The Motions of Water Molecules in Zeolite Chabazite: Molecular Dynamics Simulations

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Introduction

The presence of aluminum ions in zeolites leads to an anionic character of the framework, the negative charge in the crystalline lattice being neutralized by extra-framework cations. The presence of cations in the zeolite voids makes these materials hydrophilic and the interactions between water molecules and cations play an important role in the resulting functional properties.

The diffusion of water in Chabazite (see Fig. 1), a zeolite containing Ca^{++} ions, has been investigated by Jost $et\ al.$ [1] using the BJH [2] model. We have now extended these calculations using the SPC/E water model [3] which is computationally more efficient for our purposes. The self-diffusion coefficients (D_s) of water in chabazite at room temperature can be now obtained. In addition, the failure of the anisotropy factor prediction using the structure-correlated diffusion anisotropy has been explained.

Model and Methods

The simulation box has dimension of $26.4 \times 22.863 \times 30.2$ Å^3 ($2 \times 1 \times 2$ unit cells), containing 864 lattice atoms, corresponding to $Ca_2Al_4Si_8O_{24}$, per cage, for 24 cages. The two cations per cavity were initially put at random places. The lattice flexibility has been neglected in the MD simulations, which are carried out using the DL_POLY program, version 2.19 [4] in the canonical NVT ensemble.

The different numbers of water molecules, corresponding to loadings of 2-13 H_2O molecules per cavity, were put in the simulation box. Fig. 2 shows such a simulation box and, separately, the Chabazite lattice and the aqueous phase at a high loading. The interactions between the water have been modelled using the SPC/E potential. The potentials for the lattice-guest interaction are taken from ref [5]. Ewald summation is used to compute the long-range electrostatic interactions.
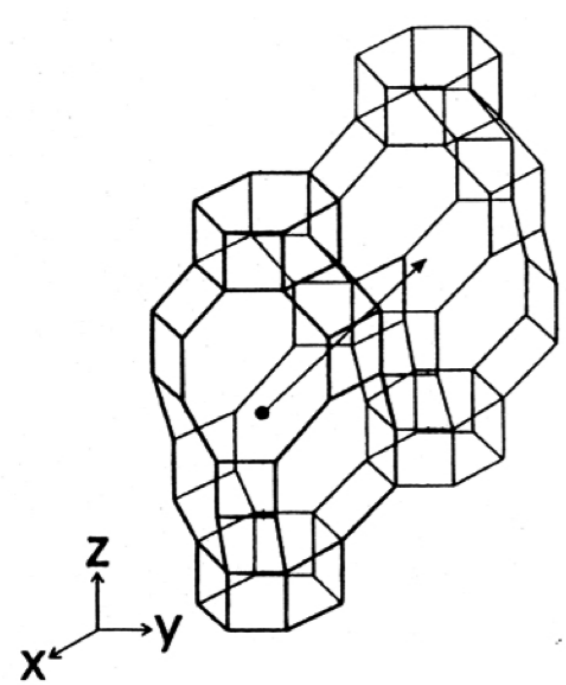
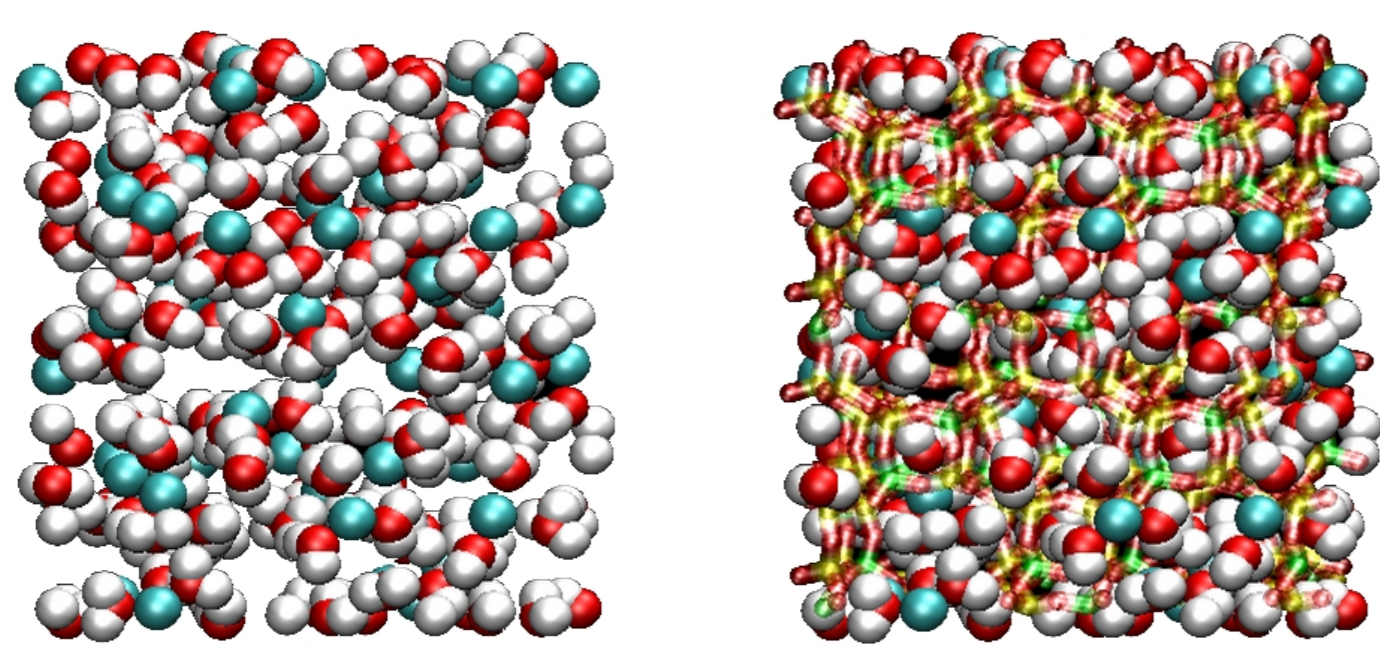Figure 1: Schematic view of the Chabazite framework

