

UNIVERSITY OF LEIPZIG

MASTER THESIS

Investigation of adsorption and diffusion of hydrogen guest molecules in the Metal-Organic Framework ZIF-11 by computer simulations

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1 Introduction:

Metal Organic Frameworks (MOFs) are promising materials for gas separation, gas storage and catalysis. One of the scientific problems at our time is to find a way to store hydrogen in a tank to use it as fuel for cars and in many industrial applications it is necessary to divide a gas mixture into its compounds. These are only two example where the Metal Organic Frameworks are a subject of interest.

The Metal Organic Frameworks have the advantage that there is a huge variety of structures that can be made from different building blocks, namely metal knots and organic linkers [13]. But this is in a way also the problem since one will need different material properties for different applications and it is hard to find the structure with the wanted properties.

The variety is big enough that it would not be the best approach to simply do measurements for all materials since a few of them are very difficult and expensive to fabricate. The other way to approach this problem is to try to do research for some promising materials to understand why their special structure is leading to a certain property. With this knowledge it might become easier to sort out some of the MOF materials and to recognise those with special properties before fabricating them.

ZIF-11 as one material of the MOF group has shown good hydrogen adsorption behaviour (see page 6) and also a good stability [21]. Therefore this material has been chosen to be one of the MOF materials of big interest.

This master thesis is investigating the behaviour of hydrogen guest molecules in ZIF-11. The main tool for the work on this master thesis were molecular dynamics simulations but also Gibbs Monte Carlo simulations were performed. The molecular dynamics simulations were carried out with the DL_Poly [12] software package while the Gibbs Monte Carlo simulations were done with a self written fortran program that was developed from a program for teaching purposes written by S. Fritzsche.

To carry out those simulations it is necessary to describe all occurring interactions. This means that one has to describe hydrogen-hydrogen interactions, the interactions of hydrogen with the ZIF-11 lattice and for a flexible simulation also the interactions of the ZIF-11 atoms with each other. All of that will be done classically in this thesis and therefore a set of parameters will be needed to describe the classical interactions. A main part of this master thesis is about the parameter research, - tests and - improving strategies. So far only one publication was found that was providing parameters for ZIF-11 [29] where the main part of the parameter set was taken directly from the Dreiding FF database. The Dreiding parameter set is known to lead to stiff bonds as it was investigated in the diploma thesis from Loreen Hertäg [11] [10]. The foundation of the parameter set of this thesis are the AMBER [5] parameters. But those parameters were

modified to reproduce the X-ray structure and a measured adsorption isotherm for hydrogen guest molecules in ZIF-11 better then the the unchanged AMBER parameters. Another big part of the master thesis was the investigation of the ZIF-11 structure. This thesis will give an insight into the different linker types that occur in ZIF-11, the 2 different pores and the window of the connection between them. The investigation of those topics has been done by self-written computer programs which were using GPUs for all expensive calculations (namely the "ISO"-, "XYZ_2_DLPOLY"- and the "ProcessHistDL2" program).

The parameter set and the structure of ZIF-11 which were obtained were used for molecular dynamics simulations to obtain values for the self-diffusion coefficient under different conditions. The behaviour of the self-diffusion coefficient is one of the main subjects of the obtained results.

Therefore it can be summarised that a lot of work for this master thesis was going into developing a force field for ZIF-11 that reproduces existing measurements and afterward this force field was used to calculate the values of unknown observables especially the self-diffusion coefficient.

2 Metal Organic Frameworks

2.1 General information:

Metal Organic Frameworks is the name for materials consisting of:

- metallic knots (metal ions like Cu(2+), Ni(2+) or Zn(2+)) and
- organic linkers (organic ligands which are able to connect to the knots e.g. Imidazolates).

Since the late 90's Metal Organic Frameworks (MOFs) have become a topic of interest for many research groups. This development started with the work of O.M. Yaghi in 1999 where he published the structure of MOF-5 [15].

The MOFs have become a topic of interest for research groups because of the huge variety of different structures that can be realized with different knots and linkers and the high inner surface areas. So there is the hope that, if we understand enough about the MOFs, we can create or choose MOFs according to the properties that we need.

MOFs can be built with a lot of different structures because of the variety of different linkers and knots which could be used as building blocks. And even if we choose the same knots and linkers they can build different lattices like the structures of ZIF-11 and ZIF-7 (see Figure 2.1).

There are many applications for porous Materials like MOFs. They can be used e.g. for: gas separation, gas storage and catalysis. In addition the Metal Organic Frameworks are promising materials for building hydrogen containers suitable for future hydrogen cars. In Table (2.1) it is shown how much hydrogen can be stored in a volume of 1 m^3 of the porous material ZIF-11 and in an empty container with the same volume for one temperature.

	Hydrogen in a free volume	Hydrogen in $1m^3$ of
	of $1m^3$, at standard pressure	ZIF-11 (MOF) at 77 K $$
	and 77 K, treated as an ideal gas	and standard pressure [21]
Amount Sorbed	158 mol	6800 mol

Table 2.1: Adsorption amount in different porous materials and in a free volume



Figure 2.1: ZIF-11 (left) and ZIF-7 (right) with the same knots and linkers but different structures

2.2 ZIFs - a subgroup of the Metal Organic Frameworks:

ZIFs (zeolitic imidazolate frameworks) are a subgroup of the Metal Organic Frameworks. The linkers of ZIFs are imidazoles (see figure 2.2) and the knots are transition metals like Zn,Co or In. The reason for the term "zeolitic" is that the structures of Zeolites and ZIFs are very similar [21]. The metal ions are building a tetrahedral structure with the 4 connecting nitrogen atoms of the imidazole derivatives. This is equivalent to the Si(Al)O₄ units in the zeolites [22]. In addition the angle between two metal ions connected by a Linker is close to 145° which is also commonly found in many zeolites between two silicon atoms connected by oxygen (see figure 2.3) [21].

2.3 ZIF-11

So far there are only a few papers about ZIF-11, mostly of experimental nature ([3], [14], [21], [27], [29], [9]). The organic Linker of ZIF-11 is shown in figure 2.5.

The linkers and knots are forming a framework of 1392 atoms per unit cell (see figure 2.6). The structure of ZIF-11 is known from X-ray diffraction measured by the group of Omar M. Yaghi [21] and was provided by the Cambridge structural data base.

The unit cell has a cubic shape with a length of 28.76 Å.

ZIF-11 has two different pores in the structure. The pores of each type are connected to 8 pores of the other type. One definition of a pore diameter is the diameter of the biggest sphere that still fits into the framework and that not intersects the van der Waals



Figure 2.2: Example for Imidazolderivates [3]



Figure 2.3: The bridging angles (M=metal ion, IM=Imidazol) [21]

surface of the lattice atoms. The van der Waals surface means here the sum of spheres around the lattice atoms a with the radius $r = 2^{1/6} \sigma_{a,a}$. With this method a diameter of 14.12 Å for pore type one and 13.89 Å for pore type 2 was obtained. To distinguish these pores they will get separate names: the Centre Pore (containing the red ball in figure 2.7) and the Edge Pore (containing the blue ball in figure 2.7).

According to the force field that was developed in this thesis and the X-ray structure there should only be one type of channels (marked with the red circle in figure 2.6) between the pores for hydrogen. This can be concluded with an equipotential surface picture and will be explained in chapter 8. Therefore this thesis contradicts the statement from the paper of Pavel Kortunov [14] where it is said that the window of ZIF-11 is a 8-ring window since the window that was identified in this thesis is a 6-ring window. The window diameter of this connection of adjacent cavities is 3.02 Å where it was testes what the smallest circle is that fits into the window and that does not intersect with the van der Walls surface of the lattice atoms.

The lattice structure will be shown and explained in further detail in section 5.1.



Figure 2.4: The Linker of ZIF-11



Figure 2.5: Scanning electron microscope pictures of ZIF-11 [27]



Figure 2.6: ZIF-11 framework



Figure 2.7: ZIF-11 pore types (the biggest fitting sphere for the Centre Pore is red; the biggest fitting sphere for the Edge Pore is blue)

3 Hydrogen in adsorption experiments

An adsorption experiment with a porous material can be imagined with the simplified setup that a piece of porous material is placed in a container together with a gas. This gas will have a pressure and a temperature and it will be adsorbed by the porous material partially.

This chapter is about the properties of the surrounding gas which is not adsorbed into the porous material and which will in our case be hydrogen. It is important to know the difference that this surrounding hydrogen will act like an ideal gas, while the hydrogen in the porous material should not be described in that way.

The conditions for the surrounding hydrogen in this thesis are ranging form 77 K up to 298 K in a pressure range of up to 10 bar. It has been checked that the assumption to treat hydrogen as an ideal gas is justified under those conditions.

Figure 3.1 shows an isotherm of free hydrogen gas at 77 K. The agreement of the hydrogen data obtained from NIST Chemistry WebBook [6], the ideal gas equation and the van der Waals equation is good enough to accept the ideal gas approximation. In fact the hydrogen van der Waals parameters are amongst the smallest that a gas can have. Zero van der Waals parameters would mean a perfect ideal gas and since the hydrogen parameters are very small [31] it is reasonable that the ideal gas equation approximates hydrogen behaviour in a wide range compared to other liquids.

If we plot again an adsorption isotherm for 298 K and again for a pressure up to 10 bar we get a very similar picture that also shows a good agreement of hydrogen data, the ideal gas equation and the van der Waals equation. Therefore we have looked at the limits of the conditions that this thesis will be dealing with. We assume that in the regions between those limits the ideal gas approximation also holds. This assumption will be needed for the fugacity expansion (chapter 7) and the pressure evaluation from molecular dynamics simulations (section 9.3.1).



Figure 3.1: Free hydrogen isotherm at $77~\mathrm{K}$



Figure 3.2: Free hydrogen isotherm at 298 K

4 Theory of molecular dynamics computer simulations

The dynamical behaviour of particles due to acting forces are classically described by the Newton Equations. Those differential equations can, in most cases, not be solved analytically, especially when a lot of molecules with complex interactions are involved. One approach to this problem is to do the integration of the equations of motion numerically. Therefore one gets approximated trajectories with a behaviour that is realistic enough to look at the statistical behaviour. From that predictions for the values of some observables of interest can be gained (see for example [7]).

To carry out such molecular dynamics simulations it takes a set of initial conditions and the description of the interaction potentials of the atoms with each other. Then a computer program is used to do the numerical time integration to get trajectories of the particles. For this master thesis the software package DL_Poly [12] was used.

The last step is then (if the time integration software does not provide it) to use additional computer programs to calculate from the obtained trajectories the statistical behaviour of observables of interest.

4.1 Periodic boundary conditions and the minimum image convention

For computer simulations one has to find a balance between two things: accuracy and reasonable computation time. In principle one could try to start a simulation with 1 mol of particles but the computational time, with the computers we have toady, would very likely exceed the live time of the scientists who started the simulation. The world record for a particle number in a computer simulation is $1.1 \cdot 10^{11}$ (value from June 2011 [28]) and therefore far away from the avogadro constant.

The periodic boundary conditions are dealing with the fact that in many cases we can't treat a system with realistic dimensions. This master thesis is about a metal organic framework and therefore a crystal structure. Here the idea is rather intuitive to do simulations only for one small fraction of the system that is repeating itself periodically in space. To apply this method the simulation cell has to be big enough that particles can not interact via short range potentials with their own images.

The simulation computes the dynamics of one original simulation cell and when a particle for example leaves the simulation box through the right Y-Z plane, the periodical image of this particle in the left hand cell will enter the simulation box through the left Y-Z plane (see red arrows in figure 4.1). Of course this periodicity of the system is not realistic and some large scale effects can not be observed with this assumption. But for some quantities it is reasonable to conclude from the behaviour of one small fraction that is repeating itself periodically to the behaviour of a real macroscopic MOF. In this thesis only one unit cell of ZIF-11 will be included in the simulation box to have acceptable computation time.

The minimum image convention deals with the fact that in many cases short range potential values can be set equal to zero for a atom distance greater than or equal to half of the simulation box length. Therefore the one particle energy of - and the force acting on particle i are calculated by summing up over the nearest images to particle i. This means for example that, if particle j is in the original box together with particle i but they have a distance bigger then half the box length in one spatial direction, than not j will contribute to the one particle energy of i but j' which is in one of the neighbouring periodically images of the original simulation box (see green arrows in figure 4.1). For further explanations and details about this topic see [7] [2].

4.2 Velocity-Verlet integration algorithm

The velocity Verlet integration algorithm is one of the common algorithms for the integration of the Newton equations of motion.

The starting data for one time are the spatial coordinates and velocities of the particles. It is then the task to approximately calculate the spatial coordinates and the particle velocities after a discrete time step h according to the equations:

$$\dot{\vec{x}} = v \tag{4.1}$$

$$\dot{\vec{v}} = \frac{\vec{F}}{m}.$$
(4.2)

The way the velocity-verlet time integration algorithm does the integration for the spatial coordinates is the aborted Taylor expansion. When we know the first two derivatives of a function for one time t we can approximate the value for t+h with a second order Taylor expansion. The second derivative will be the acting force that can be calculated with the known interaction potential. Then we get for the next time step the approximation like:

$$\vec{x}(t+h) = \vec{x}(t) + h \cdot \vec{v}(t) + \frac{h^2}{2m} \vec{F}(t).$$

We only have the first derivative of the velocity, namely the acceleration. Therefore another technique is implemented for the time integration of \vec{v} . The integration algorithm for the velocity matches the trapezoidal rule:



Figure 4.1: Periodic boundary condition and minimum image convention

$$\int_{a}^{b} f(x) dx \approx (b-a) \frac{f(a) + f(b)}{2}$$

For \vec{v} we get:

$$\vec{v}(t+h) = \vec{v}(t) + \frac{h}{2m} \cdot (\vec{F}(t+h) + \vec{F}(t)).$$

Therefore the integration in the velocity-verlet algorithm is done with:

$$\begin{aligned} \vec{x}(t+h) &= \vec{x}(t) + h \cdot \vec{v} + \frac{h^2}{2m} \vec{F}(t) \\ \vec{v}(t+h) &= \vec{v}(t) + \frac{h}{2m} \cdot (\vec{F}(t+h) + \vec{F}(t)). \end{aligned}$$

4.3 Force Field

The force field describes all interactions of the atoms with each other. For a classical simulation those interactions are approximated by potential functions which are known to give good results. It should be noticed that for example the Lennard-Jones potential can not be complete and strictly derived from fundamental laws.

The interaction potential can be divided into bonded and non bonded potential functions. The non bonded potential functions are very important for the freely moving guest particles in a pore. The bonded interactions are only acting on the atoms in the lattice structure and they are keeping the structures in shape.

From the potential function one gets the forces as: $-\nabla U(x, y, z) = F(x, y, z)$.

The potential function that were used in this thesis will be described in the following text.

Lennard-Jones-Potential [30]

The Lennard-Jones potential is a common empirical potential function to describe non bonded interactions.

Lennard Jones potential:

$$U(r_{i,j}) = 4\epsilon_q \left[\left(\frac{\sigma_q}{r_{i,j}} \right)^{12} - \left(\frac{\sigma_q}{r_{i,j}} \right)^6 \right]$$

The variables are:

- ϵ_q the depth of the potential at the minimum $U(r_{\min}) = -\epsilon_q$ in dependence on the atom type index q
- σ_q is related to the position of the potential minimum r_{\min} by $\sigma = 2^{-\frac{1}{6}} \cdot r_{\min}$; it also depends on the atom type index q

Harmonic bond potential [30]

The bond potential conserves the average distance $r_{i,j}$ between lattice atoms. It is a harmonic potential concerning the distance of the bonded atoms, therefore it can be seen as a second order Taylor expansion around r_0^m with $\frac{\partial}{\partial r}U(r)|_{r=r_0^m} = 0$ and a neglected constant term.

Harmonic bond potential: $U(r_{i,j}) = \alpha_m (r_{ij} - r_0^m)^2$

The variables are:



Figure 4.2: Lennard-Jones interaction

- α_m is a force constant similar to the stiffness of an imaginary spring between the atoms in dependence on the bond type index m
- r_0^m is a parameter to fix the mean distance between the two atoms in dependence on the bond type index m



Figure 4.3: Harmonic bond interaction

Valence angle potential [30]

The valence angle potential conserves the average angle $\Phi_{i,j,k}$ between 3 lattice atoms. It is a harmonic potential regarding the angles between two bonds (this can also be seen as a second order Taylor expansion around the potential minimum).

Valence angle potential:

$$U(\Phi_{i,j,k}) = \beta_n (\Phi_{i,j,k} - \Phi_0^n)^2$$

The variables are:

- β_n is a force constant that is defining the flexibility of changes of the angle between two bonds and that depends on the valence angle type index n
- Φ_0^n is a parameter to fix the mean angle between two bonds which is depending on the valence angle type index n



Figure 4.4: Lennard-Jones interaction

Dihedral angle potential [30]

The dihedral angle potential conserves the angle $\theta i, j, k, l$ between to bonds which are attached to 2 sites of a third bond (as you can see in figure 4.5).

dihidral angle potential: $U(\theta i, j, k, l) = \gamma_o \cdot \cos(p_o \theta_{i,j,k,l} - \theta_0^o)$

The variables are:

- γ_o is a force constant that is defining the torsion flexibility of the j-k bond (figure 4.5) which is depending on the dihedral angle type indice o
- θ_0^o is a parameter to fix the mean dihedral angle which is depending on the dihedral angle type index o
- p_o is in most cases an integer value and describes for how many dihedral angles the dihedral potential possess a minimum; this parameter also depends on the dihedral angle type index o



Figure 4.5: Dihedral angle potential

electrostatic potential [30]

The electrostatic potential as a non bonded interaction depends on the atom distance r_{ij} and is defined as:

$$U(r_{ij}) = \frac{1}{4\pi\epsilon_0} \frac{q_i q_j}{r_{ij}}.$$

The variables are:

- q_i, q_j the charges of particle i and j
- ϵ_0 vacuum permittivity

The electrostatic interactions were not included in the molecular dynamics simulations for this thesis because of the properties of hydrogen. The reasons are explained in further detail in chapter 5.2.1.

But generally they are a part of classical molecular dynamics simulations and they should be calculated with a method like the so called Ewald summation ([7], [2]) due to the fact that they are long range interactions.

4.4 Molecular dynamical ensembles

There are different statistical ensembles defined by theoretical physics. Two of the most common ones are:

- the micro canonical ensemble (NVE ensemble)
- the canonical ensemble (NVT ensemble).

