

Computer Simulations of Self-Diffusion of Adsorbed Water in a Model for Microporous Portland Cement

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Abstract

Microporous cement materials such as some types of Portland cement show swelling and shrinkage with strong hysteresis depending on the humidity. A quantitative theoretical explanation is based on the existence of strong forces mediated by adsorbed water between the pore walls and the resulting elastic response of the solid [1]. We have performed Monte-Carlo simulations of the adsorption equilibrium in the microcapillaries. The microcapillary structure of cementitious materials has been modelled using Tobermorite slit pores. We have found huge pressures and pressure anisotropy within the adsorbed water layers. Accordingly, we obtained self-diffusion coefficients on the surfaces that correspond in magnitude to coefficients in liquid water under high pressure in a three-dimensional bulk volume. Significant differences were observed in lateral diffusion (parallel to the walls) and normal diffusion (perpendicular to the walls). The diffusion kinetics strongly depends on the width of the slit pores. The diffusion coefficients were determined by tracking the mean square displacement of water molecules during the simulations. The pressure and diffusion curves are in accordance with density profiles and radial distribution functions calculated from our simulations.

Keywords

Microporous Portland Cement, Water Adsorption, Microcapillaries, Monte Carlo Simulation, Anisotropy of Pressure and Diffusion

Introduction

Microporous cement materials such as Portland cements show swelling and shrinkage with strong hysteresis depending on humidity (Fig 1). The dimensional change measured between two fixed points on the surface of the sample is a measure of the volume change at constant mass of the solid body. We proposed a quantitative theoretical explanation of the appearance of the huge hysteresis of the shrinkage/swelling curves during water desorption/adsorption cycles. This model is based on the existence of strong forces mediated by adsorbed water layers between the pore walls and the resulting elastic response of the solid [1].

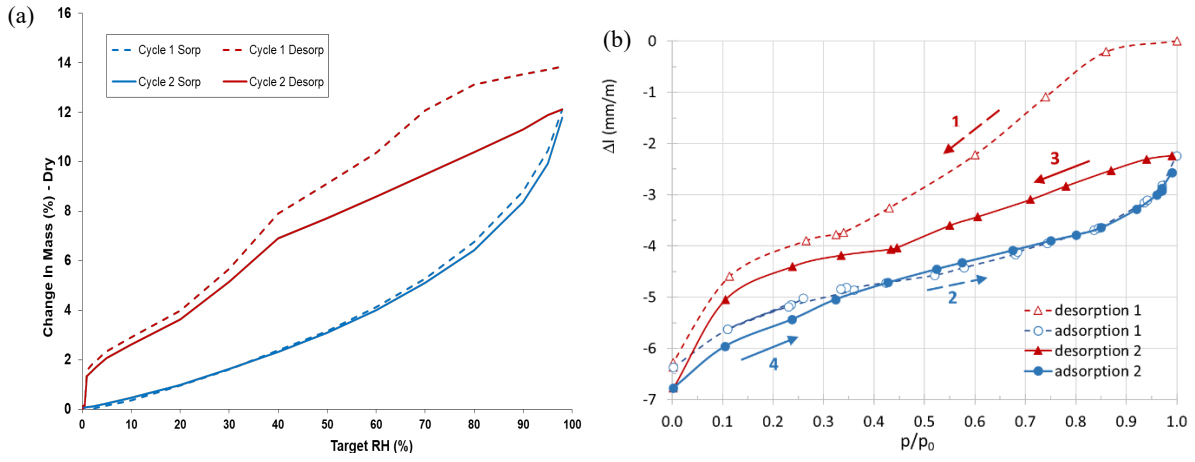


Fig. 1. Humidity depended mass change (a), and dimensional change (b, shrinkage/swelling) for a Portland cement sample during desorption/adsorption cycles at 300 K, $RH = 100\% \cdot p/p_0$ (relative humidity).

Monte Carlo Simulations of Water Adsorption in Microcapillaries

To further study forces and pressures induced by the water adsorption in the cement pores and microcapillaries, we have performed Monte-Carlo simulations of the adsorption equilibrium in the grand canonical ensemble at 300K. The micro-capillary structure of the cementitious material has been modelled as C-S-H interlayer space similar to Tobermorite slit pores (Fig. 2). Water molecules are parametrized according to the SPC model [2].