Figure 2: Simulation box for Chabazite with 312 water molecules. Left: water molecules (red: oxygen, white: hydrogen) and Ca^{++} ions (blue). Right: Chabazite lattice (stick style), water molecules and Ca^{++} ions.

The D values were determined from the mean square displacements (MSDs) of water molecules:

$$\mathrm{MSD}(t) = \langle (\rho_i(t-t_0) - \rho_i(t_0))^2 \rangle_{i,t_0}$$

where the ρ_i are their positions in the lab-system. The average $\langle \rangle_{i,t_0}$ is carried out over all time origin t_0 and equivalent molecules i. A linear function (Einstein's relation)

$$\langle (\rho_i(t-t_0) - \rho_i(t_0))^2 \rangle_{i,t_0} = \alpha \cdot D_s^i \cdot t + \alpha$$

is then fitted to the computed MSDs; $\alpha = 2D$ is equal to 2, 4, or 6 depending on the dimensionality of the motion. D_s^i is the self-diffusion coefficient, and β a fitting parameter. Fig 3 gives an example.

System	Number of water molecules	Number of Ca^{++} ions	Ca^{++} hydration water			
			total		per ion	
			300K	600K	300K	600K
Load 7	168	48	148.8	145.8	3.10	3.04
Load 13	312	48	212.3	208.8	4.42	4.35

