,11] and those with small or no changes of the cell parameters but a reorientation of certain parts, e.g. of the organic linker molecules (often referred to as “gate-opening”) [12–14].

While many MOF's are not very stable there are subgroups of them that are stable under a wide range of thermal conditions

and loadings with different guest molecules including water. Among these MOF's, the zeolitic–imidazolate frameworks (ZIF's) play a prominent role [15–19]. Recently, experimental results showed that bulky guest molecules could be found in the cavities of ZIF's with small pore openings (windows) which connect adjacent cavities [13,20–26]. In some cases, the adsorption isotherms of guest molecules in these systems exhibited a pronounced S-shape or inflection [27,13,14]. Combined adsorption and in-situ XRD studies revealed reversible structural changes in the inflection region, induced by the adsorption of guest molecules [12,14,28]. This is the above mentioned effect of “gate-opening”, generated by a reorientation of the linker molecules.

For the prediction of these effects and the knowledge-based use of such responsive ZIF's a depiction by molecular simulations is highly desirable but turned out to be a challenging task. Among the ZIF-family, ZIF-8, with methylimidazolate as linker molecule, is the most prominent representative. First attempts to describe the influence of gate-opening in ZIF-8 involved Monte–Carlo simulations with rigid lattices of the two different structures for low and high loadings of N₂ that allowed to reproduce the adsorption isotherms well [12,21]. Considering the Rietveld window size of 3.4 Å is clear that the structural flexibility has to be taken into

* Corresponding authors.

E-mail addresses: siegfried.fritzsche@uni-leipzig.de (S. Fritzsche), supot.h@chula.ac.th (S. Hannongbua).

account to capture the dynamics of guest molecules correctly, even for small guest molecules like methane with a critical diameter of 3.8 Å [29]. Flexible structures were widely investigated in a series of simulation studies [1,29–36], using several sets of parameters describing the interaction of lattice atoms and the interaction of guest molecules with the ZIF lattice (see e.g. [29,32,33,37]). However, it was only recently that the continuous structural transition of ZIF-8 upon guest uptake could be captured in classical MD simulations [27]. In their work, Zhang et al. focus on the adsorption of N₂ at low temperatures and of CH₄ and CO₂ at 298 K.

In this paper, we will examine in detail the interplay of structural properties and self-diffusion of adsorbed guest molecules. We demonstrate, that the parameter set suggested earlier in [30] is able describe the structural change in the ZIF-8 lattice induced by the N₂ adsorption and compare the predictions for the guest dynamics with the values obtained using the parameters suggested in [27]. NPT simulations have been done for the comparison of different parameter sets on the ZIF-8 lattice structure while the investigations of the structural and diffusion properties have been carried out in the NVE ensemble. To the best of our knowledge this represents the first study in which the impact of the dynamic structural change of ZIF-8 on guest diffusion is examined in detail in molecular simulations.

2. Computational details

2.1. General features of the simulations

All MD simulations reported in this paper are done using the DL_POLY program, version 2.20 (see e.g. [29]). Ewald summation was applied for the electrostatic fields that are connected with the particle charges. Interaction parameters are given in the [supporting material](#). The simulation time step was 1 fs.

In this paper we compare two flexible models of ZIF-8 and refer to them as *parameter set A* (Chokbunpiam et al. [30]) and *parameter set B* (Zhang et al. [27]), respectively. The parameter values for N₂ were taken from the transferable potential for phase equilibria (TraPPE, Potoff et al. [38]). This force field describes nitrogen by three force centers namely the two N atoms and a fictive charge center placed at the center of mass of the N₂ molecule to maintain charge neutrality. N₂ is a nonpolar molecule. The bond lengths between the three centers are fixed. Further details of the parameters used in the simulations are given in the [supplementary material, Sections 1–6](#).