Molecular dynamics simulations try to give the user the possibility to do statistics for the wanted ensemble. The easiest case is the NVE ensemble because the Newton equations of motion conserve the energy and only the numerical errors can lead to an energy change. But normally the temperature will not be the same for each time step and to realise an NVT ensemble is more complicated. To deal with this problem thermostats were developed which are applying forces or directly changing the velocities to maintain an average temperature close to a requested one. There are many different versions of such thermostats and a lot of them lead to some unrealistic behaviour in some test cases.

For this master thesis no thermostat was used and the NVE ensemble was chosen instead. By setting the starting kinetic energy to a fitting value it is possible to maintain the average temperature and the behaviour of the simulation becomes comparable to an experiment at a fixed temperature.

For more information about statistical ensembles in simulations see [7].

4.5 The software package DL_POLY [12]

DL_Poly is a software package for the calculation of trajectories of atoms or molecules. It was developed at Daresbury Laboratory by W. Smith and T.R. Forester and is written in Fortran. It provides the most common thermostats, time integration algorithms and interaction potentials and is capable of parallel computing.

DL_Poly needs 3 input files as a starting point for the trajectory computation.

CONFIG file

The CONFIG file contains in any case all initial atom positions and therefore a configuration of the system. The order of the atoms in that file is crucial since they will be referenced to in the FIELD file by the continuous number they get in the CONFIG file. In addition the initial velocities and forces of the atoms can also be included. In the header one can find variables to set the periodic boundary conditions, the dimensions of the simulation box and some other variables.

FIELD file

The Field file structures all atoms into molecule groups and contains all interaction parameters. At the start the number of different molecules is stated and they are defined by naming all of the molecules atoms and how often they occur. The mass and charge of the atoms is defined and they can be set into an immobile state or as free particles. After that all intermolecular potentials are defined with their parameters and by naming the CONFIG file number of the involved atoms.

The last part of the FIELD file describes all non bonded interactions like the Lennard-Jones potential.

CONTROL file

The CONTROL defines what procedures DL_Poly should use and some input variables for those procedures. It gives a huge amount of possible option settings and only a few will be named here:

- the integration algorithm that should be used for the simulation
- the time step for the integration algorithm
- the temperature that a thermostat can use
- the statistical ensemble as which the system should be treated
- the number of time steps that should be carried out
- the intervals in which the configuration data should be printed
- the cut off radius

and many more.

5 Force field development and the lattice shape determination for ZIF-11

The flexible force field of ZIF-11 is the foundation for the flexible molecular dynamics simulation that will be used to determine diffusions coefficients for hydrogen guest molecules in ZIF-11 and other observables.

While it was often sufficient to treat zeolites (another type of porous materials) as a rigid lattice the flexibility of the metal organic framework is in most cases much more important. It was investigated by many researchers, for example by K. Seehamart et al. [25] [26] or Loreen Hertäg et al. [11] [10] that the flexibility plays an important role for the properties of ZIF-8. Therefore ZIF-11 was directly approached with a flexible molecular dynamics simulations.

The force field of a porous material describes all interaction potentials. This includes the interaction between the guest molecules and the interaction of the guest molecules with the lattice. If we want to have a flexible framework, like we do for ZIF-11, we also need the interactions between the lattice atoms.

In this work it was the aim to get a force field that reproduces the average atom positions of the measured X-ray structure and an experimental adsorption isotherm for hydrogen in ZIF-11. This were the so far available experimental data for hydrogen behaviour in ZIF-11. The following chapter will describe how the the force field for ZIF-11 was developed and how the framework structure was found.

5.1 The lattice shape obtained by X-ray diffraction data

One of the most common ways to determine the structure of a crystal is X-ray diffraction. The Cambridge Crystallographic Data centre [1] collects and provides structures determined by X-ray diffraction of varied substances. Those crystal structures determined by X-Ray diffraction will be called X-ray structures in the following text.

The structure of ZIF-11 was published in [21] and was measured at a temperature of 258 K. It is freely available at the Cambridge Crystallographic Data Center. It would have been favorable to have the X-ray structure at a temperature of 77 K since the X-ray structure and an adsorption isotherm at 77 K will be reference measurements to evaluate and adapt the force field. But since this X-ray structure at 258 K and the adsorption isotherm at 77K are the only available data so far they were used in this combination for this thesis. The X-ray structure at 258 K will certainly be deformed in comparison with the X-ray structure at 77 K.

The structure files are containing the information about the smallest part of the lattice

that can be used to complete the hole lattice framework with some structure information (done for example by the mercury program [16]). ZIF-8 as a simple example for that is shown in figure 5.2(a) and 5.2(b).



Figure 5.1: Imidazolate Linker of ZIF-11



Figure 5.2: X-ray structure of ZIF-8

A special property of the X-ray structure file of ZIF-11 is, that there are multiple positions for hole or parts of the linkers. In the X-ray structure file it is mentioned that this is due to fact that some of the carbon atoms were found to be disordered over 2 sites. This means for the force field development that a reasonable combination of those possible linker configurations has to be chosen.

In figure 5.3(a) one can see that there are carbon atoms which are very close to each other. In comparison with figure 5.1 one can notice that those carbon atoms which are very close to each other are forming 2 possible configurations of the linkers (please note that there are only halves of the linkers in figure 5.3(a)).

Therefore one gets that next to one metal node there are 4 Linkers where 3 of them do have 2 possible configurations. The choice of those 3 linker configurations will be explained in the following text and each of the linker types will get a separate name to distinguish them.



(a) smallest part of ZIF-11 that can be used to complete one unit cell



(b) one unit cell of ZIF-11

Figure 5.3: X-ray of ZIF-11

wall linker

Figure 5.4 shows 4 wall linkers as they were chosen out of the 2 possible configurations. One Unit cell of ZIF-11 fits into a cubic box and the face wall linkers are those nearly parallel to the wall of the simulation box as it was chosen in this thesis. In figure 5.4 the top and the bottom linker are nearly parallel to the box wall while the left and right linker are bent towards the viewer. These are the two possible configurations for those linkers. They can be either straight or bent. This would normally give us a lot of possibilities how the wall linkers can be chosen (not only the one shown in figure 5.4). The first possibility would be that all wall linkers would be straight but this leads to the



Figure 5.4: 4 wall linkers

problem that the hydrogen atoms attached to the 6 membered carbon rings would only have a distance of 1.1 Å. This is too tight for non bonded atoms and would lead to very strong forces (for example Lennard Jones forces) on the atoms which would destroy the lattice shape. The second possibility would be to bend all 4 linkers. Then the distance between their hydrogen atoms would go up to 2.16 Å which is still tight for non bonded atoms but not as critical as before. But this possibility is also ruled out by the fact that the distance to the hydrogen atoms of the neighbouring simulations box image would go down to 0.9 Å which is also much too close for non bonded atoms.

Therefore the only possible solution is to alternate bent and straight wall linkers to keep them at a reasonable distance. They have to be chosen with respect to the neighbour unit cell in a way that a bent wall linker is always next to a straight one. If then one of the linkers is chosen the others are completely determined.

corner linker



Figure 5.5: 8 corner linkers

The situation for the corner linkers (figure 5.5) is very similar to the wall linker case. The Linkers can again be straight or bent. They were named corner linkers because of their occurrence in the X-ray structure. They were occurring in the corners of the chosen simulation box.

If all linkers would be straight the hydrogen distance would go down to 1.3 Å which is again too tight. If all linkers would be bent the distance to the linker above would go down to 1.4 Å and therefore this possibility is also rejected.

Therefore the only solution is again to alternate them leading to a reasonable structure as shown in figure 5.5.

Another hint to the alternating configurations of the corner linkers and the wall linkers is that this can also explain the two measured configurations via X-ray diffraction. Since X-ray measures a lot of unit cells at once it would get a mixed picture like figure 5.3(a). In the publication from Bassem Assfour [3] there were also pictures of those configurations which were obtained with density functional theory and showed those alternating configurations of the Corner - a) and wall linkers c) (see figure 5.6).



Figure 5.6: 8 corner linkers

window linkers

The window linkers are most important for the diffusion of guest molecules from one pore to another. They are forming the connection between the two different pores and are therefore essential for the question whether guest molecules will diffuse or not. The choice of the configuration for those linkers is more difficult than for the wall linkers and corner linkers. Only the first possibility where all linkers would be straight can be

ruled out because it would lead to a hydrogen distance of 1.88 Å. This leaves the two possibilities that all window linkers could be bent (see figure 5.7(a))

or that in each window two linkers could be bent and one straight (see figure 5.7(b)). Molecular dynamical test simulations were done for both cases and with interaction parameters which were fitted via rigid Monte Carlo simulations to measured adsorption isotherms separately for both cases. In the case in which one of the window linkers was bent there was no diffusion between pores for more than 20 ns and the value of the potential inside the window that is connecting the pores was around 4.7 kJ/mol while at 77 K the kinetic energy for hydrogen treated as a Lennard Jones particle is only around 1 kJ/mol. Therefore the diffusion from one pore to another one is highly improbable.

Due to the fact that one does only know from the so far measured data that hydrogen is



Figure 5.7: X-ray structure of ZIF-8

diffusing but not how fast, it is not possible to make a strict conclusion that one of the structures can be ruled out. But it is highly probable that one would see no diffusion for the 2 bent,1 straight window linker structure or that the diffusion coefficient would be much smaller than the real one.

In this thesis the window linkers will be treated to be all bent, were the height of the potential in the window is below 0 kJ/mol and diffusion between pores is very probable.

straight linker

It was mentioned that there are 4 different linker types were 3 of them do have 2 possible shapes. Therefore there is 1 linker type left which will only be called the straight linker. Figure 5.8 shows where those straight linkers are located.



Figure 5.8: 4 straight linkers

5.2 Force field parameters

The interactions for the classical molecular dynamics simulations for this thesis were described in chapter 4.3 as:

$$\begin{split} E &= \sum_{i}^{N} \sum_{j>i}^{N} 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right] \\ &+ \sum_{i}^{N} \sum_{j>i}^{N} \frac{1}{4\pi\epsilon_0} \frac{q_i q_j}{r_{ij}} \end{split}$$

$$+ \sum_{m_{bond}(i,j)}^{N_{bond}} \frac{1}{2} \alpha_m (r_{ij} - r_m)^2 + \sum_{n_{angel}(i,j,k)}^{N_{angel}} \frac{1}{2} \beta_n (\phi_{ijk} - \phi_n)^2 + \sum_{o_{torsion}(i,j,k,l)}^{N_{torsion}} \gamma_o \left[(1 + \cos(p_o \theta_{i,j,k,l} - \theta_o)) \right].$$
(5.1)

Each of the interaction potentials (Lennard-Jones, electrostatics, harmonic bond potentials, valence angel potentials, dihedral potentials) does contain several parameters. Those parameters have to be determined from measurements and ab initio quantum mechanical calculations or other resonable methods.

The parameters that were used in this thesis came out of 4 sources:

- Amber force field [5]
- Paper: Force Field for Molecular Dynamics Computations in Flexible ZIF-8 Framework, Bin Zheng, Marco Sant,* Pierfranco Demontis, and Giuseppe B. Suffritti [32]
- Paper: Molecular Dynamics Simulations of Alcohol Dehydrogenase With a Fouror Five-Coordinate Catalytic Zinc Ion, Ulf Ryde [23]
- fitting done by Gibbs Monte Carlo simulations and the fugacity expansion

Amber Force Field [5]

The AMBER force field is a collection of interaction parameters for organic molecules which was derived by several fitting techniques and ab initio methods. The parameters were tested for many different organic molecules and compared with reference data.

The Amber force field parameters will be used in this thesis to describe the interaction parameters of the organic linkers. Therefore most of the interaction parameters are taken from Amber.

The AMBER "parm10.dat" database is organised in a way that real atom types like carbon are divided into subgroups like CB,CK,CA etc. Those subgroups are defined by the environmental conditions in which they occur.

One has to choose the atom types according to their environment.

The atom types used in this thesis are:

- CA: carbons in the six membered ring
- **CB**: carbons that form the junction between the six membered and four membered ring

- CK: carbon in the 5 membered ring next to nitrogen
- NB: nitrogen in the 5 membered ring connected to Zn
- HA: hydrogen attached to the CA carbons
- H5: hydrogen attached to the CK carbon
- **Zn:** the zinc atom

AMBER only provides self interaction parameters $\sigma_{a,a}$, $\epsilon_{a,a}$ for the Lennard-Jones interaction of the lattice molecules. The Lorentz-Berthelot mixing rules were applied to get the interaction parameters for the mixed interactions $\sigma_{a,b}$, $\epsilon_{a,b}$.

Lorentz-Berthelot mixing rules

$$\sigma_{a,b} = \frac{\sigma_{a,a} + \sigma_{b,b}}{2}$$
$$\epsilon_{a,b} = \sqrt{\epsilon_{a,a}\epsilon_{b,b}}$$



Figure 5.9: the atom types of the ZIF-11 linker

Paper: Force Field for Molecular Dynamics Computations in Flexible ZIF-8 Framework, Bin Zheng, Marco Sant,* Pierfranco Demontis, and Giuseppe B. Suffritti [32]

This paper has described a molecular dynamics force field for the Framework ZIF-8. Due to the similarities of the linkers of ZIF-8 and ZIF-11 some of the interaction parameters

that are missing in Amber can be obtained from this paper. Since ZIF-11 and ZIF-8 do have 5-membered rings made of carbon, nitrogen and hydrogen the environment of the nitrogen and zinc atoms are very similar and the interaction parameters should be comparable. Therefore the bond potential Zn-N and the angel potentials Zn-NB-CK, Zn-NB-CB and NB-Zn-NB are taken from this paper. It was shown in this paper that those parameters had led to a very stable framework.

Paper: Molecular Dynamics Simulations of Alcohol Dehydrogenase With a Four- or Five-Coordinate Catalytic Zinc Ion, Ulf Ryde [23]

The torsion potential parameters for X-Zn-NB-X are the last missing parameters (the X's are indicating that the type of those atoms does not matter for the interaction parameters). The parameters for this interaction are set to zero in the paper of Marco Sant to guarantee a high flexibility of the linkers. But it was not mentioned in this paper why this interaction potential should be completely neglected. This thesis will use a small torsion potential instead and the necessary parameters were obtained from the paper of Ulf Ryde.

This paper is providing torsion interaction parameters for several neighbour atoms of the Zn-N bond. Because it did not include the exact neighbours NB-Zn-NB-CK and NB-Zn-NB-CB the X-Zn-NB-X torsion potential value was obtained by averaging over the given parameters for the given neighbours. The $\gamma_{X-Zn-NB-X}$ value of equation 5.1 is therefore set to 2.038 kJ/mol which still is very low in comparison to all other used torsion interaction parameters. The $p_{X-Zn-NB-X}$ parameter was set to 3 and the $\theta_{X-Zn-NB-X}$ value was calculated from the structure determined from the X-ray diffraction analysis.

Atom types $n Zn4 C_{in} (kJ/mol)$					
HC	С	OC-	Zn	3	0.27
С	C	OC-	Zn	3	0.27
HC	C	\mathbf{S}^{-}	Zn	3	0.76
С	С	\mathbf{S}^{-}	Zn	3	0.76
HC	\mathbf{Ca}	Na	Zn	1	-196.8
С	Ca	Na	Zn	1	73.8
Na	Ca	Na	\mathbf{Zn}	1	80.0
HO	N	Zn	O=C	3	-1.03
HO	N	Zn	OH	3^{a}	-0.75
HO	N	Zn	OH2	3^a	-0.19
HO	N	Zn	OH^-	3	-5.45
HO	N	Zn	OC^-	3	-4.02
HO	N	Zn	\mathbf{S}^{-}	3	-0.79
Ca	Na	Zn	0=C	2	11.8
Ca	Na	Zn	OH	2	11.8

Figure 5.10: Zn-N torsion parameters [23]

Fitting done by Gibbs Monte Carlo simulations and the fugacity expansion

The hydrogen molecule was treated as a Lennard Jones particle in this thesis [4]. The parameters were obtained by fitting the results of rigid Gibbs Monte Carlo simulations to measured data from [21] with the result shown in figure 5.11. The fugacity expansion was used for comparison. The Gibbs Monte Carlo Simulation will be explained in chapter 6, the fugacity expansion in chapter 7. The unit of the amount of adsorbed particles will be explained in appendix 15.1.



Figure 5.11: Measured [21] data in comparison to Gibbs Monte Carlo simulation data for the fitted hydrogen values

5.2.1 The Coulomb interactions

The parameters for the Coulomb interactions are the partial charges of the lattice atoms. A set of partial charges for ZIF-11 was obtained by a progress report by Oraphan Saengsawang [24] who has calculated them with the "antechamber" module of Amber. For the final set of the previously described parameters the partial charges were included. This simulation has had a larger deviation of the average atom positions from the X-ray structure than the simulation without partial charges (see table 5.1). The deviation from the X-ray structure was big enough to open connections of adjacent cavities at room temperature which should be closed according to the X-ray structure (see figures 5.12 and 5.13; and chapter 8 for the interpretation of equipotential surface pictures). A NPT simulation revealed that the inclusion of charges also lead to a shrinking lattice (see table 5.2).

example	mean deviation from the X-ray structure per particle in Å
MD simulation	0.238245
including charges	
MD simulation	0.06133
excluding charges	

Table 5.1: Table of mean deviation of the average atom positions from the X-ray structure





Figure 5.12: ISO surface picture at 3 kJ/mol calculated from the average atom positions of a NVE simulation including charges

Figure 5.13: ISO surface picture at 3 kJ/mol calculated from the average atom positions of a NVE simulation excluding charges

Therefore the inclusion of Coulomb interaction would have lead to many unwanted effects conflicting with measured data. For the neutral hydrogen the inclusion of charges would have only a direct effect on the lattice-lattice interaction and would not directly have an effect on the lattice-guest interactions. For those reasons the simulations for this master thesis were neglecting the partial charges and therefore the Coulomb interactions. This means that the resulting force field, as it is, should only be used for neutral guest molecules.

Since it would be desirable to have a force field for all kinds of guest molecules chapter 10 makes a proposal for compensating the Coulomb and Lennard Jones forces by adjusting

example	stable box length in Å
MD simulation	26.56
including charges	
MD simulation	28.44
excluding charges	
X-ray structure	28.76

Table 5.2: Table of the stable box lengths

the structural interaction parameters. This method was not used because it would have gone beyond the time limit of a master thesis.

