Scientific Report

Introduction

For practical application of zeolites such as selective adsorption, diffusion, and catalysis [1, 2], it is of crucial importance to understand their adsorption properties. The selection or design of a zeolite for a particular use requires knowledge of the interaction between the zeolite and the adsorbate. This interaction can be determined from experiments, however, an experiment must be performed for each zeolite and substance and these experiments can be time-consuming [3]. Alternatively, given a sufficiently accurate force field, molecular simulation techniques can be used to quantitatively predict the adsorption and diffusion behaviour of a substance in a zeolite. Developing force fields is still a major task as it requires a very large number of molecular simulations. Therefore, there is a significant interest in reducing their number.

Purpose of the visit

The purpose of my visit was to develop a method to fit the force field parameters for describing adsorption in zeolites in a computationally easier and less expensive way.

In a previous work we developed a force field for describing the adsorption of carbon dioxide in all silica and aluminosilicate zeolites with sodium extra framework cations. The method used was extremely high CPU-time consuming. Therefore, in this project we want to develop a better method to fit force field parameters describing guest-host interactions.

The crucial idea is to develop a method to describe the outcome of a molecular simulation without performing the simulation itself. This will reduce drastically time-consuming molecular simulation and become a powerful tool to accurate describe the interactions between the guest molecules themselves and the host material.

Description of the work carried out during the visit

During 12 weeks spent with the research group of Prof. Vlugt at Delft University of Technology we developed a new method to calibrate force field for guest-host interactions in zeolites.

We model the zeolite as one-dimensional pore where the zeolite is considered as an annulus with the oxygen atoms distributed uniformly on its inner surface. The model has four parameters, the inner and outer radii, the density of the oxygen atoms and a potential offset. These parameters can be fitted using Henry coefficient and heat of adsorption values, obtained from either experiments or simulations.
This model is several orders of magnitude more efficient than molecular simulation and we can estimate the force field parameter more rapidly than in the standard way.

The model parameters can be linked to the force field parameters in the molecular simulations. Once these parameters are estimated, the model can be used in place of the simulations in order to optimize the Lennard-Jones parameters for the guest-host interactions (diameter σ and strength ε).

Therefore, optimization of the force field parameters can be performed using the model thus reducing the number of required molecular simulation.

Main results

Methane is modelled with a united atom approach and the zeolite is modelled as an annulus. The guest-host interactions in the model are described by the inner radius R_1 and the outer radius R_2 of the annulus, a potential offset U_{min} and the surface density of dispersive oxygen atoms λ. The outer radius R_2 accounts for the inaccessible part of the zeolite. The dominant interactions between the guest molecule, methane, and the zeolites occur at the oxygen atoms in the zeolite and are described by the dispersive interaction modelled with a Lennard-Jones potential.

To test whether our proposed model can describe the outcome of molecular simulations, we fitted the parameters of the model to adsorption data obtained from molecular simulations. The following zeolite framework types were considered: AFI, LTL, TON, ITQ-29 and MTT. First, we perform standard Monte Carlo simulation to calculate the heat of adsorption and Henry coefficient. The simulations were performed for different values of the Lennard-Jones parameters for guest-host interactions ε/k_B and σ. The values were chosen around the values found for the interaction between CH_4 and O according to Dubbeldam [4]. These values are 115 K for ε/k_B and 3.47Å for σ. For this reason the values for ε/k_B are chosen between 113 K and 117 K and the values for σ between 3.0 Å and 4.0 Å.
In figures 1 and 2 a comparison of the model and simulations for Henry coefficient and the heat of adsorption for methane are shown in zeolites AFI and ITQ-29. From these figures it is clear that the model can correctly describe how the outcome of a simulation depends on the force field parameters.

