Molecular Dynamics Simulation of Benzene Diffusion in MOF-5: Importance of Lattice Dynamics**

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In recent years, metal organic frameworks (MOFs), a class of porous 3D linked coordination polymers, have attracted increasing attention.[1] Owing to the discrete molecular nature of the building blocks, fine tuning their properties appears possible,[2] and they hold great potential for applications in a number of fields, for example, for the storage of hydrogen and other gases, for gas separation, as gas sensors, and also as catalysts.[3,4] In all these areas the diffusivity of the guest molecules through the porous material is of crucial importance. Experimental information on diffusion in MOFs is, however, still scarce. Very recently Stallmach et al. published the first measured self-diffusion coefficients for MOF-5,[5] which is one of the most intensively studied systems. MOF-5 is the parent structure of the isoreticular frameworks (and is also abbreviated as IRMOF-1); in these frameworks Zn_4O tetrahedra are connected by terephthalic acid linkers, forming a three-dimensional cubic network.[6,7] In the case of zeolites, theoretical molecular dynamics (MD) simulations have been used extensively to study guest molecule diffusion.[8] If an accurate molecular mechanics forcefield is used, diffusion coefficients can be predicted. In addition, insight into the diffusion mechanism can be gained, which is of pivotal importance for a rational design of porous materials.

Since then a number of such theoretical studies of guest diffusion have been performed also for MOFs.[9–13] To our knowledge, all simulations have excluded the lattice dynamics by freezing the experimental geometry of the framework. This is mainly because of to the inability of the (often generic) forcefields used in these studies to reproduce the framework structure. In some cases the nonbonding interaction parameters (especially for H_2) have been reparameterized.[10,14,15] However, for an accurate description of the diffusion of larger guests the inclusion of lattice motion and deformation is crucial. We have therefore extended the MM3 forcefield,[16] which is well known to accurately describe structures and conformational energies of organic molecules, with parameters for the Zn_4O moiety, based on first principles DFT

calculations of nonperiodic model systems.[17] Our extended MM3 forcefield correctly predicts the structure of MOF-5 and reproduces DFT-calculated vibrational modes of the model fragments reasonably well. Note that this is in contrast to the very recently published forcefield focusing on a noncovalent description of the Zn−O interaction.[18] The forcefield parameters are given in the Supporting Information, and the details of the parameterization and validation will be published separately.[17] As a first test of our new forcefield we investigated diffusion of benzene, focusing on the effect of lattice dynamics.[5,19]

To determine the self-diffusion coefficient D_{self} and its temperature dependence, we sampled 15 MD trajectories (0.5 ns equilibration and 2.5 ns sampling time) for a system of 10 benzene molecules within the 424-atom unit cell (uc) of MOF-5 at temperatures of 250, 300, 350, and 400 K (see the Supporting Information). We used 10 guest molecules to improve statistics;[13] this umber is between the loadings of the experimental studies (6.3 molecules per unit cell in reference [5] and 15.8 molecules per unit cell in reference [19]). Judging from the results of the load dependence of D_{self} in MOF-5, this value is still on the lower limit.[12] In a second set of calculations the framework atoms were kept fixed at their optimized positions. In Figure 1 the mean square displace-

Figure 1. Mean square displacements (averaged from multiple time origins) with respect to the time interval Δt at 300 K for a flexible lattice (thin lines: individual trajectories, thick line: averages). The inset shows the double logarithmic plot of the average, giving a slope of 1 (light gray line) for larger time intervals.

ment (MSD) curves (averaged over multiple time origins) of the benzene centers of mass (COM) over the corresponding time intervals Δt are given (flexible framework at 300 K).
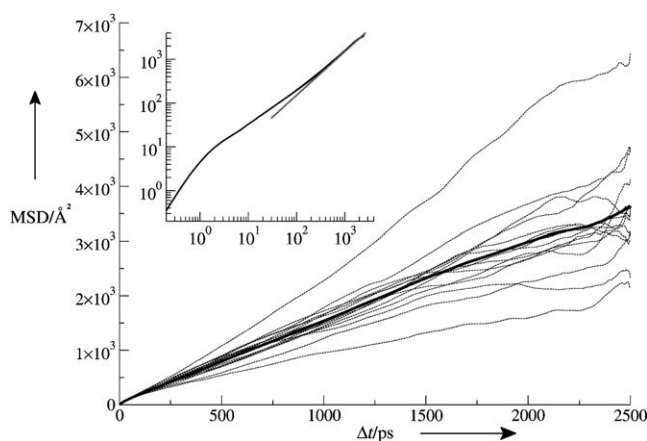
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According to Einstein's equation [Eq. (1)] the self-diffusion coefficient can be derived from the slope of these curves.[20]

$$D_{self} = \frac{1}{6}\lim_{t\to\infty} d/dt \langle |r(t)-r(0)|^2 \rangle \qquad (1)$$