5.3 Improvement of the structural parameters

It was mentioned in Section 5.1 that the linkers of ZIF-11 occur in different shapes. The AMBER force field provides only one set of parameters and therefore all the linkers would take the same average shape. Since it is important for the diffusion behaviour which shape the Window Linkers have (the height of the potential wall in the window depends strongly on the linker configuration) it was not sufficient to use the amber structural parameters.

Therefore all the distances-, angles- and torsional angel parameters were not taken from the AMBER force field. Those parameters were chosen as the real angles and distances from the X-ray structure. This of course leads to a low deviation of the average lattice shape from the X-ray structure, see table 5.3.

Test calculations:			
example	mean deviation from the X-ray strucutre per particle in Å		
amber parameters	0.2257		
own structural parameters	0.0613		

Table 5.3: Table of the mean deviation of the average atom positions from the X-ray structure

5.4 The XYZ_2_DLOLY program

The spatial coordinates of ZIF-11 were obtained as a CIF file from the Cambridge structural data base. The software mercury was used to obtain an XYZ file from this CIF file which is the input data for the self written XYZ_2_DLPOLY program (see appendix 15.2).

As the name suggests this program was written to create the DL_Poly input files: FIELD and CONFIG out of an XYZ file and all necessary interaction data.
It is relatively easy to create a CONFIG file. One only has to print out the simulations box dimensions, the spatial coordinates of all atoms and some other variables. It is a more difficult task to create a FIELD file. The FIELD file contains all lattice interactions and therefore all information about the lattice structure. Each bond, valance angle and dihedral angle has to occur in the file with the index of the atoms which are part of the interaction. Therefore the FIELD file for ZIF-11 has more than 9000 lines. The idea of the XYZ_2_DLPOLY program was to store the lattice structure by saving it into C++ objects. The linkers were saved into a linker object and all knots with their neighbour atoms were saved into a knot object. This offered the possibility to describe all the interactions for only one linker and one knot and print it out for all linkers and knot by making a loop over all the objects. Therefore this program is able to create the FIELD and CONFIG file where all interactions and the initial situation are described. The XYZ_2_DLPOLY program calculates also the angles and harmonic bond distances which are used as parameters for the bonded interaction potentials.

5.5 Summary of the interaction parameters

The summary of the interaction parameters has now become a bit more complicated due to the different linker types described in section 5.1.

To have a complete set of parameters all the rest valence angles, bond lengths and torsion angels should be given with respect to the linkers in which those interactions occur. Therefore big tables are necessary to describe all interactions which will be given in appendix 15.3.

6 Theory of Gibbs Monte Carlo computer simulations

Gibbs Monte Carlo simulations are a common way to calculate adsorption behaviour of porous materials. The challenge of this problem is that a simulation that is dealing with the adsorbed gas and the surrounding gas in one big system would in most cases be dominated by surface effects since the number of atoms that can be simulated is limited. One solution for this problem are Gibbs Monte Carlo simulations [20]. The idea is to simulate two separate subsystems: a bulk simulation box of the adsorbed gas and a bulk simulation box of the surrounding gas. Therefore the interface is completely out of consideration. Those two systems should be kept at the same temperature and the total number of guest molecules is fixed. But the two systems are allowed to exchange particles with a certain probability.

Such a simulation does two different steps. It moves particles in the volumes like for separate NVT Monte Carlo simulations for each system and it exchanges particles with a certain acceptance rate. The acceptance rate for the move and exchange of particles will be motivated in the next two sections. For further details see [2] [7].

The Gibbs Monte Carlo simulation program was starting from a Fortran code of S. Fritzsche (supervisor of this thesis) that was designed for teaching purposes. This code was modified and extended to investigate the adsorption behaviour of hydrogen in ZIF-11.

The simulation starts with a random configuration and distribution of the particles over the two subsystems. After a number of simulations steps a Gibbs Monte Carlo simulation will arrive at an equilibrium and will provide average values for the observables of interest. By varying for example the volume of the surrounding gas it is possible to change the pressure of this gas. Therefore it is possible to get the amount of adsorbed molecules in relation to the pressure of the surrounding gas.

It is also important to take care that particles are not placed into low energy regions which can not be reached by particles. Some low energy regions are separated from the pores and the kinetic energy at the considered temperature is not sufficient to overcome the potential walls to get to those regions. It is important to identify those places and either directly reject the moves there or set the particle energy to such a high value that the particles will not get there. Figure 6.1 shows an equipotential surface where the marked region has a very low energy and can not be reached by particles due to a potential wall. To identify trials in those regions a sphere was placed around this region and for each trial it is tested whether the particle would be placed in such a sphere. This was also done for other low energy regions where particles should not be placed. A visualisation of the excluded regions is shown in figure 6.2.



Figure 6.1: ISO surface picture at 3 kJ/mol calculated from the average atom positions of an NVE simulation

6.1 Monte Carlo Steps (like for an NVT-ensemble)

The Monte Carlo Algorithm estimates average values for a statistical observable A [19]:

$$\langle A \rangle = \frac{\int_{\Pi} \exp\left[-\beta H(X)\right] A(X) dX}{\int_{\Pi} \exp\left[-\beta H(X)\right] dX}$$
(6.1)

where Π is the configuration space, X is a point in the configuration space, $\frac{\exp(-\beta H(X))}{Z}$ $\left(Z = \int_{\Pi} \exp\left[-\beta H(X)\right]\right) dX$ is the probability density and H(X) is the energy in state X.

The principle of a Monte Carlo simulation is now not to directly compute the integrals of equation 6.1 but to generate a series of L states X_i that occur with the probability distribution $N(X) = \frac{\exp[-\beta H(X)]}{Z}$ with $Z = \int_{\Pi} \exp[-\beta H(X)] dX$ [2] [7]. In this case the observable average can be approximated with:

$$\langle A \rangle \approx \frac{1}{L} \sum_{i=1}^{L} A(X_i).$$



Figure 6.2: ISO surface picture at 3 kJ/mol calculated from the average atom positions of an NVE simulation with the geometrical objects (in green) for the excluded volume tests

The difficulty is to generate a series of states with the wanted probability. A method to do that is the importance sampling.

Importance sampling

The motivation of the acceptance rate will start from the aim to have a series of states which has the probability distribution $N(X_i)$ where i denotes different states of the configuration space. The series will be produced by changing an old state X_o to a new state X_n and accept the new state with a certain probability. To do the next step the new state will be interpreted as the old state. If we really produce a series of states with the wanted probability distribution the state i will occur in average $m(X_i)$ times where $m(X_i)$ should be proportional to $N(X_i)$. To keep $m(X_i)$ proportional to $N(X_i)$ the average number of changes of X_i to a random other state X_j should be equal to the average number of changes from a random other state X_j to X_i . If this condition is written as an equation it looks like:

$$\sum_{j} m(X_i)\pi(i \to j) = \sum_{j} m(X_j)\pi(j \to i) \Leftrightarrow \sum_{j} N(X_i)\pi(i \to j) = \sum_{j} N(X_j)\pi(j \to i)$$

where $\pi(i \to j)$ is the probability that X_i will be changed to X_j .

It is convenient to impose the stronger condition (detailed balance) :

$$N(X_i)\pi(i \to j) = N(X_j)\pi(j \to i).$$
(6.2)

For further details see for example: D. Frenkel and B. Smit. Understanding Molecular Simulation [7].

This relation will be used to determine a possibility to fix $\pi(i \to j)$ in a way that X_i will be distributed according to $N(X_i)$.

We directly get from equation 6.2:

$$\frac{N(X_i)}{N(X_j)} = \frac{\pi(j \to i)}{\pi(i \to j)}.$$

Where we know that:

$$\frac{N(X_i)}{N(X_j)} = \frac{\frac{exp(-\beta H(X_i))}{Z}}{\frac{exp(-\beta H(X_j))}{Z}} = exp\left(-\beta \left[H(X_i) - H(X_j)\right]\right) = \frac{\pi(j \to i)}{\pi(i \to j)}.$$
(6.3)

It was mentioned that the new state will be found by changing the old state for example by displacing a particle. Then the new state will be accepted or rejected. Therefore the probability of changing from o to n will be the product of the probability $\alpha(o \rightarrow n)$ of a trial move to n and the acceptance rate $acc(o \rightarrow n)$ of that move.

$$\pi(o \to n) = \alpha(o \to n) \cdot acc(o \to n)$$

In most cases $\alpha(o \rightarrow n)$ is chosen to be symmetric:

$$\alpha(o \to n) = \alpha(n \to o).$$

Then equation 6.3 will look like:

$$\frac{\pi(o \to n)}{\pi(n \to o)} = \frac{acc(o \to n)}{acc(n \to o)} = exp\left(-\beta\left[H(X_i) - H(X_j)\right]\right).$$
(6.4)

There are many ways to choose $acc(o \rightarrow n)$ in a way that 6.4 holds. The one of Metropolis et al. [18] is:

$$acc(o \to n) = \begin{pmatrix} exp\left(-\beta\left[H(X_i) - H(X_j)\right]\right) & \text{if } H(X_n) > H(X_o) \\ 1 & \text{if } H(X_n) \le H(X_o) \end{pmatrix}$$

It is easy to check that this choice of $acc(o \rightarrow n)$ does fulfil the condition 6.4.

This defines the Metropolis algorithm that is used to move the particles in the two separate subsystems. The next section will explain the exchange of particles of those two subsystems.

6.2 Gibbs Monte Carlo particle exchange

The particle exchange is done by choosing one particle from one of the subsystems and make a trial to move it to a random position in the other subsystem. For this particle exchange we will need again an acceptance rate.

The way of determining the acceptance rate for particle exchange is very similar to the determination of the acceptance rate for a trial move. The average for the hole system with a total number of N particles should be done in the following way:

$$=\frac{1}{Z}\sum_{n_{1}=0,n_{2}=N-n_{1}}^{N}\frac{1}{n_{1}!n_{2}!}\int_{V_{1}^{n_{1}}}\int_{V_{2}^{n_{2}}}\exp\left\(-\beta\left\[H_{1}\(\mathbf{x_{1}}\)+H_{2}\(\mathbf{x_{2}}\)\right\]\right\)A\(\mathbf{x_{1}},\mathbf{x_{2}}\)d\mathbf{x_{1}^{n_{1}}}d\mathbf{x_{2}^{n_{2}}}$$

Where Z is:

$$Z = \sum_{n_1=0, n_2=N-n_1}^{N} \frac{1}{n_1! n_2!} \int_{V_1^{n_1}} \int_{V_2^{n_2}} \exp\left(-\beta \left[H_1(\mathbf{x_1}) + H_2(\mathbf{x_2})\right]\right) d\mathbf{x_1^{n_1}} d\mathbf{x_2^{n_2}},$$

 n_1 , n_2 are the particles numbers in subsystem 1 and 2, H_1, H_2 are the total energies of subsystem 1 and 2 and V_1 and V_2 are the volumes of the two subsystems. In the next step we will introduce reduced coordinates s:

$$=\frac{1}{Z}\sum_{n_{1}=0,n_{2}=N-n_{1}}^{N}\frac{V_{1}^{n_{1}}V_{2}^{n_{2}}}{n_{1}!n_{2}!}\int\int\exp\left\(-\beta\left\[H_{1}\(\mathbf{x_{1}}\)+H_{2}\(\mathbf{x_{2}}\)\right\]\right\)A\(\mathbf{s_{1}},\mathbf{s_{2}}\)d\mathbf{s_{1}^{n_{1}}}d\mathbf{s_{2}^{n_{2}}}.$$

and get the probability for a state with a certain particle distribution between the 2 subsystems as:

$$N(s_1, s_2) = \frac{V_1^{n_1} V_2^{n_2}}{n_1! n_2!} \exp\left(-\beta \left[H_1(\mathbf{s_1}) + H_2(\mathbf{s_2})\right]\right)$$

Now we look on the probabilities for an old state:

$$N(s_1^o, s_2^o) = \frac{V_1^{n_1} V_2^{n_2}}{n_1! n_2!} \exp\left(-\beta \left[H_1(\mathbf{s_1^o}) + H_2(\mathbf{s_2^o})\right]\right),$$

and for a trial new state where one particle from subsystem 1 is placed in subsystem 2:

$$N(s_1^n, s_2^n) = \frac{V_1^{n_1-1}V_2^{n_2+1}}{(n_1-1)!(n_2+1)!} \exp\left(-\beta \left[H_1(\mathbf{s_1^n}) + H_2(\mathbf{s_2^n})\right]\right)$$

To get the acceptance rate in the same way as we got it for the particle move we have to build the ratio $\frac{N(s_1^n, s_2^n)}{N(s_1^o, s_2^o)}$:

$$\frac{N(s_1^n, s_2^n)}{N(s_1^o, s_2^o)} = \frac{n_1 V_2}{(n_2 + 1)V_1} \exp\left(-\beta \left[H_1(\mathbf{s_1^n}) - H_1(\mathbf{s_1^o}) + H_2(\mathbf{s_2^n}) - H_2(\mathbf{s_2^o})\right]\right).$$

And then we choose the acceptance rate as [7]:

$$acc(o \to n) = min\left(\frac{n_1V_2}{(n_2+1)V_1}\exp\left(-\beta\left[H_1(\mathbf{s_1^n}) - H_1(\mathbf{s_1^o}) + H_2(\mathbf{s_2^n}) - H_2(\mathbf{s_2^o})\right]\right), 1\right).$$

This acceptance rate is for a particle exchange from subsystem 1 into subsystem 2. The acceptance rate for an insertion of a particle from subsystem 2 into subsystem 1 is:

$$acc(o \to n) = min\left(\frac{n_2 V_1}{(n_1 + 1)V_2} \exp\left(-\beta \left[H_1(\mathbf{s_1^n}) - H_1(\mathbf{s_1^o}) + H_2(\mathbf{s_2^n}) - H_2(\mathbf{s_2^o})\right]\right), 1\right).$$

This defines the part of the algorithm that does the particle exchange. An overview over the hole principle algorithm of the Gibbs Monte Carlo simulation is given in figure 6.3. This algorithm approaches quickly the equilibrium and it can be seen that the evaluated chemical potentials of the two systems are in a good agreement after some statistical evaluation time.



Figure 6.3: Scheme of the Gibbs MC simulation

7 Theory of the fugacity expansion

The idea of the fugacity expansion is very similar to the starting idea of the derivation of the virial equation of state. In the virial equation of state the pressure is related to the density by a series in powers of the density. The n'th coefficient of the series is only depending on the temperature and the n-particle canonical partition sum. Since more particles will lead in many cases to a more difficult calculation this is a nice method, because you only have to put in one more particle if the result is not accurate enough. The end result of the fugacity expansion will relate the number of adsorbed particles to the pressure of the surrounding gas by a power series in p. The n'th coefficient will also depend on the n-particle partition sum of the guest molecules in the rigid lattice. The following derivation will explain the fugacity expansion in detail.

The treatment of the porous material that is surrounded by a gas

As it was done for the Gibbs simulation the hole system is divided into two separate subsystems: the surrounding gas and the adsorbed gas (see figure 7.1). Those two systems are connected by having the same temperature and chemical potential. We will look at their grand canonical partition sums.



Figure 7.1: The two subsystems

The surrounding gas/the ideal gas

In this derivation we will assume (see chapter 3) that the surrounding gas is an ideal gas. This assumption holds for example for hydrogen in a wide temperature range. Hydrogen has been used in this thesis but it has to be checked whether the surrounding gas can be treated as ideal before using this method for other gases.

The ideal gas does not consider particle interactions. Therefore the grand canonical partition sum looks like [19]:

$$\begin{split} \Xi &= \sum_{n=0}^{\infty} \frac{1}{h^{3n} n!} \int_{\Pi(\mathbf{p},\mathbf{r},n)} d\mathbf{r_1} ... d\mathbf{r_n} \ d\mathbf{p_1} ... d\mathbf{p_n} \ e^{-\beta \left(\frac{p^2}{2m} - n\mu\right)} \\ &= \sum_{n=0}^{\infty} \frac{1}{h^{3n} n!} \int_{\Pi(\mathbf{p},\mathbf{r},n)} d\mathbf{r_1} ... d\mathbf{r_n} \ d\mathbf{p_1} ... d\mathbf{p_n} \ e^{-\beta \left(\frac{p^2}{2m}\right)} \lambda^n \end{split}$$

where $\lambda = e^{\beta n \mu}$ is the fugacity and $\Pi(\mathbf{p}, \mathbf{r}, N)$ the configuration space. The kinetic part of the integral gives:

$$\int_{\Pi(\mathbf{p},n)} \frac{1}{h^{3n} n!} d\mathbf{p_1} \dots d\mathbf{p_n} \ e^{-\beta(\frac{p^2}{2m})} = \frac{1}{h^{3n} n!} \left(\frac{2m\pi}{\beta}\right)^{\frac{3n}{2}} = \frac{q(T)^n}{n!}$$

where q is defined as [17]: $q = \left(\frac{2m\pi}{\beta h^2}\right)^{\frac{3}{2}}$. For the ideal gas the configurational part is:

$$\int_{\Pi(\mathbf{r},n)} d\mathbf{r_1} ... d\mathbf{r_n} = V^n$$

and the grand canonical partition sum becomes:

$$\Xi = \sum_{n=0}^{\infty} \frac{(q\lambda V)^n}{n!} = exp(q\lambda V).$$

It is known from statistical mechanics [19] that the grand canonical potential looks like:

$$\Omega = -pV = -\frac{1}{\beta}\ln(\Xi),$$

and we get:

$$p = \frac{q\lambda}{\beta}.$$
 (7.1)

That is the result that will be needed on the ideal gas side for the fugacity expansion. It relates the chemical potential and the temperature to the gas pressure. Now we only need the number of adsorbed particles also in dependence on the chemical potential and the temperature (since those qualities should be equal for both systems). Therefore we have to look at the grand canonical partition sum of the adsorbed molecules.