2.2. Force field validation using isothermal-isobaric (NPT) ensemble

First, MD simulations were performed in the isothermal-isobaric (NPT) ensemble with a simulation box that contains 2 × 2 × 2 unit cells (initial size: 33.982 × 33.982 × 33.982 Å³) for flexible ZIF-8 framework with N₂ at different loadings between 0.5 and 30.0 molecules per cage.

The system was examined at the two temperatures, 258 and 300 K. The pressure was chosen to be 1 atm or zero to determine the box size of the empty framework, respectively. The systems were allowed to equilibrate for 1 ns and then data were collected for additional 2 ns. The van der Waals (VDW) interaction cutoff was set to be 14 Å.

2.3. Structure of the flexible ZIF-8 framework and dynamic properties of N₂ within the ZIF-8 framework (NVE ensemble)

A geometric parameter that is very important for diffusion is the diameter of the so-called window that connects adjacent cavities and has to be passed by diffusing particles. Contrary to

other force fields, this parameter was well reproduced in NVE ensemble simulations by the force field proposed in [30].

The window diameters of the 6-membered rings in ZIF-8 at 258 K (temperature of the X-ray experiment in [15]) and 300 K (room temperature) from MD simulations are compared with the window diameters of the 6-membered rings in ZIF-8 from X-ray diffraction data. These simulations of flexible ZIF-8 frameworks were started in the isochoric–isothermal ensemble (NVT) to equilibrate the system for 5 ns and then allowed to equilibrate for another 0.5 ns in the micro-canonical ensemble (NVE), followed by the production run of 5 ns (NVE). The time step was set to 1 fs. The unit cell size in our NVE simulation is the same as in the XRD data.

Again, the flexible ZIF-8 frameworks were studied at N₂ loadings between 0.5 and 30.0 molecules per cage for parameter set A and B (see Section 2.1 for their definition). These parameter sets were used to determine the window diameter of 6-membered rings of ZIF-8 and the self-diffusivity of N₂ in ZIF-8. The temperature in the simulation box was set to 300 K. To shed light on the mechanism of the gate-opening on an atomic level, the window diameter of the 6-membered rings of ZIF-8 is compared with the self-diffusivity of N₂ molecules and density plots of the N₂ location and the radial distribution functions in ZIF-8.

2.4. The dynamic properties of C₂H₆ within the ZIF-8 framework

In our earlier work (Chokbunpiam et al. [30]) no indications for the occurrence of gate-opening were evidenced for C₂H₆ diffusion in ZIF-8. Additional analysis of these data was carried out to obtain the corresponding density plots. The results of N₂ and C₂H₆ are compared to spot further details of the gate-opening effect.

3. Results and discussion

3.1. NPT versus NVE ensemble – making a choice in MD simulations

When performing molecular dynamics (MD) simulations the question arises, whether they should be done in the NPT (constant particle number *N*, pressure *P*, temperature *T*) or, in the NVE (constant particle number *N*, total energy *E*, temperature *T*) ensemble. The NPT seems to be closer to the experiment, but a reliable adsorption isotherm must be available to know for which loading of guest molecules which pressure must be chosen in the simulation. The concentration of adsorbed guest molecules would adjust itself to a chosen pressure if the gas phase which is surrounding the MOF crystal would be included into the simulation. But, this is normally not the case. Moreover, it should also be checked if isotropic pressure control is appropriate in the case of crystals with anisotropic flexibility.

The unit cell size is often used to validate the force field in NPT. For ZIF-8, the XRD cell size [15] can be better reproduced by certain interaction parameter sets [27,37] than by other sets [30]. However, only set B from Zhang et al. [27] could reproduce the size of the ZIF-8 unit cell given in [15] with decent accuracy. Interestingly, in our own calculations with set B at pressure zero (empty framework) the cell size is found to be about 0.25 Å larger than the XRD value (Fig. S2), while in [27] at a pressure of 1 atm excellent agreement was reported. Probably, the pressure in [27] is induced by N₂, although this is not mentioned explicitly. In the XRD experiments, free solvent was present in the ZIF-8 cavities and the surrounding inside the capillary was formed by the presence of a “small amount of mother liquor” and the fraction of air being present in the moment of sealing [15]. As both, solvent and atmosphere might change the unit cell size somewhat, the choice of adequate boundary conditions in comparing simulations remains debatable.