For the determination of D_{self} and its statistical error we followed the method suggested in reference [21]. Further details of the data analysis are given in the Supporting Information. The diffusion regime, with a slope of 1 in the double logarithmic plot (see inset in Figure 1) of the averaged MSD, starts at about $\Delta t = 200$ ps. From the average over all trajectories a D_{self} of $(2.49 \pm 0.29) \times 10^{-9}$ m^{2}s^{-1} is derived. This value corresponds very well to the experimental value determined by Stallmach et al., who found values of 1.8×10^{-9} m^{2}s^{-1} and 2.0×10^{-9} m^{2}s^{-1} for the intracrystalline self-diffusion coefficients of benzene, depending on the measurement parameters.[5] It can be concluded that our forcefield is able to reproduce the relevant intermolecular interactions. Note that only the MOF itself has been parametrized, whereas the intermolecular interaction parameters were taken from the standard MM3 parameter set and were not "tuned" to reproduce the experimental diffusivities.[10] Unfortunately, only the room-temperature self-diffusivity has been measured in the case of benzene.

Surprisingly, under identical conditions, a rigid MOF lattice results in substantially higher diffusion coefficients. At room temperature we find a D_{self} of $(19.5 \pm 2.0) \times 10^{-9}$ m^{2}s^{-1}, which is about an order of magnitude larger than the calculated result for the flexible lattice and the experimental value. This difference is well beyond the statistical error and is consistently observed for all temperatures. For zeolites it is often found that diffusion is decreased by a rigid lattice as a result of increased steric strain.[22] In Figure 2 D_{self} is given in a logarithmic scale versus the inverse temperature in an Arrhenius-type plot. From the slope, an energy of activation for the diffusion of 13.8 ± 1.3 kJ mol^{-1} is found for the flexible model. The corresponding activation energy for the rigid model of 4.01 ± 0.78 kJ mol^{-1} is substantially lower. In reference [5], activation energies for the diffusion of methane and ethane in MOF-5 o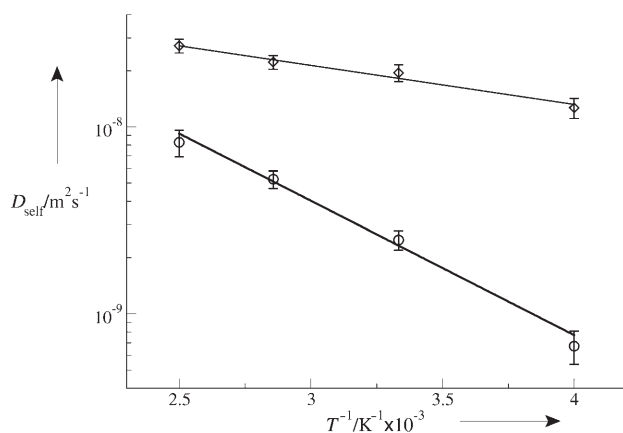f 8.5 and 9.5 kJ mol^{-1}, respectively, have been determined. Thus, for the larger benzene molecule, our calculated value for the flexible framework appears reasonable, whereas the value for the rigid model is too low.