The adsorbed gas:

For the adsorbed gas the grand canonical partition [19] function looks like:

$$\Xi = \sum_{n=0}^{\infty} \frac{1}{h^{3n} n!} \int_{\Pi(\mathbf{p},\mathbf{r},n)} d\mathbf{r_1} \dots d\mathbf{r_n} \ d\mathbf{p_1} \dots d\mathbf{p_n} \ e^{-\beta \left[\frac{p^2}{2m} + \sum_{i=0}^n \Phi(\mathbf{r_i}) + \sum_{i< j}^n W(\mathbf{r_i},\mathbf{r_j}) - n\mu\right]},$$

where $\Phi(\mathbf{r_i})$ describes the interactions of the guest molecules with the rigid lattice. Therefore the rigid lattice acts as an external potential on the guest molecules. $W(\mathbf{r_i}, \mathbf{r_j})$ describes 2 particle interactions of the guest molecules with each other. We can integrate over the momentum space and introduce again the fugacity:

$$\Xi = \sum_{n=0}^{\infty} \frac{1}{n!} \left(\int_{\Pi(\mathbf{r},n)} d\mathbf{r_1} \dots d\mathbf{r_n} \ e^{-\beta \left[\sum_{i=0}^n \Phi(\mathbf{r_i}) + \sum_{i< j}^n W(\mathbf{r_i},\mathbf{r_j}) \right]} \right) q^n \lambda^n,$$

This can be seen as a power series in lambda like:

$$\Xi = \sum_{n=0}^{\infty} a_n \cdot \lambda^n$$

with:

$$a_n = \frac{1}{n!} \left(\int_{\Pi(\mathbf{r},n)} d\mathbf{r_1} \dots d\mathbf{r_n} \ e^{-\beta \left[\sum_{i=0}^n \Phi(\mathbf{r_i}) + \sum_{i< j}^n W(\mathbf{r_i},\mathbf{r_j}) \right]} \right) q^n.$$
(7.2)

Therefore we have an expansion in the fugacity where the n'th coefficient can be calculated from the configurational part of the n-particle partition sum. We will call the configurational part Z_n .

$$Z_n = \int_{\Pi(\mathbf{r},n)} d\mathbf{r_1} \dots d\mathbf{r_n} \ e^{-\beta \left[\sum_{i=0}^n \Phi(\mathbf{r_i}) + \sum_{i$$

And therefore a_n is:

$$a_n = \frac{1}{n!} Z_n q^n.$$

We get the average particle number from the statistical relation [19]:

$$N = \lambda \frac{\partial}{\partial \lambda} \ln(\Xi).$$

Now we already have the particle number in dependence on the chemical potential and the temperature and we want to expand it in a power series:

$$N = \lambda \frac{\partial}{\partial \lambda} \ln \left(\sum_{n=0}^{\infty} a_n \cdot \lambda^n \right).$$

The approximations in this thesis will only be done up to the 2nd order but the formula above can also be used to do higher order approximations. We only take into account the first 3 terms of the sum:

$$N = \lambda \frac{\partial}{\partial \lambda} \ln(a_0 + a_1 \lambda + a_2 \lambda^2 + O(x^3)).$$

It is helpful to realise that $a_0 = 1$. If we look at equation 7.2 we can see that $q^0 = 1$ since $q \neq 0$ and $\frac{1}{0!}$ is also defined as 1. The integral still counts all possible configurations and with no particle there is only one possible state (see [17]). Therefore we have: $a_0 = 1$. And with the second order approximation of the logarithm:

$$\ln(1+x) \approx x - \frac{1}{2}x^2 + O(x^3)$$

we get N as:

$$N = \lambda \frac{\partial}{\partial \lambda} \ln(1 + a_1 \lambda + a_2 \lambda^2 + O(x^3))$$

= $\lambda \frac{\partial}{\partial \lambda} \left([a_1 \lambda + a_2 \lambda^2 + O(x^3)] - \frac{1}{2} [a_1 \lambda + a_2 \lambda^2 + O(x^3)]^2 + O(x^3) \right)$
= $\lambda \left([a_1 + 2a_2 \lambda + O'(x^3)] - [a_1 \lambda + a_2 \lambda^2 + O(x^3)] [a_1 + 2a_2 \lambda + O'(x^3)] + O'(x^3) \right).$

Now we simplify the equation by only taking into account terms with an order lower than λ^3 .

$$N \approx a_1 \lambda + (2a_2 - a_1^2)\lambda^2$$

We put in the definition of a_n and get:

$$N \approx Z_1 q \lambda + \left(2\frac{Z_2 q^2}{2!} - Z_1^2 q^2\right) \lambda^2.$$

And we arrive at the final equation:



The relation between the surrounding pressure and the number of adsorbed molecules

Now we do have the two needed relations:

$$p = \frac{q\lambda}{\beta},$$

$$N \approx Z_1 q \lambda + (Z_2 - Z_1^2) (\lambda q)^2.$$

And because both systems are treated to be at the same chemical potential and temperature we get:

$$N \approx Z_1 p\beta + (Z_2 - Z_1^2)(p\beta)^2.$$

It can be seen that the first order approximation is the ideal gas equation (by neglecting all external potentials Z_1 will become the volume). If we consider interactions we have to calculate the values of Z_1 and Z_2 numerically. How this can be done is explained in chapter 8.

But it should be mentioned that the afford for computing the integrals increases strongly with the order. The Z_3 coefficient would already need a lot of computation time.

It is important to exclude some regions of the simulation box from the fugacity expansion in the same way as for the Gibbs Monte Carlo simulation. Again all regions were exclude from the calculations which had very low energies but are not accessible for the guest particles since they are separated from the pores by high potential walls. The obtained fugacity expansion result for ZIF-11 will be shown in section 9.3.

8 GPU-Software for the calculation of the equipotential surface and the fugacity expansion coefficients

For those two tasks (calculation of the equipotential surface and the fugacity expansion coefficients) the porous material ZIF-11 was considered to be rigid. Due to the interactions with the lattice atoms a guest atom in the structure has different potential energies depending on it is position. If the surface is drawn where a guest molecule would have one special interaction energy with all lattice atoms we will get an equipotential surface for this certain energy (see figure 8.1).

This picture is helpful to determine whether a set of interaction parameters could in principle lead to a diffusion between the pores. The equipotential surface picture can be used to see the hight of the potential walls between the pores. When this value is compared to the average kinetic energy, due to the temperature, its possible to conclude how likely a travelling from one pore to another is.



Figure 8.1: Equipotential surface for 0 kJ/mol for hydrogen in ZIF-11

Using Example:

A guest molecule at 77 K has an average one particle kinetic energy of 0.96 kJ/mol. In figure 8.2 we see an equipotential surface picture for hydrogen in ZIF-11 at 3 kJ/mol. With an average kinetic energy of 0.96 kJ/mol some particles will in some cases also have a higher kinetic energy and will be able to enter regions with a higher potential energy. But the surface with a potential energy that is 3 times the kinetic energy is a boundary that the particle can only cross with a low probability. In figure 8.2 we see the centre pore and the edge pore parts with the equipotential surface as their boundary. We compare figure 8.3 and 8.2 to draw some conclusions.



Figure 8.2: equipotential surface at 3 Figure 8.3: Equipotential surface at 12 kJ/mol kJ/mol

There is a window (a connected equipotential surface marked by a red ellipse) between the edge and the centre pore even at 3 kJ/mol. By varying the energy value one finds that the potential wall between the edge and the centre pore is lower that 0 kJ/mol. This means that hydrogen has the ability to travel from the centre to the edge pores for all temperatures.

In contrast, the connection between the edge pores (marked by a green ellipse in figure 8.2) is closed at 0 kJ/mol and only slightly open for hydrogen at 12 kJ/mol. With such a big difference between the mean kinetic energy of a particle and the height of the potential wall the particle should not be able to travel from one edge pore to another because it is very unlikely to have the necessary kinetic energy at 77 K.

In addition, the connection between the Centre Pores is not even open for 12 kJ/mol (orange circle in figure 8.2 and 8.3). Therefore the only type of connections of adjacent cavities that is open for hydrogen is the one in the red circles in figure 8.2 and 8.3 which is connecting the Centre Pore and the Edge Pore. This explains the statement

that there was no 8-ring window (like in [14]) found in this thesis since the red circles are corresponding to a 6-ring window.

The implementation:

The calculation of an equipotential surface is mathematically rather easy. The simulation box is divided into a certain amount of grid cells with a resolution that can be defined by some input files of the program. To minimise the afford for creating an equipotential surface this program works again with the CONFIG and FIELD file formats of DL_Poly.

The program reads in the configuration data and the guest-lattice interaction parameters and starts to compute for each grid cell the interaction energy that a particle would have at the centre of the grid cell. This calculation is done by the graphic card because it is able to do parallel calculations for each grid cell. Therefore the graphic card is able to compute the equipotential surface for ZIF-11 in a resolution of 200x200x200 in approximately 20 sec while the CPU calculations for a resolution of 100x100x100 already needs at least 5 minutes. The reason for the time difference is that the used graphic card has 480 cores to do parallel computations for the grid cells. The implementation of the program on the graphic card and the therefore fast computation makes this program a very often used tool in the development of this master thesis.

The interaction energies are printed out as a cube file that can be used to draw equipotential surface pictures. But the obtained interaction energies for the grid cells can also be used to do the numerical integration for the fugacity expansion. For example for Z_1 :

$$Z_1 = \int_V d\mathbf{r_1} \ e^{-\beta(\Phi(\mathbf{r_1}))} \approx \sum_{grid \ cells \ i} exp[-\beta(\Phi_i)] \Delta x \Delta y \Delta z.$$

The computation for the second coefficient takes a lot more computational afford and parts of it were therefore executed on the graphic card. For each grid point j the summation is done for the hole grid:

$$I_j = \sum_{grid \ cells \ i} e^{-\beta \left(\Phi(\mathbf{r_i}) + \Phi(\mathbf{r_j}) + W(\mathbf{r_i}, \mathbf{r_j}) \right)} \Delta x^2 \Delta y^2 \Delta z^2,$$

those integral parts where again computed parallel. The summation of all those integral parts gives the approximation of Z_2 :

$$Z_2 = \int_V \int_V d\mathbf{r_1} \ d\mathbf{r_2} \ e^{-\beta(\Phi(\mathbf{r_1}) + \Phi(\mathbf{r_2}) + W(\mathbf{r_1}, \mathbf{r_2}))} \approx \sum_{grid \ cells \ j} I_j$$

Remark:

The equipotential surface gives also a big advantage in visualisation and therefore the understanding of the dynamic behaviour. If we watch the movement of guest molecules together with all the lattice molecules we do not have a good overview in which pore a guest particle is. But if we draw the trajectories together with the equipotential surface we see the boundaries of the guest molecule movement and we can distinguish in which pore a guest particle is located (see figure 8.4).



Figure 8.4: Equipotential surface for 0 kJ/mol for hydrogen in ZIF-11 together with hydrogen particles

9 Simulation results

9.1 Hydrogen-adsorption isotherm for ZIF-11 from Gibbs-Monte-Carlo

The hydrogen adsorption isotherm that was computed by Gibbs-Monte-Carlo simulations can only partly be seen as a real simulation result. The hydrogen interaction parameters were chosen in a way that the adsorption isotherm for the rigid lattice fits to experimental data. The parameter fit has only been done for 2 points of the adsorption isotherm. The plot (figure 9.1) states that the rest of the data fitted pretty well and that the experimental adsorption curve is reproducible with the X-ray structure and the obtained classical parameter set.

In principle it would also be possible to do parameter fitting for the lattice Lennard-Jones parameters but with those degrees of freedom the fitting becomes more complicated and will need much more computational afford. Since the lattice parameters of AMBER were developed by fitting them to experimental results and doing quantum mechanical calculations they were considered to work in a good agreement and that the hydrogen parameters (which are not a part of AMBER) were a good guess for the variation for a parameter fit.

The experimental data were taken from a paper from Park [21] and are therefore defining the environmental conditions where the chosen interaction parameters should work at best. The measurement was done at 77 K and in a pressure range from 0 bar $\leq p \leq 1$ bar.

9.2 Second order fugacity expansion

The fugacity expansion method was explained in chapter 7. The setup is again the same as before: a pile of ZIF-11 material that is surrounded by a gas at conditions where the gas can be treated as an ideal gas. Then the fugacity expansion method determines the coefficients of the functional relation between the ideal gas pressure and the number of guest molecules in the porous material. For calculating those coefficients we just have to know the interaction parameters between the guest- and the lattice molecules since the lattice molecules are treated to be rigid. Therefore we get a way to check the force field parameters of the guest-lattice interactions.

The first order fugacity expansion gives a straight line that should be a tangent in the zero pressure region. Figure 9.2 shows this straight line. The coefficient (slope) was calculated from the parameter set of this thesis.

It seems in the plot that the calculated slope is a good approximation to the starting



Figure 9.1: Messured [21] and simulated adsorption isotherm for hydrogen in ZIF-11 for the units of adsorption see appendix 15.1

slope of the experimental data. To compare the calculated starting slope with the experimental data a fit has been made that is represented by the green line in figure 9.2. With the fitted function it was possible to calculate an estimation for the "real" starting slope of the experimental data. A comparison in table 9.1 shows that the calculated slope is a bit smaller than the one from the fitted function. This can be explained by comparing the Gibbs Monte Carlo simulation results with the first order fugacity expansion. It can be seen that the slope for the Gibbs Monte Carlo simulation should be also slightly smaller than the one of the experimental data since the low pressure values are smaller than the experimental data. Therefore also for the Gibbs Monte Carlo simulation a fit was done with the result shown in table 9.1. The Gibbs Monte Carlo simulation and the fugacity expansion were in complete agreement as they should be since both are computational results from the same parameter set. This means that it is shown here that the fitted parameters gave a good approximation for the hole adsorption isotherm as we have seen in the previous section, but the starting slope was smaller than it should be in comparison with the experimental data, for both the Gibbs Monte Carlo simulation and the fugacity expansion.

The second order fugacity expansion is a parabola that is shown in figure 9.3 for the example of hydrogen in ZIF-11. The first fact to notice is that the plot only shows a



Figure 9.2: Measured [21] and calculated adsorption isotherm for hydrogen in ZIF-11 with the first order fugacity expansion and rigid Gibbs Monte Carlo simulation data

very low pressure region to see this parabola. And it is not easy to compare the second derivatives at zero pressure of those two curves. Therefore the calculated value of the second coefficient and the one from the experimental data are given again in table 9.1. Those two values are not in a very good agreement since the value from the experimental data is more than twice the calculated one. This questions the method of the fugacity expansion and therefore it will be explained for what the fugacity expansion method can be used.

We have seen from the comparison of the experimental results and the calculated values that the fugacity expansion should not be used for a real prediction of adsorption isotherms. This statement is supported by figure 9.4 where we see the best second order fugacity expansion that we can do since the parameters of this parabola were directly determined by the first and second derivative of the experimental data fit at zero pressure. It is just a second order Taylor expansion and this expansion works for the curve shape of the ZIF-11 adsorption isotherm only for very low pressure region. The only way to increase the pressure range where this method works would be to

calculate more coefficients, maybe up to the 4. or 5. order. But unfortunately even the 3. coefficient will need a huge amount of computation time that is unreasonable with the computers of our days.

But the method can be used to get a first evaluation of a parameter set. And in this way it was used for a previous fit to get good starting points for the Gibbs Monte Carlo simulations since the fugacity expansion is much faster than the calculation of 2 values of the Gibbs Monte Carlo data.

In addition to that a second order Taylor expansion has been also done for the hydrogen adsorption in ZIF-8 where it has worked a lot better. Therefore the applicability of this method depends much upon the porous material.



Figure 9.3: Measured [21] and calculated adsorption isotherm for hydrogen in ZIF-11 with the second order fugacity expansion

9.3 Results from molecular dynamics simulations

One of the main tools of this thesis were molecular dynamics simulations. In theses simulations interaction potentials for the particles and a starting configuration were used to numerically calculate the following trajectories of the particles. For this thesis a lot of different simulation runs were done which had produced large HISTORY files



Figure 9.4: Measured [21] and calculated adsorption isotherm for hydrogen in ZIF-11 with the second order fugacity expansion with parameters from experimental data

	first coefficient in Å	second coefficient in $Å^2$
from experimental	$1.985 \cdot 10^{7}$	$3.658 \cdot 10^{14}$
data fit		
from fugacity	$1.245 \cdot 10^7$	$1.411 \cdot 10^{14}$
expansion		
from Gibbs-MC	$1.248 \cdot 10^{7}$	$1.490 \cdot 10^{14}$
data fit		

Table 9.1: Table of the first and second coefficient of the fugacity expansion

containing the atom positions at different time steps. Those files were used to do statistical evaluations of observables of interest, especially the diffusion coefficient and the chemical potential.

The ensemble of these simulations is in all cases the NVE ensemble where the kinetic energy was chosen to correspond to a certain average value of the temperature. Therefore it is possible to talk about simulations at a certain temperature.

9.3.1 Adsorption isotherm for hydrogen in ZIF-11 at 77K

It is not an easy task to get an adsorption isotherm from molecular dynamics simulations. The problem is that the molecular dynamics simulation (MD simulation) only simulates a box of bulk material of ZIF-11 and that we have to find the pressure of the surrounding gas from this simulation. But it was mentioned several times in this thesis that the surrounding gas and the adsorbed guest molecules have to have the same chemical potential in equilibrium. Therefore the task is to get the chemical potential from the molecular dynamics simulation and to calculate the pressure of the surrounding ideal gas from this chemical potential and the constant temperature. If this is done for some molecular dynamics simulations with different particle numbers we get an adsorption isotherm.

The chemical potential of the MD simulation was evaluated with the Widom test particle method like [7]:

$$\mu = -k_b T \ln\left(\frac{V}{\Lambda^3(N+1)}\right) - k_b T \ln\left[\int d\mathbf{s_{N+1}} < \exp(-\beta\Delta U) >_N\right]$$

with:

 $k_b = \text{Bolzmann constant},$

T =temperature,

V = volume of the simulation box,

$$\mathbf{s} = \text{reduced coordinates } (\mathbf{s} = \frac{\mathbf{x}}{V}),$$

$$\beta = \frac{1}{k_b T},$$

N =particle number,

 Λ = thermal de Broglie wave length,

 $\langle \rangle_N =$ canonical ensemble average.

The calculation of the chemical potential is done by the self written

"ProcessHistDL2" (see appendix 15.2) program. The volume of the simulation box is divided into grid cells and the $\langle \rangle_N$ average is done for each one of them over a complete simulation run. This averaging is carried out on GPU cores and therefore the evaluation of a 40 ns simulation run is done in less then 10 minutes at a grid resolution of 150x150x150. With the so obtained values for the function $\langle \exp(-\beta \Delta U) \rangle_N$ the integration is done and the chemical potential is calculated.