Clearly, the presence of N_2 above the “gate-opening pressure” should be omitted as the structural transition occurring at higher N_2 -loadings leads to changes of the unit cell size.

We have performed NPT runs using parameter sets A (from Chokbunpiam et al. [30]) and B at different temperatures and a variety of N_2 loadings (see Section 7 in the supporting material). We find that set A predicts a sudden increase in the cell parameters once a loading of 18.4 molecules per cavity is crossed (Fig. S3). This is the exact loading where the gate-opening effect has been found in experiments [12]. This result gives a first indication, that also set A is capable of capturing the gate-opening effect in MD simulations. Furthermore, we note that set A returns cell size parameters which are somewhat too small. However, as discussed in the following section, all further investigations were done in the NVE ensemble.

In NVE simulations the cell size is an input parameter and exact by definition. This means that in NVE small fluctuations of the total simulation cell box size are suppressed. However, since the simulation box contains eight unit cells, the cell size of an individual unit can still fluctuate. When it comes to the dynamics of diffusing guest molecules, geometry and the size of the windows connecting adjacent cavities is far more important than small deviations in the total size of the MD box. This bottleneck must be passed by the diffusing particles. So, the bottleneck allows some guest particles to pass while others cannot. The reproduction of this important feature is now discussed in the following section.

3.2. Lattice and guest dynamics investigated by MD simulations in the NVE ensemble

As discussed in the previous paragraph we focus now on the window size to validate the force fields for investigations of the guest dynamics in the NVE ensemble. The box size is fixed at the experimentally measured values. The window diameters of the ZIF-8 framework for parameter sets A and B at 258 and 300 K are shown in Fig. 1.

The window diameters obtained from the maxima of the distributions for systems A and B are 3.375 and 3.675 Å, respectively. The FWHM (full width at half maximum) of all curves is larger than 0.6 Å, illustrating the pronounced flexibility of the windows, which allow the passage of molecules with a size notably above the XRD window size (3.4 Å). Interestingly, for both sets the window diameter did not change with temperature. For parameter set A, the window diameter of the 6-membered rings is in excellent agreement with the experimental XRD data (3.4 Å), whereas parameter set B overestimates the window size by almost 0.3 Å. Thus, parameter set A appears to be more suitable than parameter set B to reproduce dynamic properties of guest molecules, as in pore systems with larger cavities framed by narrow windows of similar

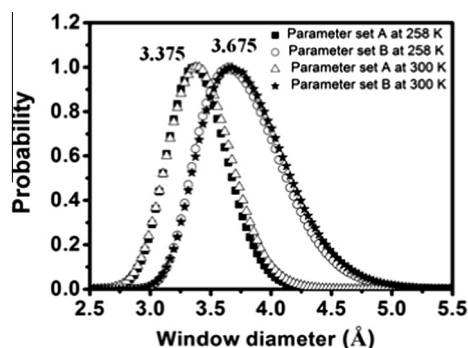


Fig. 1. Distributions of the diameter of the 6-membered rings (windows) of ZIF-8 at 258 and 300 K for parameter sets A and B.

size as the diffusion molecules usually the window size dictates the molecular mobility.

In-situ XRD experiments evidenced a relocation of the linker molecules occurring at higher N_2 -loadings [12]. As both parameter sets A and B predict a change in the box size at the expected loading in NPT simulations, we also expect to find a sudden increase in the window size if the “gate-loading” loading is exceeded. In fact, such changes are observed for both parameter sets at 300 K (see Fig. 2a).