Table 1: Details of simulated system and results

References

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Acknowledgments

Results

Ionic Hydration

Figure 4 shows the loading dependence of the distribution of hydration numbers of the Ca^{++} ions at 300 K. The hydration numbers increase with loading up to a more or less full hydration with an average hydration number of about 4, at the concentration of about 8 molecules per cavity. Table 1 shows that at a loading of 7 water molecules per cavity, virtually all water is in the hydration shells of the ions. This number of hydration water decreases only slightly with temperature, indicating the stability of these shells.
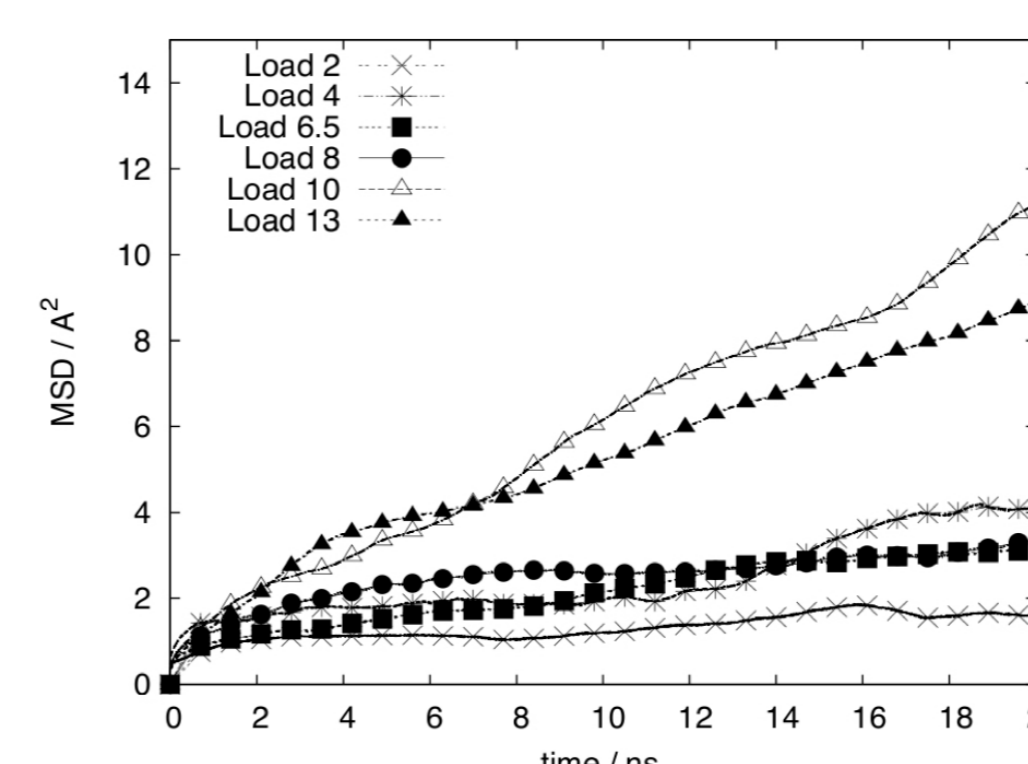