Afterwards it is easy to obtain the surrounding pressure with the chemical potential relation for an ideal gas (see 7.1):

$$p = \frac{q\lambda}{\beta}$$

MD simulations were carried out for several different numbers of particles in the simulation box at a temperature of 77 K with the result shown in figure 9.5. It is noticeable that for higher pressures the number of adsorbed particles was for the flexible MD simulation higher than for the rigid Gibbs Monte Carlo simulation. To see whether this could be a numerical effect, since the deviations are relatively small, some rigid MD simulations were done and the resulting points were in good agreement with the experimental data and the rigid Gibbs Monte Carlo simulation. The conclusion is therefore that the flexible lattice was containing a slightly larger amount of molecules at the same pressure.



Figure 9.5: Adsorption isotherm for hydrogen in ZIF-11 at 77K from: experimental data [21], MD flexible simulation, MD rigid simulation, Gibbs Monte Carlo simulation; for the units of adsorption see appendix 15.1

This of course questions the method of fitting the hydrogen Lennard Jones parameters to the measured adsorption isotherm with rigid Gibbs Monte Carlo simulations. The parameters could be slightly improved either by flexible Gibbs Monte Carlo simulations or fitting via flexible MD simulations which would take a lot more time. But it is still the opinion of the author that it is a good first approach to use the rigid parameters and afterwards to do the fitting with flexible simulations only if a high accuracy of the data is needed.

9.3.2 Self-Diffusion Coefficients

The self-diffusion coefficient is a value that shows how far a particle will be displaced in average after a certain time when there is no concentration gradient. The self-diffusion coefficient can only be measured in molecular dynamics simulations since Monte Carlo simulation are not simulating the time dependent behaviour of the hydrogen guest molecules.

To get values for the self-diffusion coefficient was one of the main aims of this master thesis. The obtained parameter set was now used to gain values for the self-diffusion coefficients where there is nearly no literature value for comparison.

The self-diffusion coefficient was evaluated out of the moments of the probability distribution of finding a particle at a certain distance of a starting point after a certain time. The diffusion equation for a constant diffusion coefficient \tilde{D} looks like [17]:

$$\frac{\partial \rho(\mathbf{r},t)}{\partial t} = -\tilde{D}\Delta\rho(\mathbf{r},t)$$

(where $\rho(\mathbf{r}, t)$ is the density). In the case of self-diffusion ($\tilde{D} = D$ = self-diffusion coefficient) the density ρ becomes the probability density ω and a solution looks like:

$$\omega(\mathbf{r},t) = (4\pi Dt)^{-3/2} \cdot \exp\left[-\frac{(\mathbf{r}-\mathbf{r_0})^2}{4Dt}\right]$$

The second moments of this distribution can be found as:

$$< |\mathbf{r} - \mathbf{r_0}|^2 >= 6Dt.$$

Therefore the statistical value of $< |\mathbf{r} - \mathbf{r_0}|^2 >$ can be used to determine the value of D for example with:

$$D = \frac{1}{6} \frac{\partial \langle |\mathbf{r} - \mathbf{r_0}|^2 \rangle}{\partial t}.$$

By using this relation the self-diffusion coefficient of hydrogen in ZIF-11 was calculated. Two different dependencies of the self-diffusion coefficient were investigated: the temperature dependency and the dependency on the loading of ZIF-11 with different amounts of guest molecules.

So far there is no measured value for the self-diffusion of hydrogen in ZIF-11. The only value that was found in the literature is a simulation from Aaron W. Thornton [29] at a pressure of 10 bar and 298 K. This value was:

$$D = 7.2 \times 10^{-9} \frac{\mathrm{m}^2}{\mathrm{s}}.$$

A simulation of 5 particles per unit cell at a temperature of 298 K has given a self-diffusion coefficient of:

$$D = 8.65 \times 10^{-9} \frac{\mathrm{m}^2}{\mathrm{s}},$$

those conditions correspond to a pressure of 14 bar. Therefore it can be seen that the coefficients are in the same order of magnitude.

The temperature dependence

In many cases the temperature dependency of the self-diffusion coefficient can be described with the so called Arrhenius equation [8]:

$$D(T) = D_0 \cdot exp\left(-\frac{E_A}{k_b T}\right).$$
(9.1)

 E_A describes an activation energy that in many cases can be related to a threshold within the system while D_0 is a pre exponential factor and the self diffusion coefficient would be equal to D_0 in the limiting case of infinite temperature.

A logarithmic plot of the self-diffusion coefficients in dependence on $\frac{1}{T}$ is found in figure 9.6. The Arrhenius equation would give a straight line and the simulated values are in a good agreement with a straight line. The values for E_A and D_0 from equation 9.1 were found as:

$$D_0 = (3.59 \pm 0.44) \times 10^{-8} \frac{\text{m}}{\text{s}^2}$$

 $E_A = (3.724 \pm 0.16) \frac{\text{kJ}}{\text{mol}}.$

The errors were calculated from the error of the linear fit.

The simulations were carried out with 5 particle per unit cell. The obtained values are given in table 9.2 In the regarded temperature region and at this loading it is therefore sufficient to use the Arrhenius equation.

The loading dependence

For different loading of the ZIF-11 material simulations were carried out and a self-diffusion coefficient was obtained. The result can be seen in figure 9.7. The self-diffusion coefficient was increasing up to a range of 60-80 particles per unit cell, afterward the self-diffusion coefficient goes down for higher loadings.



Figure 9.6: Relation between the self-diffusion coefficient and the temperature for the self-diffusion of hydrogen in ZIF-11

The increasing self-diffusion coefficient for an increasing amount of adsorbed particle for low loadings could be explained by the fact that particles will be adsorbed into deep potential minima (especially at low temperatures). Under those conditions a higher amount of particles will mean that some of those potential minima are already occupied by hydrogen atoms. Therefore it will take in average a longer time until a hydrogen atom is again adsorbed into such a minimum. This would explain that hydrogen self-diffusion is faster at higher loadings.

In figure 9.8, a hydrogen molecule is displayed, out of an MD simulation for 40 hydrogen molecules per unit cell. This hydrogen molecule (in the red circle) is trapped in a region with a potential energy of less then -8.0 kJ/mol.

The molecule is plotted again together with the equipotential surface at -3.5 kJ/mol. If it has the necessary kinetic energy to get up to this potential value the hydrogen molecule will be able to travel inside the centre pore to other potential minima. But as we can see this equipotential surface is still not connected to the equipotential surface of the window to the next pore in the blue circle. Therefore at this energy it will not be able to travel out of the pore.

The last figure (figure 9.10) shows this particle (red circle) together with an

temperature in K	self-diffusion coefficient in $\frac{m^2}{s}$
100	5.61×10^{-10}
120	1.21×10^{-9}
150	2.86×10^{-9}
200	4.58×10^{-9}
250	6.9×10^{-9}
298	8.65×10^{-9}

Table 9.2: Table of self-diffusion coefficients for different temperatures at a loading of 5 hydrogen molecules per unit cell

equipotential surface at -2.4 kJ/mol. Here we have the first thin connection (green circle) to the neighbour pores. But therefore the energy difference between the potential minima and the necessary energy for leaving the pore is 5.6 kJ/mol. One additional way to show that the explanation for the increasing self-diffusion coefficient for increasing particle numbers could work is to look at the probability density distributions for different particle numbers. It can be calculated that for 80 hydrogen molecules per unit cell the probability for being in a potential minimum is less than for a loading of 40 hydrogen molecules. For example for the position of the hydrogen molecule of figure 9.8 to 9.10 the probability density has a value of $2.1 \times 10^{28} \frac{1}{m^2}$ for the 40 particles per cell simulation and a value of $1.0 \times 10^{28} \frac{1}{m^2}$ for the 40 particles per cell simulation and a value of $1.0 \times 10^{28} \frac{1}{m^2}$ for the some the for higher loadings. Therefore the hydrogen molecules will spend less time in the energy minima for high loadings. This leads to the conclusion that there is an increased amount of freely moving particles.

The effect of a decreasing self-diffusion coefficient for high loadings is well known and interpreted as a hindering of the movement of the particles due to the interaction with each other, since they have a very tiny free path until they interact again with the next guest molecule. Figure 9.11 shows a configuration of 120 hydrogen molecules at 77 K in an MD simulation.

Different test simulations for the same conditions (88 guest particles at 77 K; see figure 9.7) have revealed an error of: $0.3 \times 10^{-11} \frac{\text{m}^2}{\text{s}}$ for the values of the self-diffusion coefficient at 77 K.



Figure 9.7: Relation between the self-diffusion coefficient and the loading for the self-diffusion of hydrogen in ZIF-11 at 77 K



Figure 9.8: A particle trapped in a potential minima (red circle) together with the equipotential surface at -8.0 kJ/mol



Figure 9.9: A particle trapped in a potential minima (red circle) together with the equipotential surface at -3.5 kJ/mol; the blue circle marks the location of the window between the pores



Figure 9.10: A particle trapped in a potential minima (red circle) together with the equipotential surface at -2.4 kJ/mol; the blue circle marks the location of the window between the pores; the green circle marks the connection of the window to the potential minima



Figure 9.11: A snapshot from the trajectory of 120 hydrogene molecules in a unit cell of ZIF-11 at 77 K

10 Proposal for the the compensation of lattice deformations caused by Coulomb forces

It was mentioned in section 5.2.1 that the Coulomb interactions were neglected in this work since they had a negative effect on the stability (NPT-Simulation) and the maintenance of the X-ray structure. For hydrogen guest molecules the Coulomb interactions are not that important since the hydrogen molecule is electrically neutral. But it would be most desirable to have a force field which is capable of handling all kinds of guest molecules (also the charged ones).

The introduction of charges into the lattice should not lead to a deformation of the lattice structure. The following text will give a proposal how this could be accomplished by adapting the structural interaction parameters. The realisation has not been done in this work due to a lack of time.

The principle idea

The idea is to compensate the Lennard-Jones and Coulomb forces with the forces from the bonded interaction potentials. Therefore the X-ray structure would correspond to the minima of the total lattice energy and at low temperatures to the average atom positions.

We introduce the condition that the quantity:

$$\sum_{i}^{N} |\mathbf{F}_{i} + (\mathbf{B}_{i} + \mathbf{V}_{i} + \mathbf{T}_{i})|^{2}$$
(10.1)

should be minimal to compensate the Lennard Jones - and Coulomb forces in the most effective way.

Where we use the following nomenclature:

 $\mathbf{F_i} = \text{the Coulomb} + \text{Lennard Jones force acting on particle i}$

 $\mathbf{B}_i = \mathrm{the}$ harmonic bond forces acting on particle i

 \mathbf{V}_i = the valence angle forces acting on particle i

 $\mathbf{T}_i = \mathrm{the}\;\mathrm{dihedral}\;\mathrm{forces}\;\mathrm{acting}\;\mathrm{on}\;\mathrm{particle}\;\mathrm{i}$

Each lattice atom is a part of some bond interactions. For example in figure 10.1

particle	involved in the interactions:
1	b1,v1,d1
2	b1, b2, v1, v2, d1
3	b2,b3,v1,v2,d1
4	b2,v2,d1

Table 10.1: Particles and the interactions in which they are involved; b stands for harmonic bond -, v for valence angle - and d for dihedral interaction

particle 1 and 2 are included in the harmonic bond interaction 1, particle 2 and 3 are included in the harmonic bond interaction 2 and so on (see table 10.1).



Figure 10.1: Exemplary confirmation of 4 atoms

The first aim will be now to rewrite the forces which are acting on the particles due to the bond interactions in some way.

The bond force on one particle depends on the interaction parameter set of the bonded interaction s and the positions of all atoms which are a part of this structural interaction $\{\mathbf{x}\}_s$. For example, particles 1-3 are included in valence angle interaction v1 and all particles are included in the dihedral interaction d1 in figure 10.1. The parameters of s would be β and Φ_0 for the valence angle interaction v1 and γ , n and Ψ_0 for the dihedral interaction d1. If we know all these parameters and the positions of the atoms which are included in the interaction we are able to calculate the force acting on the involved particles. For compensating the Coulomb forces only the structure defining parameters: Φ_0, Ψ_0 and r_0 will be varied. The other parameters (elasticities) will be considered to be constants.

We want to rewrite the force on one particle due to one structural interaction now in a way that it factorises into a first factor that is depending on the parameters of s and the atom positions $\{\mathbf{x}\}_s$ and another factor that gives the direction and is only depending on $\{\mathbf{x}\}_s$. The first factor should be the same for each particle of the list $\{\mathbf{x}\}_s$. For the dihedral forces in figure 10.1 this means:

$$\begin{split} \mathbf{F_1} &= \tilde{F}_1(\theta_0, \{\mathbf{x}\}_s) \mathbf{e_{s1}}(\{\mathbf{x}\}_s) \\ \mathbf{F_2} &= \tilde{F}_1(\theta_0, \{\mathbf{x}\}_s) \eta_2(\{\mathbf{x}\}_s) \mathbf{e_{s2}}(\{\mathbf{x}\}_s) \\ \mathbf{F_3} &= \tilde{F}_1(\theta_0, \{\mathbf{x}\}_s) \eta_3(\{\mathbf{x}\}_s) \mathbf{e_{s3}}(\{\mathbf{x}\}_s) \\ \mathbf{F_4} &= \tilde{F}_1(\theta_0, \{\mathbf{x}\}_s) \eta_4(\{\mathbf{x}\}_s) \mathbf{e_{s4}}(\{\mathbf{x}\}_s), \end{split}$$

where **e** means a unit vector and therefore the previously mentioned second factor is a combination of η and **e**. It has to be proven separately that each interaction can be rewritten in that way.

Harmonic bond interaction

At first we will define a unit vector for the force \mathbf{F}_1 :

$$\mathbf{e_{b1}} = rac{\mathbf{r_1} - \mathbf{r_2}}{|\mathbf{r_1} - \mathbf{r_2}|}$$

(b stands for harmonic bond interaction)

The force on one of the particles can be computed directly from the harmonic bond interaction potential and can be written as a scalar times e_{s1} :

$$\mathbf{F_1} = \nabla \alpha (r_{ij} - r_0)^2 = \tilde{F}_1 \cdot \mathbf{e_{b1}}.$$

The sum of both forces should be zero $\mathbf{F_1} + \mathbf{F_2} = 0$. The force on the second particle can be found as:

$$\mathbf{F_2} = -\tilde{F_1} \cdot \mathbf{e_{b1}} = \tilde{F_1} \cdot \mathbf{e_{b2}}.$$

Therefore we have the form:

$$\begin{aligned} \mathbf{F_1} &= \tilde{F}_1(r_0, \{\mathbf{x}\}_b) \mathbf{e_{b1}}(\{\mathbf{x}\}_b) \\ \mathbf{F_2} &= \tilde{F}_1(r_0, \{\mathbf{x}\}_b) \eta_2(\{\mathbf{x}\}_b) \mathbf{e_{b2}}(\{\mathbf{x}\}_b) \end{aligned}$$
where:

$$\eta_2(\{\mathbf{x}\}_b) = 1$$

This means that it is possible to rewrite the harmonic bond interaction in the required way.

Valence angle interaction

Again the first force will be directly computed from the interaction potential:

$$\mathbf{F}_1 = -\nabla U(\Phi_{ij}) = -\nabla \beta (\Phi_{ij} - \Phi_0)^2 = F_1 \cdot \mathbf{e}_{\mathbf{F}_1}.$$

It can easily be shown in which direction this force will act. This problem will be considered in spherical coordinates where the origin is particle 2 (see figure 10.2) and the z-axis has the direction of the connection between particle 2 and 3.

In this coordinate system the position of particle 1 can be expressed easily with the spherical coordinates r, ϕ and θ where θ is the valence angle. While doing the spatial derivative in this coordinate system one notices that $\frac{\partial U(\Phi_{ij})}{\partial r}$ and $\frac{\partial U(\Phi_{ij})}{\partial \phi}$ are equal to zero and that the force can therefore only act in the \mathbf{e}_{θ} direction.

$$\mathbf{F_1} = -\nabla \mathbf{U} = -\left(\mathbf{e}_r \frac{\partial U}{\partial r} + \mathbf{e}_\theta \frac{1}{r} \frac{\partial U}{\partial \theta} + \mathbf{e}_\varphi \frac{1}{r \sin \theta} \frac{\partial U}{\partial \varphi}\right)$$



Figure 10.2: Configuration of 3 atoms in spherical coordinates

A reasonable definition of a unit vector for \mathbf{F}_1 out of the structure is therefore:

$$\mathbf{e_{s1}} = \frac{\left[(\mathbf{r_1} - \mathbf{r_2}) \times (\mathbf{r_3} - \mathbf{r_2}) \right] \times (\mathbf{r_1} - \mathbf{r_2})}{\left| \left[(\mathbf{r_1} - \mathbf{r_2}) \times (\mathbf{r_3} - \mathbf{r_2}) \right] \times (\mathbf{r_1} - \mathbf{r_2}) \right|}.$$

With this unit vector $\mathbf{F_1}$ can be written as:

$$\mathbf{F_1} = \tilde{F}_1 \mathbf{e_{s1}}.$$

With the same argumentation like for particle 1 (spherical coordinates) the direction of the force acting on particle 3 can be derived and we obtain a choice for a unit vector for $\mathbf{F_3}$ as:

$$\mathbf{e_{v3}} = -\frac{[(\mathbf{r_1} - \mathbf{r_2}) \times (\mathbf{r_3} - \mathbf{r_2})] \times (\mathbf{r_3} - \mathbf{r_2})}{|[(\mathbf{r_1} - \mathbf{r_2}) \times (\mathbf{r_3} - \mathbf{r_2})] \times (\mathbf{r_3} - \mathbf{r_2})|}.$$

The forces F_1 and F_3 are orthogonal to the connecting vectors $\overline{12}$ and $\overline{23}$, respectively. Due to this fact it is easy to calculate the total torque which has to be zero:

$$(r_1 - r_2) \times F_1 + (r_3 - r_2) \times F_3 = 0$$

which is equivalent to:

$$|\mathbf{r_1} - \mathbf{r_2}| \frac{(\mathbf{r_1} - \mathbf{r_2})}{|\mathbf{r_1} - \mathbf{r_2}|} \times \tilde{F_1} \mathbf{e_{v1}} = -|\mathbf{r_3} - \mathbf{r_2}| \frac{(\mathbf{r_3} - \mathbf{r_2})}{|\mathbf{r_3} - \mathbf{r_2}|} \times \tilde{F_3} \mathbf{e_{v3}}$$

or:

$$\tilde{F}_{1}|\mathbf{r_{1}}-\mathbf{r_{2}}|\left(\frac{(\mathbf{r_{1}}-\mathbf{r_{2}})}{|\mathbf{r_{1}}-\mathbf{r_{2}}|}\times\mathbf{e_{v1}}\right) = -\tilde{F}_{3}|\mathbf{r_{3}}-\mathbf{r_{2}}|\left(\frac{(\mathbf{r_{3}}-\mathbf{r_{2}})}{|\mathbf{r_{3}}-\mathbf{r_{2}}|}\times\mathbf{e_{v3}}\right).$$

Since the two vectors on both sides in the last equation are unit vectors which are parallel to each other but point in opposite directions we get for \tilde{F}_3 :

$$\tilde{F}_3 = \tilde{F}_1 \frac{|\mathbf{r_1} - \mathbf{r_2}|}{|\mathbf{r_3} - \mathbf{r_2}|}.$$

The last force that we have to express in that form is $\mathbf{F_2}$. Since the total force has to vanish $(\mathbf{F_1} + \mathbf{F_2} + \mathbf{F_3} = 0)$ we get:

$$\mathbf{F_2} = -(\mathbf{F_1} + \mathbf{F_3}) = -\left(\tilde{F_1}\mathbf{e_{v1}} + \tilde{F_1}\frac{|\mathbf{r_1} - \mathbf{r_2}|}{|\mathbf{r_3} - \mathbf{r_2}|}\mathbf{e_{v3}}\right) = -\tilde{F_1} \cdot \left(\mathbf{e_{v1}} + \frac{|\mathbf{r_1} - \mathbf{r_2}|}{|\mathbf{r_3} - \mathbf{r_2}|}\mathbf{e_{v3}}\right)$$

 $\mathbf{F_2} = \tilde{F_1} \kappa_2 \mathbf{e_{v2}}.$

All forces are therefore in the form:

$$\begin{aligned} \mathbf{F_1} &= F_1(\theta_0, \{\mathbf{x}\}_v) \mathbf{e_{v1}}(\{\mathbf{x}\}_v) \\ \mathbf{F_2} &= \tilde{F}_1(\theta_0, \{\mathbf{x}\}_v) \kappa_2(\{\mathbf{x}\}_v) \mathbf{e_{v2}}(\{\mathbf{x}\}_v) \\ \mathbf{F_3} &= \tilde{F}_1(\theta_0, \{\mathbf{x}\}_v) \kappa_3(\{\mathbf{x}\}_v) \mathbf{e_{v3}}(\{\mathbf{x}\}_v). \end{aligned}$$

So it is also possible to rewrite the valence angle interaction in the required way.