Both parameter sets predict a slight decrease in the window size as the loading is increased from zero to 18.44 molecules per cage, followed by a substantial increase afterwards by 0.36 Å for set A and 0.58 Å for set B, respectively. While in set A this increase proceeds gradually as the loading rises from 18.44 to 24.7 molecules per cage, set B suggests a steep increase only when the loading crosses 24.7 molecules per cage. With indicating a transition point for a structural change near to a concentration of 18.44 N_2 molecules per cage, set A matches closely the gate-opening loading found in experiments by Fairen-Jiminez et al. [12]. We demonstrate in Section 3.3 that this structural change resembles exactly the change of the ZIF-8 framework from the close to the open form as discussed in [12].

In analogy to Fig. 1, the distributions of the window size for set A in dependence of the loading is displayed in Fig. S4. Interestingly, the curves are shifted as a whole without a change in the FWHM. Hence, the fluctuations in the window size occur independently of the rotation of the linkers. If the broad width of the size distribution would be solely caused by a rotation of the linkers, the width should strongly decrease above the “gate-opening loading” of 18.44 molecules per cavity, as the open form would mark the upper limit of the window size.

Most surprisingly, the sudden change in the window size is not accompanied by an enhancement of the self-diffusivity (see Fig. 2b). The D_s values from both parameter sets slightly increase until a loading of 18.44 N_2 molecules per cage and amount between 10^{-9} and 10^{-10} m^2/s . Afterwards, the diffusivity starts to decrease and then drops sharply by 2–3 orders of magnitude in the high coverage region between 25 and 30 N_2 molecules per cage. The reason for this strong decrease is simply that at very high loadings the mutual hindrance of the N_2 molecules becomes the dominating factor and strongly reduces the mobility. The magnitude of the diffusivity is in accordance with experiments and simulations of other small molecules. For CH_4 and CO_2 self-diffusivities in the range of $1-3 \times 10^{-10}$ m^2/s were measured [35]. Studies based on molecular simulations with a flexible lattice report numbers in the range of 10^{-11} – 10^{-9} m^2s^{-1} , depending on the chosen set of parameters [29,31,32,34,35]. The mobility of H_2 or D_2 is mostly reported in the order of 10^{-9} – 10^{-7} m^2s^{-1} [29,31,36]. As general characteristics one finds a weak dependence of the self-diffusivity on loading. Our values for N_2 fall in between the intervals reported for H_2/D_2 and CH_4/CO_2 , as expected based on the kinetic diameter of these molecules. Also, the trend of the loading-dependence for low-intermediate pore fillings agrees well with the results for other molecules. The counter-intuitive finding that the increase of the window size does not result in a corresponding speed-up in the molecular mobility will be examined in more detail in Section 3.3.

Fig. 2b also shows that the self-diffusion coefficients D_s from MD are nearly equal for the parameter sets A and B in spite of the notably different window diameters. N_2 is a small molecule and the correct window size is more important for the diffusion of larger molecules.

3.3. More detailed examination of the gate-opening effect

The structural transition observed using parameter set A is visualized in Fig. 3. In (a) and (b) a projection of a whole cavity

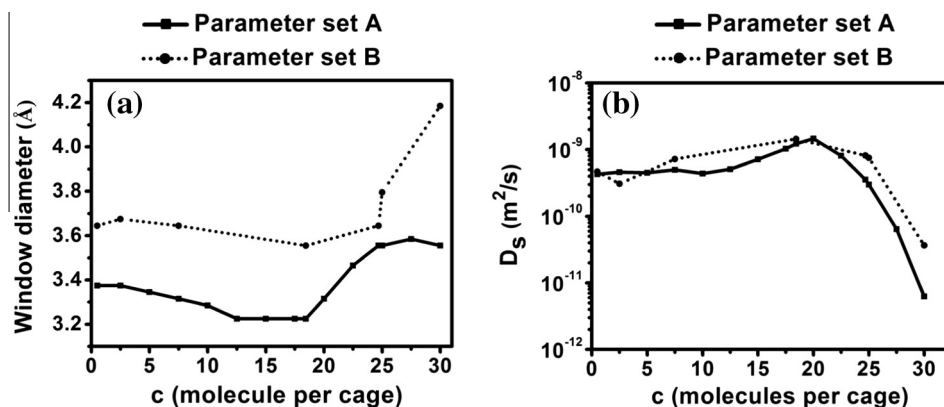


Fig. 2. (a) Window diameter and (b) self-diffusivity D_s for N_2 molecules in a ZIF-8 framework for the parameter sets A and B as a function of nitrogen loading.