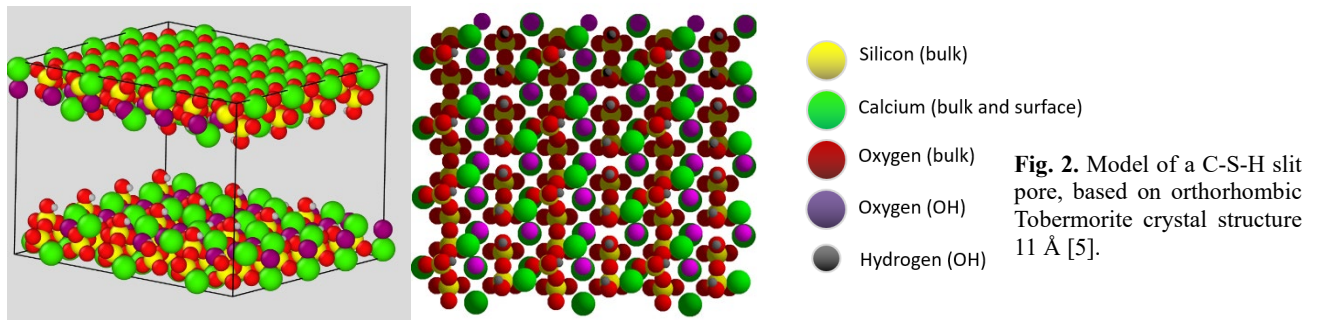


Fig. 2. Model of a C-S-H slit pore, based on orthorhombic Tobermorite crystal structure 11 Å [5].

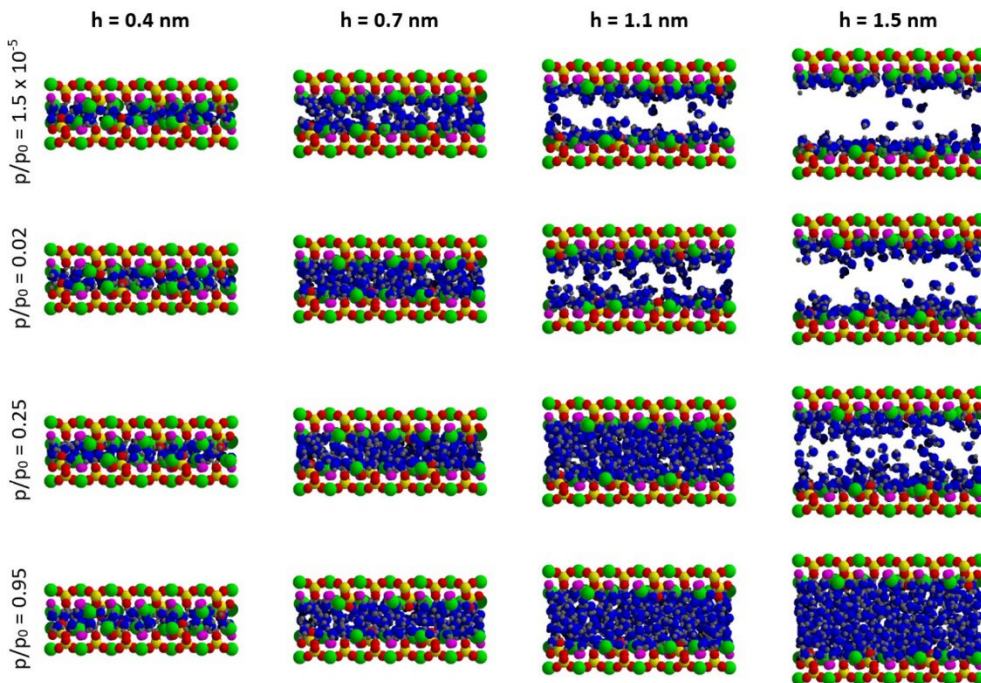


Fig. 3. Cross sections of snapshots of adsorbed water in Tobermorite-like slit pores with different pore width at selected humidities p/p_0 .

We have used the parameters of the Clay Force Field [3] for bonded and nonbonded interactions within the LAMMPS Software Package [4]. The size of the simulation box is 3.38 nm in x-direction, 2.95 nm in y-direction, and varies between 1.3 nm and 2.4 nm in z-direction. The range of slit widths in the z-direction is from 0.4 nm to 1.5 nm (Fig. 3). As results of the Monte Carlo runs, we analyzed the water phase structure in the adsorption equilibrium of water in the slit pores. Some examples of the equilibrated systems are shown in Fig.3.