Dihedral interaction

The force on the first particle can again be calculated from the interaction potential:

$$E(\Theta) = \gamma \cdot \cos(p\theta - \theta_0).$$

The direction of the force on particle 1 can be predicted by looking at the problem in cylindrical coordinates with the origin at particle 3 (see figure 10.3). In this coordinate system particle 1 has the coordinates r, θ, z (where θ is the dihedral angle) and the force on particle 1 is calculated with ∇ in cylindrical coordinates:

$$\mathbf{F} = -\nabla E = -\left(\mathbf{e}_{\mathbf{r}}\frac{\partial E}{\partial r} + \mathbf{e}_{\phi}\frac{1}{r}\frac{\partial E}{\partial \phi} + \mathbf{e}_{\mathbf{z}}\frac{\partial E}{\partial z}\right).$$

The force on particle 1 has therefore only a component in \mathbf{e}_{ϕ} direction. And the same can be done for particle 4.



Figure 10.3: dihedral interaction configuration

Therefore a reasonable definition of unit vectors for $\mathbf{F_1}$ and $\mathbf{F_4}$ is:

$$\mathbf{e_{d1}} = -\frac{[(\mathbf{r_1} - \mathbf{r_2}) \times (\mathbf{r_3} - \mathbf{r_2})]}{|[(\mathbf{r_1} - \mathbf{r_2}) \times (\mathbf{r_3} - \mathbf{r_2})]|}$$

$$\mathbf{e_{d4}} = -\frac{[(\mathbf{r_4} - \mathbf{r_3}) \times (\mathbf{r_2} - \mathbf{r_3})]}{|[(\mathbf{r_4} - \mathbf{r_3}) \times (\mathbf{r_2} - \mathbf{r_3})]|}.$$

And the force on particle 1 will be rewritten as:

$$\mathbf{F_1} = F_1 \mathbf{e_{d1}}.$$

Another point that has to be mentioned before starting some calculations is that the forces on particle 2 and 3 can not have a contribution in z direction. This can be explained with the fact that the dihedral force (as the potential) only depends on the angle between the two planes in which particle 1,2 and 3 and particle 2,3 and 4 are laying, respectively. If the positions of particle 2 or 3 are varied in z-direction it would not change the angle between the 2 planes. Therefore the change of the interaction energy is zero in this direction. This means that the forces in z-direction of particle 2 and 3 are zero.

The total torque can be calculated by looking at all position vectors and forces. The coordinate system will be chosen according to figure 10.4 (cartesian coordinates). All gathered information about the coordinates and the force directions will be taken into account.



Figure 10.4: Dihedral interaction configuration

$$\mathbf{r_1} = x_1\mathbf{e_1} + y_1\mathbf{e_2} + z_1\mathbf{e_3}$$

 $\mathbf{r_2} = z_2\mathbf{e_3}$
 $\mathbf{r_3} = z_3\mathbf{e_3}$
 $\mathbf{r_4} = x_4\mathbf{e_1} + y_4\mathbf{e_2} + z_4\mathbf{e_3}$

$$F_{1} = f_{x1}e_{1} + f_{y1}e_{2}$$

$$F_{2} = f_{x2}e_{1} + f_{y2}e_{2}$$

$$F_{3} = f_{x3}e_{1} + f_{y3}e_{2}$$

$$F_{4} = f_{x4}e_{1} + f_{y4}e_{2}$$

If there is no external force than the total torque has to be zero:

 $\mathbf{M} = \mathbf{0} = \mathbf{r_1} \times \mathbf{F_1} + \mathbf{r_2} \times \mathbf{F_2} + \mathbf{r_3} \times \mathbf{F_3} + \mathbf{r_4} \times \mathbf{F_4}.$

$$0 = (x_1\mathbf{e_1} + y_1\mathbf{e_2} + z_1\mathbf{e_3}) \times (f_{x1}\mathbf{e_1} + f_{y1}\mathbf{e_2}) + (z_2\mathbf{e_3}) \times (f_{x2}\mathbf{e_1} + f_{y2}\mathbf{e_2}) + (z_3\mathbf{e_3}) \times (f_{x3}\mathbf{e_1} + f_{y3}\mathbf{e_2}) + (x_4\mathbf{e_1} + y_4\mathbf{e_2} + z_4\mathbf{e_3}) \times (f_{x4}\mathbf{e_1} + f_{y4}\mathbf{e_2})$$

$$0 = x_1 f_{x1} \mathbf{e_1} \times \mathbf{e_1} + y_1 f_{x1} \mathbf{e_2} \times \mathbf{e_1} + z_1 f_{x1} \mathbf{e_3} \times \mathbf{e_1} + x_1 f_{y1} \mathbf{e_1} \times \mathbf{e_2} + y_1 f_{y1} \mathbf{e_2} \times \mathbf{e_2} + z_1 f_{y1} \mathbf{e_3} \times \mathbf{e_2} + f_{x2} z_2 \mathbf{e_3} \times \mathbf{e_1} + f_{y2} z_2 \mathbf{e_3} \times \mathbf{e_2} + f_{x3} z_3 \mathbf{e_3} \times \mathbf{e_1} + f_{y3} z_3 \mathbf{e_3} \times \mathbf{e_2} + x_4 f_{x4} \mathbf{e_1} \times \mathbf{e_1} + y_4 f_{x4} \mathbf{e_2} \times \mathbf{e_1} + z_4 f_{x4} \mathbf{e_3} \times \mathbf{e_1} + x_4 f_{y4} \mathbf{e_1} \times \mathbf{e_2} + y_4 f_{y4} \mathbf{e_2} \times \mathbf{e_2} + z_4 f_{y4} \mathbf{e_3} \times \mathbf{e_2}$$

$$0 = -y_1 f_{x1} \mathbf{e_3} + z_1 f_{x1} \mathbf{e_2} + x_1 f_{y1} \mathbf{e_3} - z_1 f_{y1} \mathbf{e_1} + f_{x2} z_2 \mathbf{e_2} - f_{y2} z_2 \mathbf{e_1} + f_{x3} z_3 \mathbf{e_2} - f_{y3} z_3 \mathbf{e_1} - y_4 f_{x4} \mathbf{e_3} + z_4 f_{x4} \mathbf{e_2} + x_4 f_{y4} \mathbf{e_3} - z_4 f_{y4} \mathbf{e_1}$$
(10.2)

That the total torque is zero means that each component has to be zero. We will look at each component of the torque to get relations between the forces F_2 , F_3 and F_4 to the force F_1 .

Z-component of the total torque (eqn. 10.2):

$$0 = x_1 f_{y1} - y_1 f_{x1} + x_4 f_{y4} - y_4 f_{x4}$$
(10.3)

If we call $\mathbf{r_1^{\perp}}$ the projection of the vector $\mathbf{r_1}$ on the *x-y* plane we get:

$$\mathbf{r}_1^{\perp} = x_1 \mathbf{e} \mathbf{1} + x_2 \mathbf{e} \mathbf{2}.$$

Since the forces $\mathbf{F_1}$ and $\mathbf{F_4}$ are also not having a contribution in z-direction, $\mathbf{F_1} \times \mathbf{r_1^{\perp}}$ and $\mathbf{F_4} \times \mathbf{r_4^{\perp}}$ only have a contribution in z-direction that equals:

$$(\mathbf{r_1^{\perp} \times F_1})_z = x_1 f_{y1} - y_1 f_{x1}$$

 $(\mathbf{r_4^{\perp} \times F_4})_z = x_4 f_{y4} - y_4 f_{x4}.$

If we take into account equation 10.3 we get:

$$\mathbf{r}_1^\perp \times \mathbf{F_1} = -\mathbf{r}_4^\perp \times \mathbf{F_4}$$

$$\begin{split} |\mathbf{r}_{1}^{\perp}| \frac{\mathbf{r}_{1}^{\perp}}{|\mathbf{r}_{1}^{\perp}|} \times \tilde{F}_{1} \mathbf{e}_{\mathbf{d}1} &= -|\mathbf{r}_{4}^{\perp}| \frac{\mathbf{r}_{4}^{\perp}}{|\mathbf{r}_{4}^{\perp}|} \times \tilde{F}_{4} \mathbf{e}_{\mathbf{d}4} \\ \\ \tilde{F}_{1}|\mathbf{r}_{1}^{\perp}| \left[\frac{\mathbf{r}_{1}^{\perp}}{|\mathbf{r}_{1}^{\perp}|} \times \mathbf{e}_{\mathbf{d}1} \right] &= -\tilde{F}_{4}|\mathbf{r}_{4}^{\perp}| \left[\frac{\mathbf{r}_{4}^{\perp}}{|\mathbf{r}_{4}^{\perp}|} \times \mathbf{e}_{\mathbf{d}4} \right] \end{split}$$

and since the vectors on both sides are parallel unit vectors with opposite direction we can express $\mathbf{F_4}$ like:

$$\tilde{F}_4 = \frac{r_1^{\perp}}{r_4^{\perp}} \cdot \tilde{F}_1,$$
$$\mathbf{F}_4 = \tilde{F}_4 \mathbf{e_{d4}}.$$

Y-component of the total torque (eqn. 10.2):

$$z_1 f_{x1} + f_{x2} z_2 + f_{x3} z_3 + z_4 f_{x4} = 0 aga{10.4}$$

We combine this relation with the condition that the total force has to vanish:

$$F_1 + F_2 + F_3 + F_4 = 0. (10.5)$$

Therefore we have:

$$f_{x1} + f_{x2} + f_{x3} + f_{x4} = 0$$

$$f_{x2} = -(f_{x1} + f_{x3} + f_{x4}). \tag{10.6}$$

We get from 10.4 and 10.6: $\,$

$$z_1 f_{x1} - (f_{x1} + f_{x3} + f_{x4}) z_2 + f_{x3} z_3 + z_4 f_{x4} = 0$$

which will lead to:

$$f_{x3} = \frac{f_{x1}(z_2 - z_1) + f_{x4}(z_2 - z_4)}{(z_3 - z_2)}.$$

We all ready got ${\bf F_4}$ and ${\bf F_1}$ in the wanted form:

$$f_{x4} = \mathbf{F_4e1} = \tilde{F}_4 \mathbf{e_{14}e_1} = \frac{r_1^{\perp}}{r_4^{\perp}} \cdot \tilde{F}_1 \mathbf{e_{d4}e_1}$$

and:

or:

$$f_{x1} = \mathbf{F_1}\mathbf{e1} = \tilde{F_1}\mathbf{e_{d1}}\mathbf{e_1}.$$

Therefore we get for f_{x3} :

$$f_{x3} = \frac{f_{x1}(z_2 - z_1) + f_{x4}(z_2 - z_4)}{(z_3 - z_2)} = \tilde{F}_1 \frac{\mathbf{e_{d1}}\mathbf{e_1}(z_2 - z_1) + \frac{r_1^{\perp}}{r_4^{\perp}}\mathbf{e_{d4}}\mathbf{e_1}(z_2 - z_4)}{(z_3 - z_2)} = \tilde{F}_1 \tilde{\lambda}_3^1(\{\mathbf{x}\}_d)$$

X-component of the total torque (eqn. 10.2):

$$-z_1f_{y1} - f_{y2}z_2 - f_{y3}z_3 - z_4f_{y4} = 0$$

or

$$z_1 f_{y1} + f_{y2} z_2 + f_{y3} z_3 + z_4 f_{y4} = 0 aga{10.7}$$

We get again from 10.5 for f_{y2} :

$$f_{y2} = -(f_{y1} + f_{y3} + f_{y4}). (10.8)$$

We mix 10.7 and 10.8:

$$0 = z_1 f_{y1} - (f_{y1} + f_{y3} + f_{y4})z_2 + f_{y3}z_3 + z_4 f_{y4}$$

and get:

$$f_{y3} = \frac{f_{y1}(z_2 - z_1) + f_{y4}(z_2 - z_4)}{(z_3 - z_2)}.$$

The last step looks again like before:

$$f_{y4} = \mathbf{F_4}\mathbf{e2} = \tilde{F}_4\mathbf{e_{d4}}\mathbf{e_2} = \frac{r_1^{\perp}}{r_4^{\perp}} \cdot \tilde{F}_1\mathbf{e_{d4}}\mathbf{e_2}$$

 $f_{y1} = \mathbf{F_1}\mathbf{e2} = \tilde{F_1}\mathbf{e_{d1}}\mathbf{e_2}.$

End we end up with:

$$f_{y3} = \frac{f_{y1}(z_2 - z_1) + f_{y4}(z_2 - z_4)}{(z_3 - z_2)} = \tilde{F}_1 \frac{\mathbf{e_{d1}} \mathbf{e_2}(z_2 - z_1) + \frac{r_1^\perp}{r_4^\perp} \cdot \mathbf{e_{d4}} \mathbf{e_2}(z_2 - z_4)}{(z_3 - z_2)} = \tilde{F}_1 \tilde{\lambda}_3^2 (\{\mathbf{x}\}_d)$$

which means that $\mathbf{F_3}$ looks like:

$$\mathbf{F_3} = \tilde{F}_1 \cdot \begin{pmatrix} \tilde{\lambda}_3^1(\{\mathbf{x}\}_d) \\ \tilde{\lambda}_3^2(\{\mathbf{x}\}_d) \\ 0 \end{pmatrix} = \tilde{F}_1 \lambda_3(\{\mathbf{x}\}_d) \mathbf{e_{d3}}$$

Now we have ${\bf F_1},\,{\bf F_3}$ and ${\bf F_4}$ in the wanted form and we get ${\bf F_2}$ from:

$$F_1 + F_2 + F_3 + F_4 = 0$$

by the simple step:

$$\mathbf{F_2} = -(\mathbf{F_2} + \mathbf{F_3} + \mathbf{F_4}) = -\left(\tilde{F}_1 \mathbf{e_{d1}} + \tilde{F}_1 \lambda_3 \mathbf{e_{d3}} + \tilde{F}_1 \frac{r_1^{\perp}}{r_4^{\perp}} \mathbf{e_{d4}}\right) = \tilde{F}_1 \lambda_2 \mathbf{e_{d2}}.$$

Therefore all 4 forces are now in the required form:

$$\begin{aligned} \mathbf{F_1} &= \tilde{F}_1(\theta_0, \{\mathbf{x}\}_d) \mathbf{e_{d1}}(\{\mathbf{x}\}_s) \\ \mathbf{F_2} &= \tilde{F}_1(\theta_0, \{\mathbf{x}\}_d) \lambda_2(\{\mathbf{x}\}_d) \mathbf{e_{d2}}(\{\mathbf{x}\}_d) \\ \mathbf{F_3} &= \tilde{F}_1(\theta_0, \{\mathbf{x}\}_d) \lambda_3(\{\mathbf{x}\}_d) \mathbf{e_{d3}}(\{\mathbf{x}\}_d) \\ \mathbf{F_4} &= \tilde{F}_1(\theta_0, \{\mathbf{x}\}_d) \lambda_4(\{\mathbf{x}\}_d) \mathbf{e_{d4}}(\{\mathbf{x}\}_d). \end{aligned}$$

The force (im)balance equation

Now it is shown for all 3 structural interaction forces that they can be expressed in a special way. This will now be used to find a way to minimise the quantity 10.1:

$$\sum_{i}^{N} |\mathbf{F_i} + (\mathbf{B_i} + \mathbf{V_i} + \mathbf{T_i})|^2.$$

In an ideal case we will be able to compensate all Coulomb and Van der Waals forces with the structural forces. Then we would have the 3N conditions:

$$\begin{array}{l} B_{x}^{1}+V_{x}^{1}+T_{x}^{1}=F_{x}^{1}\\ B_{y}^{1}+V_{y}^{1}+T_{y}^{1}=F_{y}^{1}\\ B_{z}^{1}+V_{z}^{1}+T_{z}^{1}=F_{z}^{1}\\ & & \\ &$$

Each particle will be a part of various structural interactions:

$$\begin{split} \mathbf{B}_{\mathbf{i}} &= \sum_{bond \ j} F_{j}^{b} \eta_{i,j}(\{\mathbf{x}\}_{j}) \mathbf{e}_{\mathbf{i},\mathbf{j}}(\{\mathbf{x}\}_{j}) \\ \mathbf{V}_{\mathbf{i}} &= \sum_{valence \ angles \ k} F_{k}^{v} \kappa_{i,k}(\{\mathbf{x}\}_{k}) \mathbf{e}_{\mathbf{i},\mathbf{k}}(\{\mathbf{x}\}_{k}) \\ \mathbf{T}_{\mathbf{i}} &= \sum_{dihedral \ angles \ l} F_{k}^{d} \lambda_{i,l}(\{\mathbf{x}\}_{l}) \mathbf{e}_{\mathbf{i},\mathbf{l}}(\{\mathbf{x}\}_{l}). \end{split}$$

It should be noticed that the sum for one particle i is running over all bond-, valence angle- and dihedral angle potentials that there are. Therefore a lot of the $\eta_{i,j}(\{\mathbf{x}\}_s)$ are going to be zero since one particle is only involved in a few interaction potentials.