including the surrounding lattice atoms on a plane is shown for the high density and the low density configuration, respectively. The two kinds of windows are marked by different colors. The re-orientation of the imidazolate linkers in the ZIF-8 framework from closed (Fig. 3a) to open form (Fig. 3b) is exactly the structural change which has been discovered in the high-pressure experiment of Moggach et al. [28] and in the work of Fairen-Jiminez et al. [12] and Zhang et al. [27] for N_2 adsorption. The re-orientation of the linkers is easily recognized when both structures are superimposed (see close-up views of the 4- and 6-membered ring windows in Figs. 3c,d).

To shed some light on the physics behind the loading dependence of the N_2 diffusivity we consider in the following the probability density plots for location of the N_2 molecules at different loadings as derived from our MD simulations using parameter set A at 300 K in the NVE ensemble (see Fig. 4). The results are

compared with the density plots for C_2H_6 , as obtained from the MD runs presented in [30].

The plots show the sites of the center of masses of the guest molecules at every 100 steps from the last 50000 steps of the production run in order to visualize the probability density to find a particle at a given site. To aid the interpretation of the density plots the radial distribution functions (RDFs) were calculated in addition (see Section 9.2 in the supporting material). The density plots at N_2 loadings between 2.5 and 18.4 molecules per cage (Fig. 4a–d) show a high density of N_2 molecules in the funnel shaped entry region to the 6-ring windows and a lot of N_2 molecules passing the windows. The entry region was also specified for CH_4 and CO_2 as preferred adsorption sites [16] and also C_2H_6 seems to prefer this region (Fig. 4g–h). As already stressed in [28] and [1] and confirmed in our own RDF calculations (see Section 9.2 in the supporting material), the structural transition at 18.4 N_2 molecules per cavity is accompanied by a packing rearrangement of the guest molecules. Now, also sites near the 4-ring windows (see Fig. 3) are populated – which is only possible when the linkers are distorted. The linear shape of the N_2 molecules together with the rearrangement then allows to accommodate more molecules in the cavities. The picture looks similar to density plots of the phase transition in hard sphere or LJ liquids. At high loadings, the RDFs reveal also a particularly strong interaction of the N_2 molecules with the atoms at the CC and CT positions (Fig. S5). Obviously, the force constants describing the dihedral (stretching and bending) of the linker are of vital importance to capture the structural change in molecular simulations. In [27] it was concluded that their treatment of the dihedral of the imidazolate linker is similar to the description of the dihedral (X–CT–CT–X) in the AMBER force field, in which CT are sp^3 hybridized carbon atoms. In our simulations we use the AMBER force field which may explain partially why the gate opening effect is similarly described by both parameter sets.

A population of the sites near the 4-ring windows is also observed for high C_2H_6 loadings, however without a swing-effect of the linkers [30]. As revealed by the work of Fairen-Jiminez et al. [12], Ania et al. [1] and Zhang et al. [27], the occurrence of guest-induced structural transitions in ZIF-8 is the consequence of a complex interplay of different factors, including guest size, shape, packing and interaction with the linker molecules and related changes in the energy landscape of the host structure. So, most likely, it is not only a consequence of the somewhat larger size of C_2H_6 compared to N_2 , that a gate-opening transition is not observed for C_2H_6 . However, the situation might change in other