Figure 3: MSD for the water molecules over 20 ns, averaged over the first 5 ns of a 25 ns trajectory, for selected loadings at 300 K.
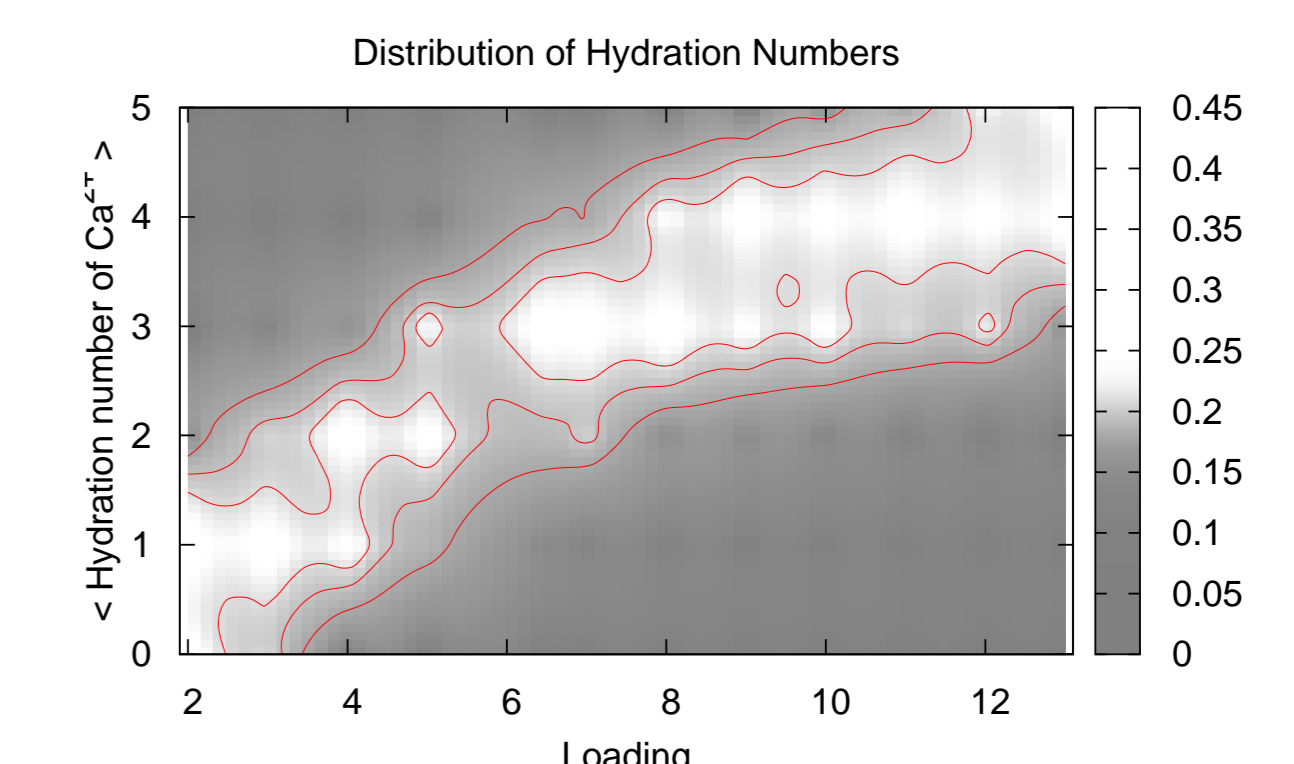

Figure 4: The hydration numbers of the Ca^{++} ions at 300 K. The probability scale is shown on the right hand sites.

Translational Self-Diffusion

Direct simulations of the self-diffusion of water were now also possible at 300 K, an improvement over the situation in Jost $et\ al.$ [1]. We can thus compare directly with experiment. It is also found that the long-ranged electrostatic interactions affect the self-diffusion at high loadings and temperatures; it gives the same trend as in Arbuckle $et\ al.$ [6].