Expressing the forces as the mentioned sums equation 10.1 looks like:

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$$\sum_{bond \ j} F_j^b \eta_{1,j}(\{\mathbf{x}\}_j) e_x^{1,j}(\{\mathbf{x}\}_j) + \sum_{valence \ angles \ k} F_k^v \kappa_{1,k}(\{\mathbf{x}\}_k) e_x^{1,k}(\{\mathbf{x}\}_k) + \sum_{dihedral \ angles \ l} F_k^d \lambda_{1,l}(\{\mathbf{x}\}_l) e_x^{1,l}(\{\mathbf{x}\}_l) = -F_x^1 \sum_{bond \ j} F_j^b \eta_{1,j}(\{\mathbf{x}\}_j) e_y^{1,j}(\{\mathbf{x}\}_j) + \sum_{valence \ angles \ k} F_k^v \kappa_{1,k}(\{\mathbf{x}\}_k) e_y^{1,k}(\{\mathbf{x}\}_k) + \sum_{dihedral \ angles \ l} F_k^d \lambda_{1,l}(\{\mathbf{x}\}_l) e_y^{1,l}(\{\mathbf{x}\}_l) = -F_y^1 \sum_{bond \ j} F_j^b \eta_{1,j}(\{\mathbf{x}\}_j) e_z^{1,j}(\{\mathbf{x}\}_j) + \sum_{valence \ angles \ k} F_k^v \kappa_{1,k}(\{\mathbf{x}\}_k) e_z^{1,k}(\{\mathbf{x}\}_k) + \sum_{dihedral \ angles \ l} F_k^d \lambda_{1,l}(\{\mathbf{x}\}_l) e_y^{1,l}(\{\mathbf{x}\}_l) = -F_y^1 \sum_{valence \ angles \ k} F_k^v \kappa_{1,k}(\{\mathbf{x}\}_k) e_z^{1,k}(\{\mathbf{x}\}_k) + \sum_{dihedral \ angles \ l} F_k^d \lambda_{1,l}(\{\mathbf{x}\}_l) e_z^{1,l}(\{\mathbf{x}\}_l) = -F_z^1 \sum_{valence \ angles \ k} F_k^v \kappa_{1,k}(\{\mathbf{x}\}_k) e_z^{1,k}(\{\mathbf{x}\}_k) + \sum_{dihedral \ angles \ l} F_k^d \lambda_{1,l}(\{\mathbf{x}\}_l) e_z^{1,l}(\{\mathbf{x}\}_l) = -F_z^1 \sum_{valence \ angles \ k} F_k^v \kappa_{1,k}(\{\mathbf{x}\}_k) e_z^{1,k}(\{\mathbf{x}\}_k) + \sum_{dihedral \ angles \ l} F_k^d \lambda_{1,l}(\{\mathbf{x}\}_l) e_z^{1,l}(\{\mathbf{x}\}_l) e_z^{1,l}(\{\mathbf{x}\}_l) = -F_z^1 \sum_{valence \ angles \ k} F_k^v \kappa_{1,k}(\{\mathbf{x}\}_k) e_z^{1,k}(\{\mathbf{x}\}_k) e_z^{1,k}(\{\mathbf{x}\}_k) + \sum_{dihedral \ angles \ l} F_k^d \lambda_{1,l}(\{\mathbf{x}\}_l) e_z^{1,l}(\{\mathbf{x}\}_l) e_z^{1,l}(\{\mathbf{x}\}_l) e_z^{1,l}(\{\mathbf{x}\}_l) e_z^{1,l}(\{\mathbf{x}\}_l) = -F_z^1 \sum_{valence \ angles \ k} F_k^v \kappa_{1,k}(\{\mathbf{x}\}_k) e_z^{1,k}(\{\mathbf{x}\}_k) e_z^{1,k}(\{\mathbf{x}\}_l) e_z^{1,$$

$$\sum_{bond j} F_{j}^{b} \eta_{N,j}(\{\mathbf{x}\}_{j}) e_{x}^{N,j}(\{\mathbf{x}\}_{j}) + \sum_{valence \ angles \ k} F_{k}^{v} \kappa_{N,k}(\{\mathbf{x}\}_{k}) e_{x}^{N,k}(\{\mathbf{x}\}_{k}) + \sum_{dihedral \ angles \ l} F_{k}^{d} \lambda_{N,l}(\{\mathbf{x}\}_{l}) e_{x}^{N,l}(\{\mathbf{x}\}_{l}) = -F_{x}^{N,k} \sum_{bond \ j} F_{j}^{b} \eta_{N,j}(\{\mathbf{x}\}_{j}) e_{y}^{N,j}(\{\mathbf{x}\}_{j}) + \sum_{valence \ angles \ k} F_{k}^{v} \kappa_{N,k}(\{\mathbf{x}\}_{k}) e_{y}^{N,k}(\{\mathbf{x}\}_{k}) + \sum_{dihedral \ angles \ l} F_{k}^{d} \lambda_{N,l}(\{\mathbf{x}\}_{l}) e_{y}^{N,l}(\{\mathbf{x}\}_{l}) = -F_{y}^{N,k} \sum_{bond \ j} F_{j}^{b} \eta_{N,j}(\{\mathbf{x}\}_{j}) e_{z}^{N,j}(\{\mathbf{x}\}_{j}) + \sum_{valence \ angles \ k} F_{k}^{v} \kappa_{N,k}(\{\mathbf{x}\}_{k}) e_{z}^{N,k}(\{\mathbf{x}\}_{k}) + \sum_{dihedral \ angles \ l} F_{k}^{d} \lambda_{N,l}(\{\mathbf{x}\}_{l}) e_{z}^{N,l}(\{\mathbf{x}\}_{l}) = -F_{z}^{N,k} \sum_{bond \ j} F_{j}^{b} \eta_{N,j}(\{\mathbf{x}\}_{j}) e_{z}^{N,j}(\{\mathbf{x}\}_{j}) + \sum_{valence \ angles \ k} F_{k}^{v} \kappa_{N,k}(\{\mathbf{x}\}_{k}) e_{z}^{N,k}(\{\mathbf{x}\}_{k}) + \sum_{dihedral \ angles \ l} F_{k}^{d} \lambda_{N,l}(\{\mathbf{x}\}_{l}) e_{z}^{N,l}(\{\mathbf{x}\}_{l}) = -F_{z}^{N,k} \sum_{bond \ j} F_{j}^{b} \eta_{N,j}(\{\mathbf{x}\}_{j}) e_{z}^{N,j}(\{\mathbf{x}\}_{l}) + \sum_{valence \ angles \ k} F_{k}^{v} \kappa_{N,k}(\{\mathbf{x}\}_{k}) e_{z}^{N,k}(\{\mathbf{x}\}_{k}) + \sum_{dihedral \ angles \ l} F_{k}^{d} \lambda_{N,l}(\{\mathbf{x}\}_{l}) e_{z}^{N,l}(\{\mathbf{x}\}_{l}) = -F_{z}^{N,k} \sum_{b \in D} F_{k}^{N,k}(\{\mathbf{x}\}_{k}) e_{z}^{N,k}(\{\mathbf{x}\}_{k}) + \sum_{dihedral \ angles \ l} F_{k}^{d} \lambda_{N,l}(\{\mathbf{x}\}_{l}) e_{z}^{N,l}(\{\mathbf{x}\}_{l}) e_{z}^{N,l}(\{\mathbf{x}\}_{l}) = -F_{z}^{N,k} \sum_{b \in D} F_{k}^{N,k}(\{\mathbf{x}\}_{k}) e_{z}^{N,k}(\{\mathbf{x}\}_{k}) e_{z}^{N$$

This can be rewritten as a matrix operation (The force (im)balance equation):

/

$$= \mathbf{R} \cdot \vec{S} = \vec{Y}$$

where:

$$b_{i,j}^{k} = \left(\eta_{i,j}(\{\mathbf{x}\}_{j})e_{k}^{i,j}(\{\mathbf{x}\}_{j})\right)$$
$$v_{i,j}^{k} = \left(\kappa_{i,j}(\{\mathbf{x}\}_{j})e_{k}^{i,j}(\{\mathbf{x}\}_{j})\right)$$
$$d_{i,j}^{k} = \left(\lambda_{i,j}(\{\mathbf{x}\}_{j})e_{k}^{i,j}(\{\mathbf{x}\}_{j})\right)$$

with:

$$k \in \{x, y, z\}.$$

Now it hopefully becomes clear why the forces had to be rewritten as done above, since the equation could therefore be interpreted as a matrix multiplication. Therefore the minimisation problem has become linear and can be approached, for example, with the linear regression method.

In most cases there will be much less parameters than equations and therefore this relation is a so called inconsistent equation (Not solvable for the unknowns by one set of values = force imbalance). Therefore one can apply some methods to find the minimum of:

$$\sum_{i}^{N} |\mathbf{F_i} + (\mathbf{B_i} + \mathbf{V_i} + \mathbf{T_i})|^2.$$

The Hill climbing method would for example give an iterative approximation for the best \vec{S} while the linear regression method will directly compute the best \vec{S} . With the approximating \vec{S} the parameters r_0, ϕ_0, θ_0 can be calculated. Those parameters, used in an MD simulation, should lead to average atom positions which are close to the X-ray structure atom positions. How near they get to the X-ray structure will depend upon the temperature and to which extent the Coulomb and Lennard Jones forces were compensated.

11 Remaining problems

11.1 General problems

This chapter was included to display the remaining problems that I see for my own work which were beyond the time limits of this master thesis. This chapter should help the reader to be aware of those problems and inspire him to think about solutions and own ways to work on the topic of this thesis.

Window Linker choice

The first remaining problem is located in the chapter where the linkers were chosen from the X-ray structure. It became clear where the different configurations for the wall linkers and corner linkers came from. But the question why the Window Linkers had different possible configurations in the X-ray structure file remains unanswered. A quantum mechanical approach, for example by density functional theory, could reveal whether both configurations should occur.

Rigid lattice fit

The hydrogen Lennard Jones parameters were fitted by rigid Gibbs Monte Carlo simulations. Since the simulation results have shown that they do depend upon the flexibility of the lattice it should not be neglected in the fitting process. The Outlook (chapter 12) will mention ways to fit the interaction parameters to flexible simulations. Unfortunately a parameter fit with a flexible lattice will need a huge amount of time.

The neglected charges

The third remaining problem concerns the neglect of charges in this thesis. For hydrogen guest molecules the interaction of hydrogen with ZIF-11 is not directly influenced by this neglect. But the lattice will show slightly different behavior when the charges are included and therefore some of the given values of this thesis will be influenced by that. A proposal has been made to include charges and maintain the X-ray structure at the same time, but the implementation is beyond the time limits of a master thesis.

Balance between theory and results

One additional remaining problem concerns the amount of simulation data in this thesis. In this work a lot of theory and preparatory work has been done to get a reliable force field for ZIF-11. And the amount of gained predictions of ZIF-11 adsorption behavior is filling much less pages of this thesis than the preparations. But it was the intention to get a force field other scientist can also use and where they are aware which known properties of ZIF-11 this force field is able to reproduce. In addition to that, this thesis includes remarks and suggestions which should be easily applicable for the research on force fields for other porous materials (equipotential surface calculation, the fugacity expansion, the charge compensation suggestion).

11.2 Force-field parameters

The force field parameters that were developed in this thesis were fitted to X-ray diffraction data and an adsorption isotherm. This kind of proceeding is typical for the application of classical force fields. So far it seems that it is not possible to have one and the same set of interaction parameters for all or many applications. And there is no single set of parameters provided by the literature but there are several of them. So one has to choose which set will work best for his application or to even change the parameters to be able to reproduce measurements.

This procedure gives of course boundaries to the knowledge we can gain in that way. If we use parameters from other applications to predict adsorption behaviour that was not measured so far we can not be certain how reliable this data will be and normally we will not rely on that data too much. This is a big disadvantage that hopefully will be solved or at least approximately solved in the future and it will certainly need a new way to describe the interactions.

The idea that seems to suggests itself is to use quantum mechanics to describe the interactions between the atoms of the simulation. A lot of approaches were made to achieve that goal and there are already some promising progresses in that field. But so far it often means that one has to find fitting basis functions to get the electron densities which will most likely also mean a separate treatment of different applications. But since quantum mechanics is the best known way to describe interactions at the atomic length scale a quantum mechanical approach is a very promising one. But of course the method that was used in this thesis has still enough advantages and knowledge that we can gain from it. Even if predictions for new materials are not very reliable we are able to understand properties of the materials for which we do the research. If we are able to reproduce measurements it will probably mean that the microscopic behaviour of the simulation is a good approach to the real processes. We are in many cases able to gain knowledge from that which is not accessible for the experimentalists and that can help to identify the relation between material properties and adsorption behaviour.

12 Outlook

The force field presented in this Master thesis already reproduces the adsorption isotherm of hydrogen and the X-ray structure in a good approximation. But it was mentioned before that this force field will not work for charged guest molecules. Therefore the next step for ZIF-11 should be to develop a force field that can also handle charged guests.

This might be accomplished by the proposal of chapter 10 which will hopefully be tested in the future. If it is possible to find a parameter set with charges that also reproduces the X-ray structure than those parameters will also have an influence on the simulations for hydrogen guest molecules. This influence is expected to be rather small which of course has to be tested.

In addition to that, the guest molecule parameters were fitted via Gibbs-Monte Carlo simulations in a way that the measured adsorption isotherm was in a good agreement with the simulated adsorption isotherm. The MD simulation with the flexible lattice has shown that the flexibility lead to a slight increase of pressure for higher loadings. Therefore it would be also worthwhile to fit the hydrogen interaction parameters again with adsorption isotherms calculated from MD simulations. This will of course take a higher computational afford but should also slightly improve the parameter set. Another way to deal with the flexible lattice would be to include the flexibility into the Gibbs-Monte Carlo simulation.

If there are some additional experimental data on ZIF-11 it might also be interesting to check the agreement of the adsorption isotherm for higher pressures and additional temperatures.

This work also provides simulated values for the diffusion coefficient were there is no measured value to check the agreement. Those measurements will hopefully be done soon.

13 Acknowledgements

The first acknowledgement goes to Dr. Fritzsche who has supervised my master thesis. He was available to talk about difficulties and the interpretation of the data whenever I felt the need to talk about my work. He has given me the freedom to work independently and to follow my own ideas and ways of developing computer programs. Secondly I like to thank Steven Reichhardt who is a fellow student of mine. He was open to discuss some ideas and went through argumentations and derivations whenever I felt the need for a second opinion. It has helped a lot and I am not taking it for granted that he has found the time for that.

The next acknowledgement goes to Mr. Rost who has helped me to get my simulation runs going on the high performance computers in Leipzig. This has also helped me to avoid and fix some mistakes for my high performance computation in Dresden. Another acknowledgement should go to the DL_Poly programmers since they developed the simulation code that was used in this thesis and because they made the code freely available for scientific use.

I like also to thank Prof. Kärger for his interest in this topic and for being the second supervisor. His has checked my master thesis very carefully to give me a lot of helpful critic.

The last acknowledgement goes to the ZIH Dresden. I thank the Center for Information Services and High Performance Computing (ZIH) at TU Dresden for generous allocations of computer time. It is great that it is possible for students to do high performance computation for free.

14 Statutory Declaration

I declare on oath that I completed this work on my own and that information which has been directly or indirectly taken from other sources has been noted as such. Neither this, nor a similar work, has been published or presented to an examination committee.

Leipzig, November 12th, 2012

15 Appendix

15.1 Unit of the adsorbed amount of particles

The unit $\frac{cm^3}{g}STP$ means the volume that the amount of hydrogen, that is adsorbed into 1 g of porous material, would have as an ideal gas under the standard conditions: $T_0 = 273.15K$ and p = 101325Pa. Therefore the number of adsorbed particles for one unit cell of ZIF-11 (mass=14383 $\frac{g}{mal}$) is:

$$N = x \cdot \text{mass} \cdot 10^{-3} \cdot \frac{p_0}{k_b T_0} \approx 0.642 \frac{\text{g}}{\text{cm}^3} \cdot x$$

where x has the unit $\frac{\text{cm}^3}{\text{g}}STP$.

15.2 Self written programms for this thesis

The programms which were written in C++ but they are to big to print them in the appendix. Please contact me at $p_schierz@hotmail.de$ to get the source code.

15.3 Table of the parameters

Linker types (list 15.3):

- 1. Straight linker
- 2. Wall linker
 - a) straight
 - b) bent
- 3. Corner linker
 - a) straight
 - b) bent
- 4. Wall linker



Figure 15.1: A zinc knot with the surrounding hydrogen The numbers with dotes next to the N's are referring to the attached linkertypes of list 15.3. The numbers without dots are defining names for the bonds.