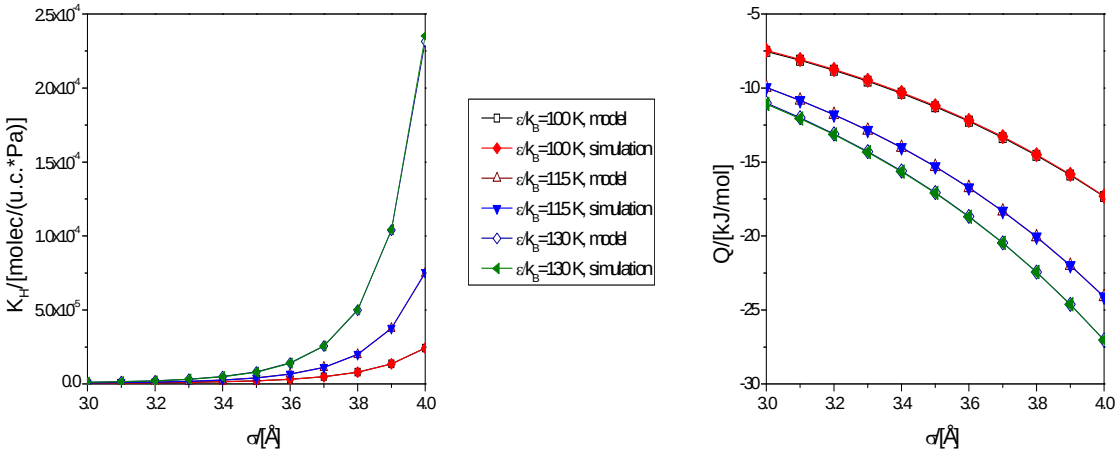

Figure 1: Henry coefficient of methane (left) and the heat of adsorption (right) in AFI zeolites at 300 K as a function of the force field parameters for guest-host interactions.

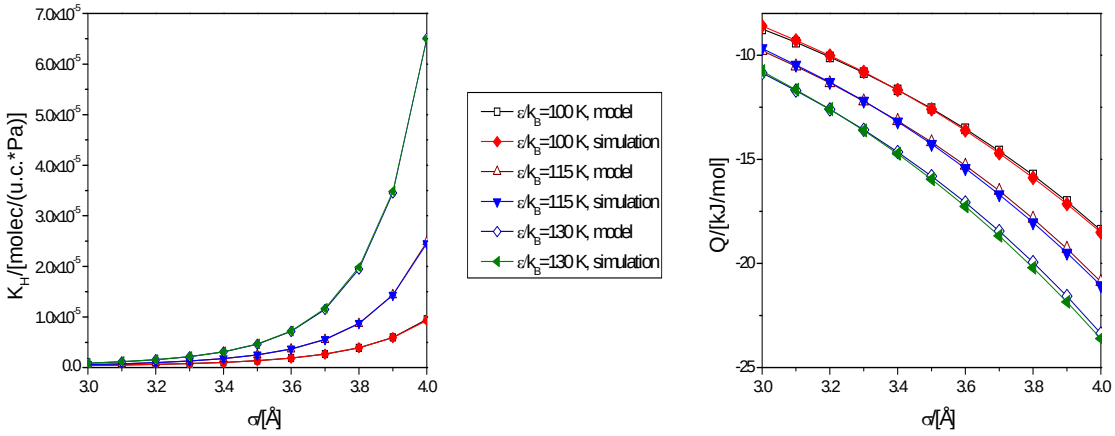

Figure 2: Henry coefficient of methane (left) and the heat of adsorption (right) in ITQ-29 zeolites at 300 K. as a function of the force field parameters for guest-host interactions.

Once the model parameters R_1, R_2, λ and U_{min} are fixed for a particular zeolite and guest species, the LJ guest-host parameters ε and σ for different guests can be predicted by the model. For each different guest, new values of these parameters can be found using known values for the Henry coefficient and the heat of adsorption. In table 1 those values are shown for methane.