In Figure 5, the long-time self-diffusion coefficient (D_{long}) increases with loading up to a loading of 10 H_2O/cavity. This is mainly due to the water molecules, which are mostly not in an hydration shell. At the highest loading, D_{long} is close to the experimental value [7]. The D of water molecules have been also calculated from the moments of the propagator. The D value from the 2nd moment agree within the error bars mentioned above with those from the long-time fits to the slope of the MSD.
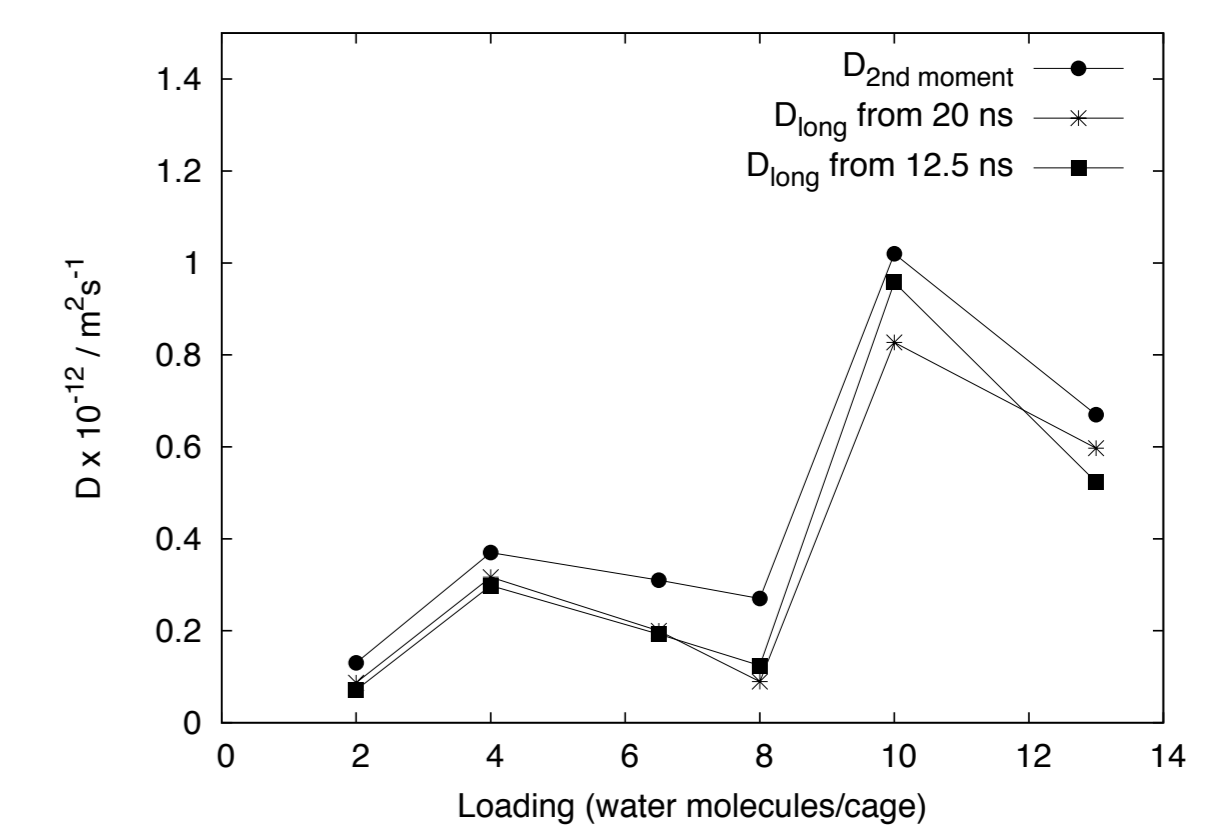

Figure 5: The loading dependence of D_{long} from MSD and from the second moment for all water at 300 K.

Structure-directed diffusion anisotropy

In Ref. [7], water diffusion in chabazite was predicted to be subject to the following equation of structure-related diffusion anisotropy