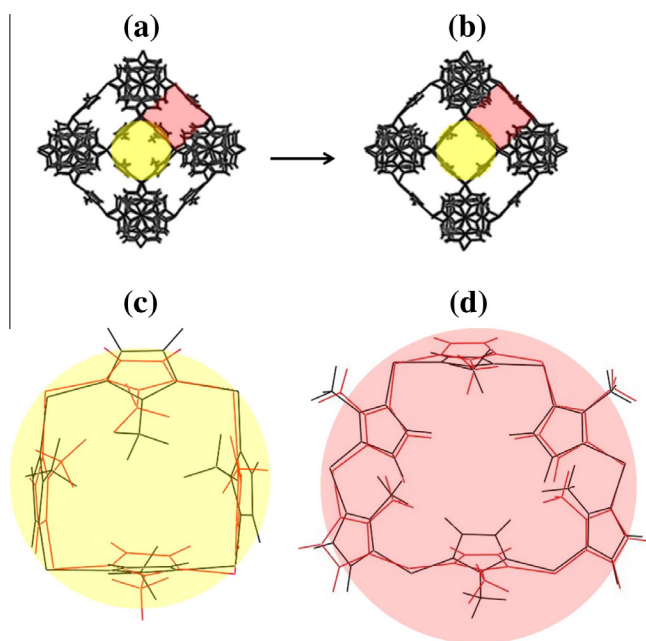


Fig. 3. The change of the orientation of the imidazolate linkers in ZIF-8 framework for (a) low (0.5 N_2 per cage) and (b) high (15.0 N_2 per cage) nitrogen loadings. Superimpositions of the low loading (black) and high loading (red) structures are shown for (c) the 4-membered ring (d), and the 6-membered ring. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

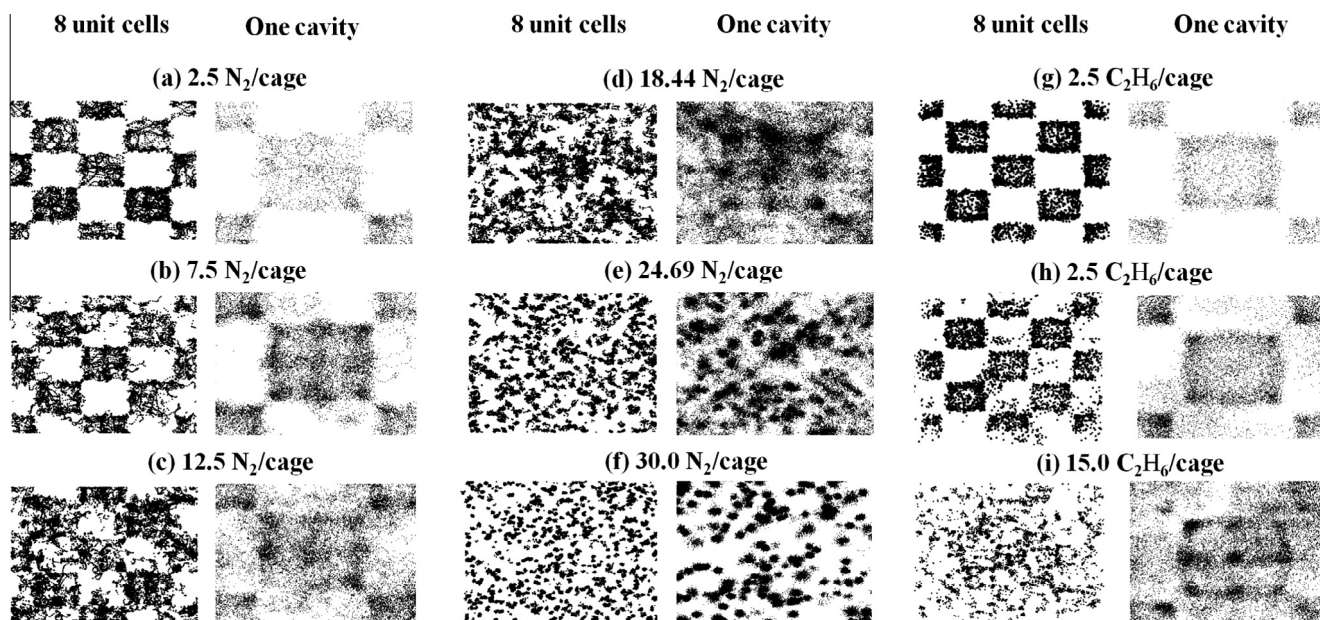


Fig. 4. Comparison of the probability density plots for N_2 and C_2H_6 molecules at different loadings in ZIF-8. In each column the right hand picture shows the projection of a single cavity centered in the picture while the left hand picture shows a larger area. Dark regions indicate high probability density.