Self-diffusion of Adsorbed Water in Microcapillaries

The pores filled partially or completely with equilibrated adsorbed water had been the starting configurations for further studying of self-diffusion coefficients of water by means of isothermal Molecular Dynamics simulations. The self-diffusion coefficients are obtained by tracking the water molecules and measuring the mean square displacement (msd) in the canonical ensemble as function of time. It is based on the simple relation $msd = 2 d D t$, where d is the dimension, D the self-diffusion coefficient and t the tracking time. By assuming a three-dimensional tracking in all pores, we have obtained effective self-diffusion coefficients. As shown in Figure 4, at all humidities, the diffusion becomes faster with increasing pore width, suggesting that confinement is a key factor in water mobility. The smaller the humidity the larger the value of the diffusion coefficient. This effect is especially strong in very narrow pores. As expected, the coefficients are smaller than the coefficients in an extended three-dimensional SPC-water volume under saturation pressure. The magnitudes of all self-diffusion coefficients of water in the pores are in line with the values for bulk water under higher pressure (Fig. 5). The pore walls act as an external force field on the water phase and give rise to water mediated forces between them which results in enormous pressure in the adsorbed water layers. Furthermore, an anisotropy is introduced by these forces. The diagonal elements of the pressure tensor corresponding to directions lateral and normal to the walls are different (Fig. 6). The water phases are inhomogeneous and display a layered structure with layers parallel to the walls. In this way, the diffusion occurs in an external field and should also show anisotropic behavior. For better understanding, we have studied the anisotropy of self-diffusion of adsorbed water in the slit pores at 95% humidity.

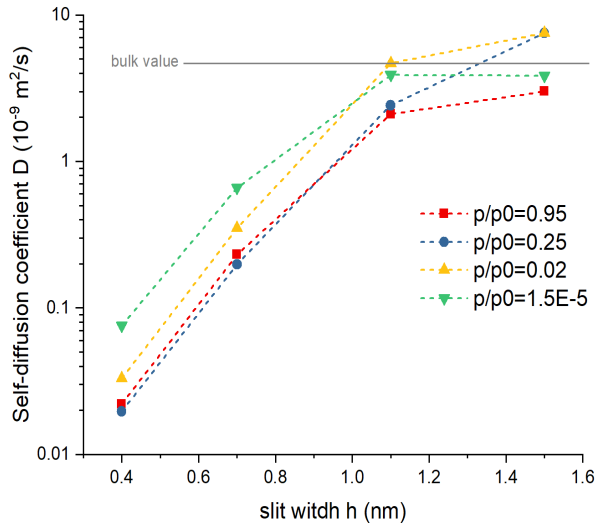


Fig. 4. Self-diffusion of water in relation to slit width at different humidity (p/p_0) at $T=300$ K.

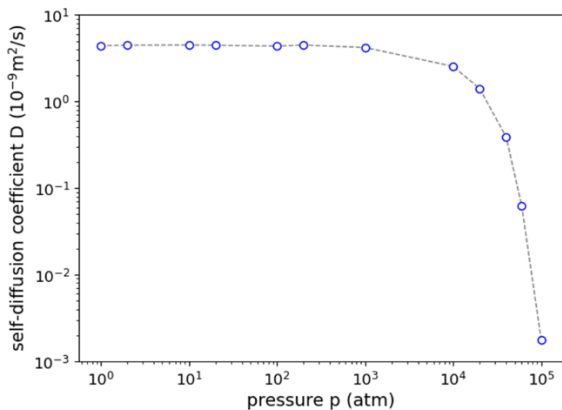


Fig. 5. Pressure dependence of the self-diffusion coefficient of SPC-water in a bulk phase at 300 K.

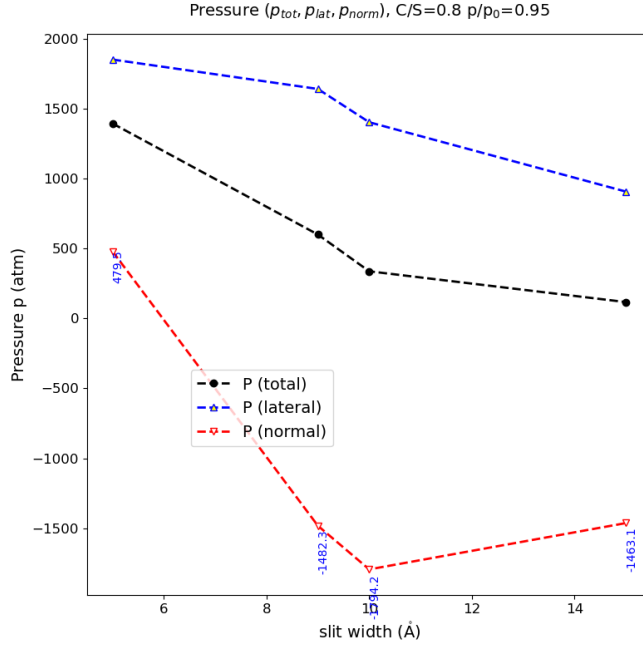


Fig. 6: Pressure anisotropy in water confined in Tobermorite slit pores at 95% humidity at 300K as function of slit width.