For insight into the diffusion mechanism we calculated the spatial probability distribution of the benzene COM at $T = 300$ K from all trajectories. An isosurface of this probability density (flexible framework) reveals 32 distinct maxima (Figure 3). The unit cell of MOF-5 consists of eight cubic
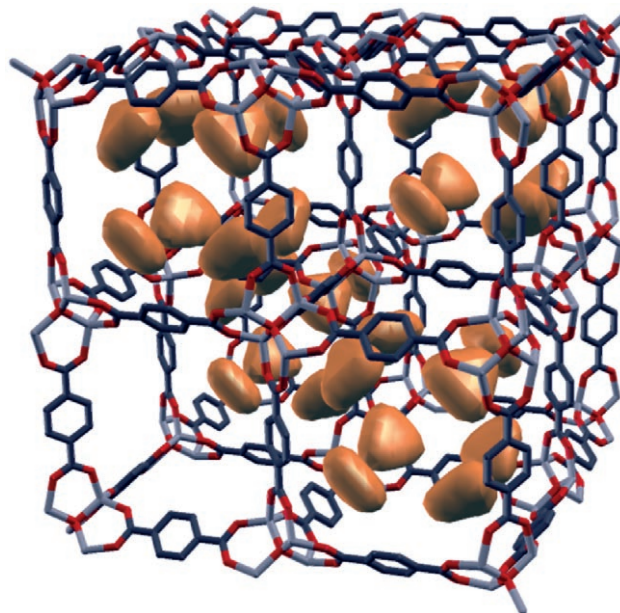

Figure 3. Probablility distribution of the benzene COM in the flexible framework at 300 K. The framework structure shown is the relaxed geometry, which was used in the rigid calculations. Hydrogen atoms are omitted for clarity. The surface is shown for a probability value of 0.0008 (probability normalized for the unit cell).

cells. In four of these cells, labeled A, the phenylene ring planes are facing inside, whereas in other B cells their sides are directed inwards. The benzene molecules accumulate in "pockets" in the corners of the A cells, just above the faces of the Zn_4O tetrahedra. As a result, on average 92.4% reside in an A cell, whereas only 7.6% are found in a B cell. A preference for this site has been found in DFT calculations for H_2 as well.[23] In a previous forcefield study on benzene (using a rigid lattice), this location was identified as the global energy minimum, but no interaction energy was given.[19] We find a total binding energy of 41.5 kJ mol^{-1} for a single benzene molecule in this pocket (flexible lattice). Note, that the COM probability distribution represents an ensemble average and includes an integration over all the remaining $3N-3$ internal and rotational degrees of freedom. The long-range diffusion results from the hopping of a benzene molecule from one A cell to the next A cell, as indicated by the solid arrow in the contour plot of the probability density on a plane through the maxima of the pockets (Figure 4a). The squared distance of the A-cell centers $(\sqrt{2} \times 12.9$ Å$)^2 =$

Figure 2. Arrhenius-type plot of D_{self} versus T^{-1}; ○: flexible framework, ◇: rigid framework.
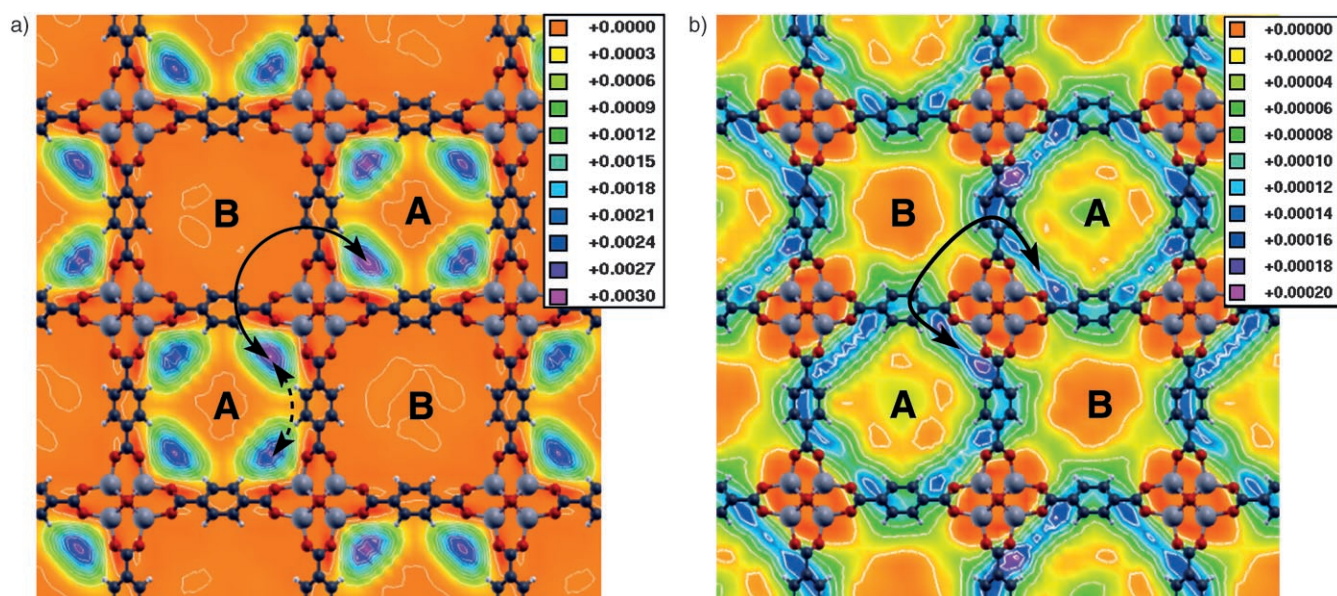
Figure 4. Contour plot of the COM probability density in planes a) through the maxima of the binding pockets and b) through the cell centers (flexible framework at 300 K). The solid and dashed arrows indicate the inter- and intracell hopping events, respectively.