Figure 15.2: numbering of the bonds



Figure 15.3: atomypes of the linker

CIII	mand bolles potential $E_{LJ} = 4c_e \left[\left(\begin{array}{c} r \end{array} \right) \right]$									
	atom type e	$\epsilon_e(kcal \cdot mol^{-1})$	σ_e (Å)							
	H5	0.063	2.42							
	$\rm CK$	0.360	3.40							
	NB	0.712	3.25							
	CB	0.360	3.40							
	\mathbf{CA}	0.360	3.40							
	\mathbf{HA}	0.063	2.60							
	Zn	0.052	1.96							

Lennard-Jones potential $E_{LJ} = 4\epsilon_e \left[\left(\frac{\sigma_e}{r} \right)^{12} - \left(\frac{\sigma_e}{r} \right)^6 \right]$

Table 15.1: Table of the Lennard Jones interactions

bond type b	$\alpha_b(kcal \cdot mol^{-1} \text{\AA}^2)$	r_{0b} Å					
		1.	2.a)	2.b)	3.a)	3.b)	4.
$(CK-H5)_1$	367.0	0.932	0.932	0.932	0.928	0.928	0.928
$(CK-NB)_{3,4}$	529.0	1.316	1.339	1.339	1.315	1.315	1.289
$(NB-CB)_{6,7}$	414.0	1.366	1.391	1.389	1.537	1.283	1.383
$(CB-CB)_8$	520.0	1.472	1.455	1.323	1.428	1.472	1.452
$(CB-CA)_{9,10}$	469.0	1.409	1.403	1.444	1.383	1.454	1.397
$(CA-HA)_{11,12}$	367.0	0.929	0.929	0.929	0.930	0.929	0.959
$(CA-HA)_{16,17}$	367.0	0.931	0.930	0.931	0.929	0.928	0.929
$(CA-CA)_{13,14}$	469.0	1.340	1.399	1.414	1.367	1.350	1.282
$(CA-CA)_{15}$	469.0	1.421	1.369	1.329	1.358	1.362	1.521
$(Zn-NB)_{2,5}$	78.50	1.976	1.988	1.988	1.986	1.986	1.966

bond potential $E_{bond} = \alpha_b (r - r_{0b})^2$

The subscripts of the bonds are corresponding to the numbers in figure 15.2.

	valence angle petential	Dena PC	(1 100)				
bond type c	$\beta_c(kcal \cdot mol^{-1}rad^2)$	$\Phi_{0c}(rad)$					
		1.	2.a)	2.b)	3.a)	$3.\mathrm{b})$	4.
(H5-CK-NB) _{1,3}	50.0	120.53	122.41	122.42	122.06	122.06	139.48
$({\rm H5-CK-NB})_{1,4}$	50.0	120.53	122.42	122.41	122.06	122.06	98.714
$(NB-CK-NB)_{3,4}$	70.0	118.94	115.17	115.17	115.88	115.88	121.8
(CK-NB-Zn) _{3,2;4,5}	48.7	130.49	126.92	126.91	130.23	130.23	128.59
(CK-NB-CB) _{3,6;4,7}	70.0	103.64	103.97	102.37	106.34	104.05	102.26
$(Zn-NB-CB)_{2,4;5,7}$	32.5	125.8	127.89	128.8	123.09	123.08	128.53
$(CB-CB-NB)_{6,8;7,8}$	70.0	106.89	106.82	109.73	105.11	107.15	106.83
$(NB-CB-CA)_{6,9;7,10}$	70.0	133.22	132.13	127.75	134.06	132.03	134.53
$(CB-CB-CA)_{8,9;8,10}$	63.0	119.88	120.56	122.39	120.78	120.24	118.61
$(CB-CA-CA)_{9,13;10,12}$	63.0	117.21	116.7	114.39	116.29	114.02	115.59
$(CA-CA-HA)_{11,13;12,14}$	50.0	121.33	121.67	122.73	121.83	123.02	110.74
$(CA-CA-HA)_{13,16;14,17}$	50.0	118.51	118.63	118.59	118.76	117.05	120.24
$(CA-CA-HA)_{16,15;15,17}$	50.0	118.59	118.65	118.4	118.36	117.27	120.1
$(CA-CA-CA)_{13,15;14,15}$	63.0	122.9	122.72	123.02	122.88	125.67	119.66
$(HA-CA-CB)_{11,9;10,12}$	50.0	121.46	121.62	122.88	121.89	122.97	124.29
bond type c	$\beta_c(kcal \cdot mol^{-1}rad^2)$	$\Phi_{0c}(rad)$					
(NB-Zn-NB) _{1,2}	35.2	107.46					
$(NB-Zn-NB)_{1,3}$	35.2	111.33					
$(NB-Zn-NB)_{1,4}$	35.2	107.04					
$(NB-Zn-NB)_{2,3}$	35.2	104.72					
$(NB-Zn-NB)_{2,4}$	35.2	109.95					
$(NB-Zn-NB)_{4,3}$	35.2	116.07					

valence angle potential $E_{bend} = \beta_c (\Phi - \Phi_{0c})^2$

The subscripts of the 3 atom types are related to the numbers of the bonds (figure 15.2 or figure 15.1) that are forming the group of 3 atoms.

bond type d	$\gamma_d(kcal \cdot mol^{-1})$	n_d	$\phi_{0d}(rad)$					
			1.	2.a)	2.b)	3.a)	$3.\mathrm{b})$	4.
$(H5-CK-NB-Zn)_{(1,3,2)}$	20.00	2	170.68	166.73	189.98	189.98	189.98	198.17
$(H5-CK-NB-Zn)_{(1,4,5)}$	20.00	2	189.32	193.27	170.02	170.02	170.02	160.98
$(H5-CK-NB-CB)_{(1,3,6)}$	20.00	2	176.85	142.93	153.16	203.16	153.16	181.11
$(H5-CK-NB-CB)_{(1,4,7)}$	20.00	2	183.15	217.07	206.84	156.84	206.84	178.04
$(NB-CK-NB-Zn)_{(3,4,5)}$	20.00	2	188.97	193.28	170.16	170.16	170.16	159.35
$(NB-CK-NB-Zn)_{(4,3,2)}$	20.00	2	171.03	166.72	189.84	189.84	189.84	200.65
$(NB-CK-NB-CB)_{(3,4,7)}$	20.00	2	182.8	217.08	206.97	156.97	206.97	176.41
$(NB-CK-NB-CB)_{(4,3,6)}$	20.00	2	177.2	142.92	153.03	203.03	153.03	183.59
$(CK-NB-CB-CB)_{(3,6,8)}$	5.10	2	181.49	200.52	194.89	167.4	194.89	178.18
$(CK-NB-CB-CB)_{(4,7,8)}$	5.10	2	178.51	159.48	165.11	192.6	165.11	181.82
$(CK-NB-CB-CA)_{(3,6,9)}$	5.10	2	178.95	184.08	176.91	162.63	176.91	174.21
$(CK-NB-CB-CA)_{(4,7,10)}$	5.10	2	181.05	175.92	183.09	197.37	183.09	185.79
$(Zn-NB-CB-CB)_{(2,6,8)}$	5.10	2	187.27	176.4	161.45	179.41	161.45	161.13
$(Zn-NB-CB-CB)_{(5,7,8)}$	5.10	2	172.73	183.6	198.55	180.59	198.55	198.87
$(Zn-NB-CB-CA)_{(2,6,9)}$	5.10	2	184.73	159.96	143.46	174.64	143.46	157.17
(Zn-NB-CB-CA) _(5,7,10)	5.10	2	175.27	200.04	216.54	185.36	216.54	202.83
$(NB-CB-CB-NB)_{(6,8,7)}$	21.80	4	180	180	180	180	180	180
$(NB-CB-CB-CA)_{(6,8,10)}$	21.80	4	175.73	151.71	149.11	172.02	149.11	173.56
$(NB-CB-CB-CA)_{(7,8,9)}$	21.80	4	175.73	151.71	210.89	187.98	210.89	186.44
$(CA-CB-CB-CA)_{(9,8,10)}$	21.80	4	180	180	180	180	180	180
$(NB-CB-CA-HA)_{(6,9,11)}$	14.00	4	181.32	210.55	208.62	200.18	208.62	225.07
$(NB-CB-CA-HA)_{(7,10,12)}$	14.00	4	178.68	149.45	151.38	159.82	151.38	134.93
$(NB-CB-CA-CA)_{(6,9,13)}$	14.00	4	182.48	209.93	207.99	200.1	207.99	78.27
$(NB-CB-CA-CA)_{(7,10,14)}$	14.00	4	177.52	150.07	152.01	159.9	152.01	281.73
(CB-CB-CA-HA) _(8,9,11)	14.00	4	175.72	173.98	168.8	189.45	168.8	216.43
$(CB-CB-CA-HA)_{(8,10,12)}$	14.00	4	184.28	186.02	191.2	170.55	191.2	143.57
$(CB-CB-CA-CA)_{(8,9,13)}$	14.00	4	176.88	173.36	168.18	189.37	168.18	69.625
$(CB-CB-CA-CA)_{(8,10,14)}$	14.00	4	183.12	186.64	191.82	170.63	191.82	290.37
$(CB-CA-CA-CA)_{(9,13,15)}$	14.50	4	183.23	186.8	192.58	170.41	192.58	291.61
$(CB-CA-CA-CA)_{(10,14,15)}$	14.50	4	176.77	173.2	167.42	189.59	167.42	68.391
(CB-CA-CA-HA) _(9,13,16)	14.50	4	183.97	186.41	192.23	170.11	192.23	292.41
$(CB-CA-CA-HA)_{(10,14,17)}$	14.50	4	176.03	173.59	167.77	189.89	167.77	67.593
(CA-CA-CA-HA) _(11,13,15)	14.50	4	184.38	186.18	191.95	170.33	191.95	164.12
(CA-CA-CA-HA) _(12,14,15)	14.50	4	175.62	173.82	168.05	189.67	168.05	195.88
(HA-CA-CA-HA) _(11,13,16)	14.50	4	185.12	185.79	191.6	170.03	191.6	164.92
(HA-CA-CA-HA) _(17,14,12)	14.50	4	174.88	174.21	168.4	189.97	168.4	195.08
(CA-CA-CA-CA) _(13,15,14)	14.50	4	180	180	180	180	180	180
(CA-CA-CA-HA)(17,15,13)	14.50	4	179.26	179.61	179.65	179.7	179.65	180.8
(CA-CA-CA-HA)(16,15,14)	14.50	4	179.26	179.61	180.35	180.3	180.35	179.2
(HA-CA-CA-HA) _(16,15,17)	14.50	4	180	180	180	180	180	180

dihedral potential $E_{dih} = \gamma_d [1 + \cos(n_d \phi - \phi_{0d})]$

The subscripts of the 4 atom types are related to the numbers of the bonds (figure 15.2) that are forming the group of 4 atoms.

	1 4111		1	
bond type d		$\gamma_d(kcal \cdot mol^{-1})$	n_d	$\phi_{0d}(rad)$
([CB(1.)]-[NB(1.)]	-[Zn]-[NB(2.a)])	0.49	3	329.34
([CB(1.)]-[NB(1.)]	-[Zn]-[NB(2.b)])	0.49	3	30.661
([CB(1.)]-[NB(1.)]	-[Zn]-[NB(3.a))])	0.49	3	19.13
([CB(1.)]-[NB(1.)]	-[Zn]-[NB(3.b))])	0.49	3	19.13
([CB(1.)]-[NB(1.)]	-[Zn]-[NB(4.)])	0.49	3	35.215
([CB(2.a)]-[NB(2.a)])	a)]-[Zn]-[NB(1.))])	0.49	3	90.485
([CB(2.a)]-[NB(2.a)])	a)]-[Zn]-[NB(3.a))])	0.49	3	84.658
([CB(2.a)]-[NB(2.a)])	a)]-[Zn]-[NB(3.b))])	0.49	3	275.34
([CB(2.a)]-[NB(2.a)])	a)]-[Zn]-[NB(4.)])	0.49	3	108.12
([CB(2.b)]-[NB(2.	b)]-[Zn]-[NB(1.))])	0.49	3	9.3948
([CB(2.b)]-[NB(2.b)])	b)]-[Zn]-[NB(3.a))])	0.49	3	15.223
([CB(2.b)] - [NB(2.b)])	b)]-[Zn]-[NB(3.b))])	0.49	3	344.78
([CB(2.b)] - [NB(2.b)])	b)]-[Zn]-[NB(4.)])	0.49	3	351.76
([CB(3.a)]-[NB(3.a)	a)]-[Zn]-[NB(1.)])	0.49	3	99.857
([CB(3.a)] - [NB(3.a)]	a)]-[Zn]-[NB(2.a))])	0.49	3	270.88
([CB(3.a)]-[NB(3.a)	a)]-[Zn]-[NB(2.b))])	0.49	3	89.118
([CB(3.a)] - [NB(3.a)]	a)]-[Zn]-[NB(4.)])	0.49	3	104.11
([CB(3,b)]-[NB(3,b)])	b)]-[Zn]-[NB(1.)])	0.49	3	12.856
([CB(3,b)] - [NB(3,b)])	b)]-[Zn]-[NB(2.a))])	0.49	3	2.1174
([CB(3,b)] - [NB(3)])	b)]-[Zn]-[NB(2,b))])	0.49	3	357.88
([CB(3,b)] - [NB(3)]	b)]-[Zn]-[NB(4,)])	0.49	3	17.107
([CB(4,)]-[NB(4,)])	-[Zn] - [NB(1,)])	0.49	3	333.57
([CB(4,)] - [NB(4,)])	-[Zn] - [NB(2,a))])	0.49	3	13.891
([CB(4,)] - [NB(4,)])	-[Zn] - [NB(2,b))])	0.49	3	346.11
([CB(4,)] - [NB(4,)])	-[Zn] - [NB(3,a))])	0.49	3	337.8
([CB(4,)] - [NB(4,)])	-[Zn] - [NB(3,b))])	0.49	3	337.8
([CK(1)] - [NB(1)])	-[Zn] - [NB(2,a)])	0.49	3	160.43
([CK(1)] - [NB(1)])	-[Zn] - [NB(2 b)])	0.49	3	199.57
([CK(1)] [NB(1)])	-[Zn] - [NB(3 a))])	0.49	3	188.04
([CK(1)] - [NB(1)])	-[Zn] - [NB(3,b))])	0.49	3	188.04
([CK(1)] [NB(1)])	-[Zn] - [NB(4)])	0.49	3	204 13
([CK(2 a)] - [NB(2 a)]	a)]-[Zn]-[NB(1))])	0.49	3	226.42
([CK(2 a)] = [NB(2 a)]	a)]- $[Zn]-[NB(3 a))]$	0.49	3	220.12 220.59
([CK(2,a)] = [NB(2,a)]	$a)]_{2n}[2n]_{2n}[NB(3b)])$	0.49	3	139.41
([CK(2,a)] [NB(2,a)] - [NB(2	a)] $[Zn] [NB(4)])$	0.49	3	244.05
([CK(2.a)] [NB(2.a)] - [NB(2.a)]	b)]- $[Zn]-[NB(1))]$	0.49	3	133 58
([CK(2.b)] [NB(2.b)] - [NB(2	b)] $[Zn] [NB(3a)]$	0.49	3	130.00
([CK(2.b)] - [NB(2.b)] - [NB	b)]-[Zn]-[NB(3 b)]]	0.49	3	220 59
([CK(2.b)] - [NB(2.b)] - [NB(2.b)] = [NB	b)] $[Zn] [NB(4)]$	0.49	3 2	115.05
([CK(2,0)] - [NB(2,0)] - [NB(3,0)] - [NB	$p_{1}^{(2n)} = [NB(1)]$	0.49	3 2	257.10
([CK(3,a)] - [ND(3,a)] ([CK(2,a)]) [ND(2,a)])	a) - [Zn] - [ND(1, j)]	0.49	ວ ໑	207.19
([CK(3.a)] - [ND(3.a)] ([CK(2.a)]) [ND(2.a)]	a)] $[Zn] - [ND(2.a))])$	0.49	ა ე	246.45
([CK(3,a)] - [ND(3,a)] - [ND(3,a)] = ([CK(3,a)] - [ND(3,a)] - [ND(3,a)] - [ND(3,a)] = ([CK(3,a)] - [ND(3,a)] - [ND(3,a)] = ([CK(3,a)] - [ND(3,a)] - [ND(3,a)] = ([CK(3,a)] - [(CK(3,a)] - [(CK(3,a)] - [(CK(3,a)] - [(ND(3,a)] = ([CK(3,a)] - [(CK(3,a)] - [(C	a)] $[Zn] [ND(4.)])$	0.49	ა ი	240.45
([CK(3.a)]-[ND(3.a)] ([CK(3.b)])	$a_{j} - [\Delta \Pi] - [ND(4, j])$ $b_{j} = [ND(1, j])$	0.49	ა ი	201.44
([CK(3.D)] - [ND(3.)] ([CK(3.D)] - [ND(3.)])	$D_{j}^{-}[Z_{II}^{-}[IND(1,j])]$	0.49	ა ი	207.19
([CK(3.D)] - [ND(3.C)] - ([CK(3.D)] - [ND(3.C)]) - ([CK(3.D)] - [ND(3.C)]) - ([CK(3.D)] - ([ND(3.C)]) - ([ND(3.C	$D_{j} - [Z_{II}] - [IND(2.a)])$	0.49	ა ი	240.40 112 FF
([CK(3.D)] - [ND(3.C)] - ([CK(3.D)] - [ND(3.C)]) - ([CK(3.D)] - [ND(3.C)]) - ([CK(3.D)] - ([ND(3.C)]) - ([ND(3.C	D) - [ZII] - [IND(2.D))]) b) $[Z_m] [ND(4)])$	0.49	ა ი	115.55
$([\mathbf{CK}(3,\mathbf{D})] - [\mathbf{INB}(3,\mathbf{CK}(4))] - [\mathbf{ND}(4)]$	$\bigcup_{j \in [\mathbf{Z}_n] \in [\mathbf{ND}(1_j)]} [\mathbf{ND}(1_j)]$	0.49	ა ი	201.44 195 C
([OK(4,)]-[IND(4,)])	$-[\Delta\Pi] - [\operatorname{IND}(1, j])$	0.49	ა ი	161.00
([OK(4,)]-[IND(4,)])	$-[\Box\Pi] - [\PiD(2.a))])$	0.49	ა ი	101.80
$([\mathbf{CK}(4,)] - [\mathbf{ND}(4,)])$	$-[\Delta \Pi] - [\Pi D(2.D)])$	0.49	ა ი	190.14
([CK(4.)] - [ND(4.)])	-[2n]-[ND(3.a))]) - $[Zn]-[NB(3.b))])$	0.49	ა ვ	109.04

dihedral potential $E_{dih} = \gamma_d [1 + \cos(n_d \phi - \phi_{0d})]$

 $\frac{([CK(4.)]-[NB(4.)]-[Zn]-[NB(3.b))])}{The numbers in brackets () are related to the numbers of the linker types (figure 15.1 and list 15.3))}{That are forming the group of 4 atoms.}$

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