Zeolite	Model Parameters			
	R_1/[Å]	R_2/[Å]	λ	$U_{min}k_B^{-1}$/[K]
AFI	5.1477	10.2550	1.4918	0.3375
LTL	4.9196	10.9750	1.0451	2.9283
TON	4.0420	8.1378	1.4223	0.4865
ITQ-29	5.3815	9.2728	1.3664	1.2072
MTT	3.9261	7.9745	1.5245	-1.9371

Table 1: Model parameters for the adsorption of methane in several zeolites.

Given target values for the Henry coefficient and the heat of adsorption, the guest-host parameters were computed following the scheme shown in Figure 3. To perform these calculations, we generated the target data values with molecular simulations using the accepted values from the literature (ε/k_B = 115 K and σ = 3.47 Å). The results for methane can be seen in Table 2. The entries in this table indicate the values of the guest-host interaction parameters after one, two and three iterations of the scheme shown in Figure 3. For the AFI-, LTL- and TON-type zeolites convergence was obtained in two iterations and for ITQ-29 and MTT a third iteration was needed.

Zeolite	Target Values		Predicted ε and σ	
	K_H/[molec./u.c./Pa]	Q/[KJ/mol]	εk_B^{-1}/[K]	σ/[Å]
First Iteration				
AFI	$3.62 \cdot 10^{-6}$	-14.91	114.00	3.4781
LTL	$3.37 \cdot 10^{-6}$	-14.33	113.22	3.5110
TON	$5.09 \cdot 10^{-6}$	-21.14	115.71	3.4626
ITQ-29	$3.38 \cdot 10^{-6}$	-20.98	110.15	3.5273
MTT	$2.26 \cdot 10^{-6}$	-13.94	112.91	3.5009
Second Iteration				
AFI	$3.62 \cdot 10^{-6}$	-14.91	115.04	3.4698
LTL	$3.37 \cdot 10^{-6}$	-14.33	114.78	3.4730
TON	$5.09 \cdot 10^{-6}$	-21.14	115.35	3.4660
ITQ-29	$3.38 \cdot 10^{-6}$	-20.98	114.23	3.4799
MTT	$2.26 \cdot 10^{-6}$	-13.94	113.68	3.4844
Third Iteration				
ITQ-29	$3.38 \cdot 10^{-6}$	-20.98	114.55	3.4753
MTT	$2.26 \cdot 10^{-6}$	-13.94	114.29	3.4760

Table 2: The guest-host parameters ε/k_B and σ for adsorption of methane predicted with the pore model using the scheme depicted in Figure 3. All values in this table were predicted starting with random initial values within the ranges 80 K $\leq \varepsilon/k_B \leq$ 130 K and 3.0 Å $\leq \sigma \leq$ 4.0 Å.

The results obtained in Table 2 show a very good approach to the accepted values from the literature. This is especially a good result since it has been obtained after very little iteration of simulation and fitting.

The time for calculating the force field parameter using the developed model required 1/15th of the amount of time that would be needed if simulations were used instead of the model at each step in the standard method using the simplex algorithm [3]. Since the computation time for fitting the force field parameters increases quadratically with the number of pair interactions, (e.g., from extra framework cations in the zeolite, or a dipole moment in the adsorbed gas) any degree of savings is crucial.