$$\frac{h^2}{2D_z} = \frac{r^2}{4D_{xy}}$$

where h is the vertical separation between two connected cavities in z-direction, r the horizontal separation between two connected cavities in x, y plane (see Figure 6). D_z and $D_{x,y}$ are the diffusivities in z-direction and in xy plane, respectively. With $h = 0.503$ nm and $r = 0.796$ nm, the equation yields an anisotropic factor of $\frac{D_z}{D_{xy}} = 0.8$. It is compared with the experiment and our MD values, see Table 2.
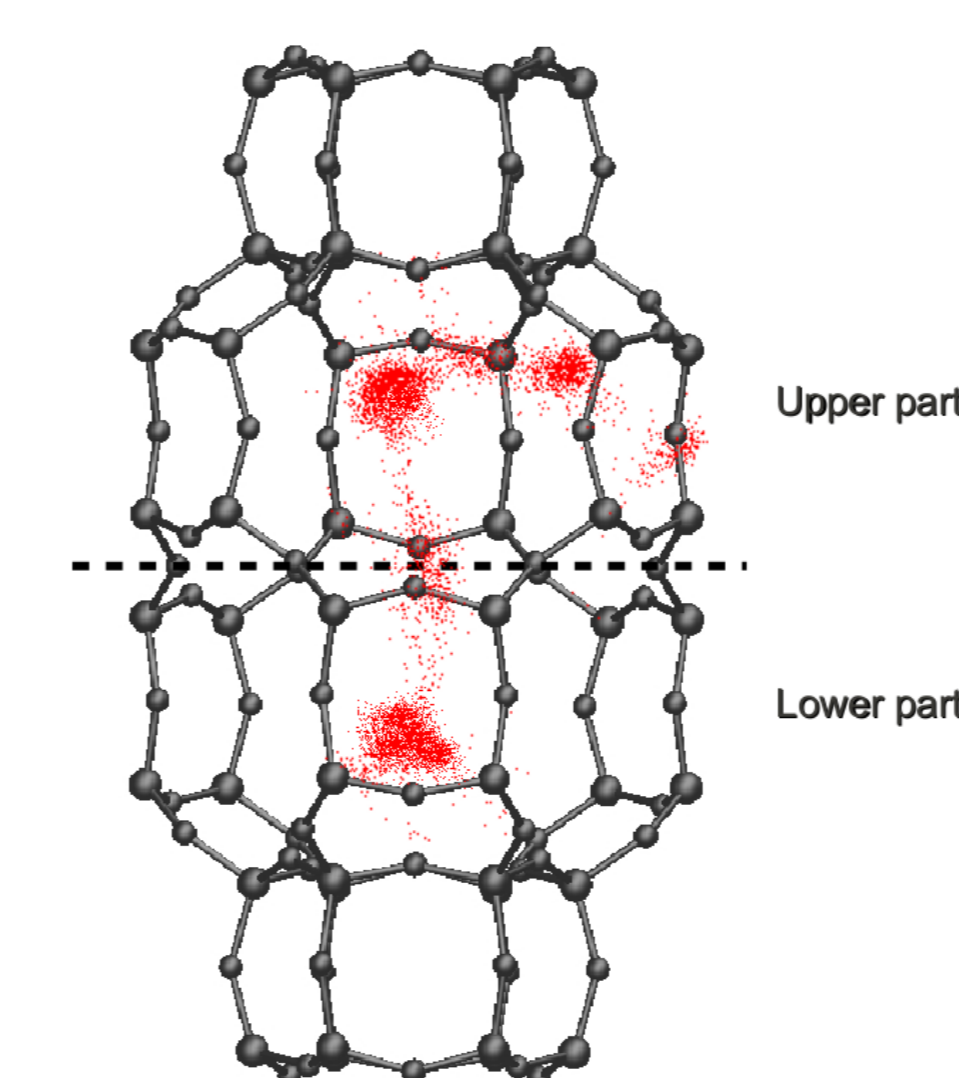

Figure 6: Positions of one water molecule within one cavity plotted with constant time increment during one simulation run.

$\alpha = D_z/D_{xy}$	Reference or Method
0.8	Bär $et\ al.$ [Jump model], Ref. [7]
0.4	Bär $et\ al.$ [PFG NMR], Ref. [7]
0.3	this work, MSD
0.23	this work, $\frac{N_{xy}}{N_{\mathrm{intra}}}$

Table 2: Anisotropy coefficient α

With the present simulations, the deviation from the assumption in Ref. [7] has been explained and this relation has been modified as:

$$\frac{h^2}{2D_z} = \tau_{\mathrm{intra}} + \frac{r^2}{4D_{xy}} = \left(\frac{N_{xy}}{N_{\mathrm{intra}}} + 1 \right) + \frac{r^2}{4D_{xy}}$$

where N_{xy} and N_{intra} denote the number of events from one cavity into an adjacent one or from one half of the cavity into the other half.

Interestingly, the transition between both parts of one cavity averaged over all particles have been found to happen less frequently than transitions to other cavities even in spite of the fact that some water molecules are adsorbed at positions close to the dividing plane and cross it more frequently.

Conclusions and Outlook

Molecular dynamics (MD) simulations are extended to room temperatures. For the self-diffusion of water in Chabazite, it is found that the procedure used to compute the long-range electrostatic interaction matters: Ewald summation is necessary for high loadings and temperatures. We thus get a better agreement between the computed and experimental anisotropy coefficients of self-diffusion. The failure of the anisotropic factor prediction has been explained and the diffusion anisotropy relation has been modified.