ZIF structures. In [13] by quantum density functional simulations of C_2H_6 in ZIF-7, a quantum mechanical explanation for the gate-opening was proposed. This underlines to the conclusion that within the highly flexible ZIF lattices a complex interplay of the host-guest system results in gate-opening effects. In case of N_2 in ZIF-8, classical simulations are accurate enough to capture its dynamic occurrence.

A structural change caused by C_2H_6 uptake was found in classical simulation for another MOF structure, viz. MOF Zn(tbip) [39,40]. At higher loadings an increase of the diameter of the bottlenecks in the channels occurred that results in a rapid increase of the self-diffusion coefficient. Interestingly, this opening of the bottleneck could only be observed for ethane, not for methane, while for ZIF-8 the classical gate-opening appears for N_2 , but not for C_2H_6 [30,34]. For N_2 in ZIF-8, the increase of the window size is not correlated with an increase in the diffusivity (Fig. 2b). Apparently, the reorientation and closer packing of the N_2 molecules at higher loadings has also implications for their mobility. Besides the size of the narrow window also the probability to jump through the window and the chance to find a free site behind contribute to the diffusivity. Induced by the structural transition and the rearrangement the possibility to find N_2 in the window region is notably increased. In addition, the closer packing makes it more difficult for the N_2 molecules to exchange their places. Both contributions overbalance the speed-up in the diffusivity which would be expected solely based on the window size and result in the decrease of the self-diffusivity above 18.4 molecules per cage (see Fig. 2b). Finally, at 30 N_2 molecules per cage the N_2 molecules can oscillate only in isolated regions (Fig. 4f), resulting in the sharp decrease of the mobility.

4. Conclusions

This work was focused on investigating the impact of structural changes on the dynamics of N_2 molecules in the MOF ZIF-8 by classical MD simulations. We have demonstrated that our parameter set proposed in [30] can well reproduce the guest-induced change of the ZIF-8 lattice structure in MD simulations performed in the NVE ensemble. The structural change witnessed in our simulations

is identical with the structural transition described earlier in experiments by Fairen-Jimenez et al. [12]. The force constants describing the stretching and bending of the linker are essential to capture the structural change at high N_2 loadings.

We compared the results with calculations using an alternative parameter set developed recently by Zhang et al. [27] which is able to reproduce the unit cell dimensions, N_2 adsorption and mechanical properties. In contrast to the parameters suggested in [27], for our set the diameter of the windows connecting adjacent cavities is found to match the X-ray values almost perfectly. As the window diameter is of crucial importance for the diffusion of molecules with diameters close to the window size, we reckon that our set may provide a more realistic prediction of guest diffusion.

In accordance with the experiments, our simulations indicate gate-opening at a high concentration of 18.4 N_2 molecules per cavity. At this critical nitrogen loading, the methylimidazolate linker have to distort to allow the adsorption of further nitrogen molecules. Most surprisingly, the pronounced increase in the window size by 0.36 Å does not result in a speed-up of the molecular mobility. The accelerating effect of the larger window size appears to be overcompensated by an interplay of different factors initiated by the relocation of the N_2 molecules above the “gate-loading”. They include stronger interactions between the N_2 molecules and the increased probability to find N_2 molecules in the window region. This leads to an increased mutual hindrance which overbalances the expected mobility increase based on the larger window size, and results in the observed decrease of the self-diffusivity. The situation might be different for a hypothetical molecule, which induces similar structural changes but has a size closer to the limiting dimensions of the windows connecting the cavities.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.micromeso.2013.12.012>.

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