330 Å^2) compares well with the onset of the diffusive regime (see inset in Figure 1). Careful inspection of the probability density reveals the most probable pathway for this hopping: starting from the A-cell pocket the guest molecules enter the B cell in the center of the connecting window and cross the B-cell diagonal, since there is a minimum of the probability density in the center of the B cells (plane through cell centers shown in Figure 4b; note that the scale is about an order of magnitude smaller than in (b)). In addition, an intracell hopping with a lower energy of activation will occur (dashed arrow in Figure 4a). It is likely that the isotropic rearrangement process measured by Gonzalez et al. with an activation energy of 6.14 kJ mol^{-1} can be assigned to this intracell hopping.[19]

An analysis of the difference of the probability distributions for flexible and rigid lattice reveals that the framework motion leads to a decreased population in the center of the cells and a significant increase in the binding pockets (see the Supporting Information for a graphical representation). Thus, a correlated motion of especially the linker phenylene rings with the benzene molecules results in an increase of the probability to find them in the A-cell pockets. Note that this is a purely dynamic effect, since the benzene binding energy in the pocket for the rigid and the flexible model differs by less than 0.1 kJ mol^{-1}. In other words, the potential well is approximately of the same depth but it becomes wider owing to the ability of the framework to adapt to the relative position of the guest molecules. As a consequence, the activation energy necessary to leave the pocket and to pass through the B cell is higher for the flexible model.

As a next step we will investigate the load dependence on the diffusion of benzene, especially for loads at and above 32 molecules per unit cell, where all binding pockets can be occupied. In addition, we are currently simulating the

diffusivity of other organic guest molecules, as well as larger (metal organic) molecules with anisotropies similar to that of benzene (e.g. ferrocene) inside MOF-5.[24] Preliminary calculations for methane diffusion, using the unmodified MM3 parameterization for alkanes, give a D_{self} of $(37.8 \pm 3.5) \times 10^{-9}$ m^{2}s^{-1} and $(87.5 \pm 8.8) \times 10^{-9}$ m^{2}s^{-1} for the flexible and the rigid model, respectively ($T = 300\,K$; 10 CH$_4$ molecules per unit cell). For the nearly spherical CH$_4$ molecule the correlation of lattice motion is much smaller, leading to a reduction of D_{self} by only a factor of two. In previous work values of around 30×10^{-9} m^{2}s^{-1} for a rigid lattice model have been calculated using different intermolecular interaction parameters.[12, 13] Thus, the theoretical values differ by a factor of three for different parameterizations and are all below the experimentally determined value of about 170×10^{-9} m^{2}s^{-1}.[5] Obviously, for the smaller and much more weakly interacting methane, a very accurate description for the host guest interaction is needed. We are currently reparameterizing the nonbonded interaction parameters for alkanes based on first-principles calculations following the strategy by Sagara et al.[15]

Our results here demonstrate that with the new extended MM3 forcefield for MOF-5 it is possible to predict the self-diffusion coefficient of a molecule like benzene with an accuracy comparable to the uncertainty in corresponding experimental measurements. This holds, however, only when the lattice motion is included, which was not the case in previous studies owing to deficiencies of existing forcefields. In addition, the simulations allow a deeper insight into the mechanism of molecular transport, which is relevant for a rational design of modified MOF systems. Since any Zn$_4$O-based isoreticular framework having an organic linker covered by the standard parameter set can be treated without further parametrization, our results set the stage for a

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theoretical prescreening. This will be a valuable tool for the further development of MOFs in gas storage, separation, or sensor applications.

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