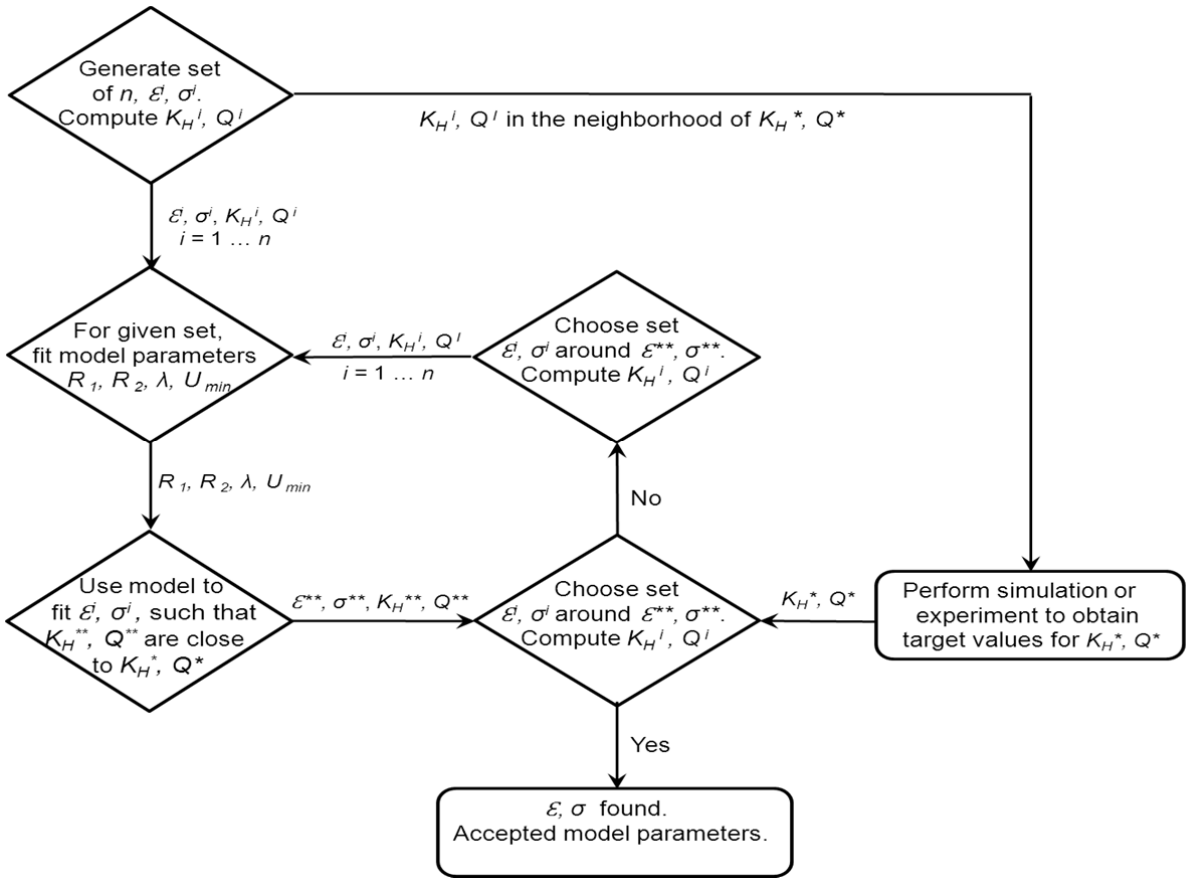

Figure 3: Schematic representation of the parameter fitting procedure.

Future collaboration with host institution and concluding remarks

The interesting result obtained during the 12 weeks in Delft with Prof. Vlugt directly trigger in a formal application for a research contract. Thanks to this contract we continued the study and extend it also to other guest molecules as ethane. The resulting work was submitted to The Journal of Physical Chemistry.

I plan to keep active collaboration with Prof. Vlugt as he is an expert in molecular simulation methods. We are thinking of extending our collaboration in new projects. Particularly we are considering the possibilities to do similar studies with other light gases and longer alkanes and also extend to other frameworks structures such as aluminosilicates, metal-organic frameworks (MOFs) and other novel host.

References:

1. Smit, B. and T.L.M. Maesen, *Molecular simulations of zeolites: Adsorption, diffusion, and shape selectivity.* Chemical Reviews, 2008. **108**(10): p. 4125-4184.
2. Caro, J. and M. Noack, *Zeolite membranes - Recent developments and progress.* Microporous and Mesoporous Materials, 2008. **115**(3): p. 215-233.
3. Garcia-Sanchez, A., et al., *Transferable Force Field for Carbon Dioxide Adsorption in Zeolites.* Journal of Physical Chemistry C, 2009. **113**(20): p. 8814-8820.
4. Dubbeldam, D., et al., *Force field parametrization through fitting on inflection points in isotherms.* Physical Review Letters, 2004. **93**(8): p. 088302.