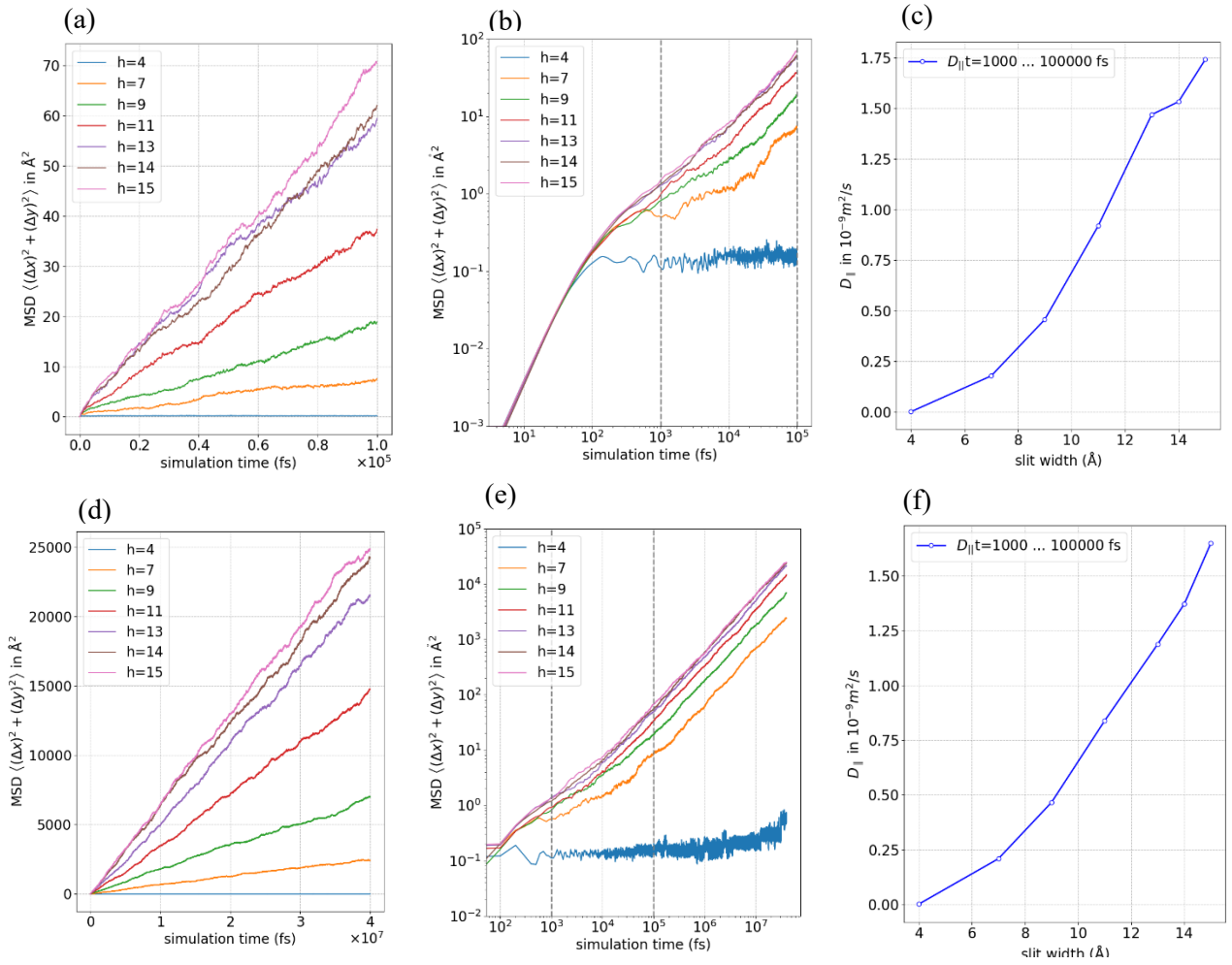


Fig. 7. Mean square displacement $MSD = \langle (\Delta x)^2 + (\Delta y)^2 \rangle$ for different slit widths h (a: linear scale, b: logarithmic scale) and c: self-diffusion coefficients $D_{||}$ (lateral direction) until simulation timestep $t = 10^5$ fs. For comparison, the values for an extended simulation time (4×10^7 fs) are given in (d) to (f).

The self-diffusion coefficients $D_{\parallel}$ in lateral direction have been obtained from the msd-values of two-dimensional tracking. The coefficients $D_{\perp}$ in normal direction were calculated from msd-values in one-dimensional tracking. Both self-diffusion coefficients display the same trend to increase with pore width. The self-diffusion coefficients in lateral direction are much larger than that ones in normal direction. Considering the anisotropy of pressure, it is seen that the higher pressure in lateral direction is related to a faster diffusion compared to the diffusion in normal direction, where the pressure is even negative (tension). In Fig. 7 and 8, the shorter timescale (a - c) shows a first diffusion regime (ballistic), whereas longer simulations (d - f) are necessary to reach the actual diffusive regime.

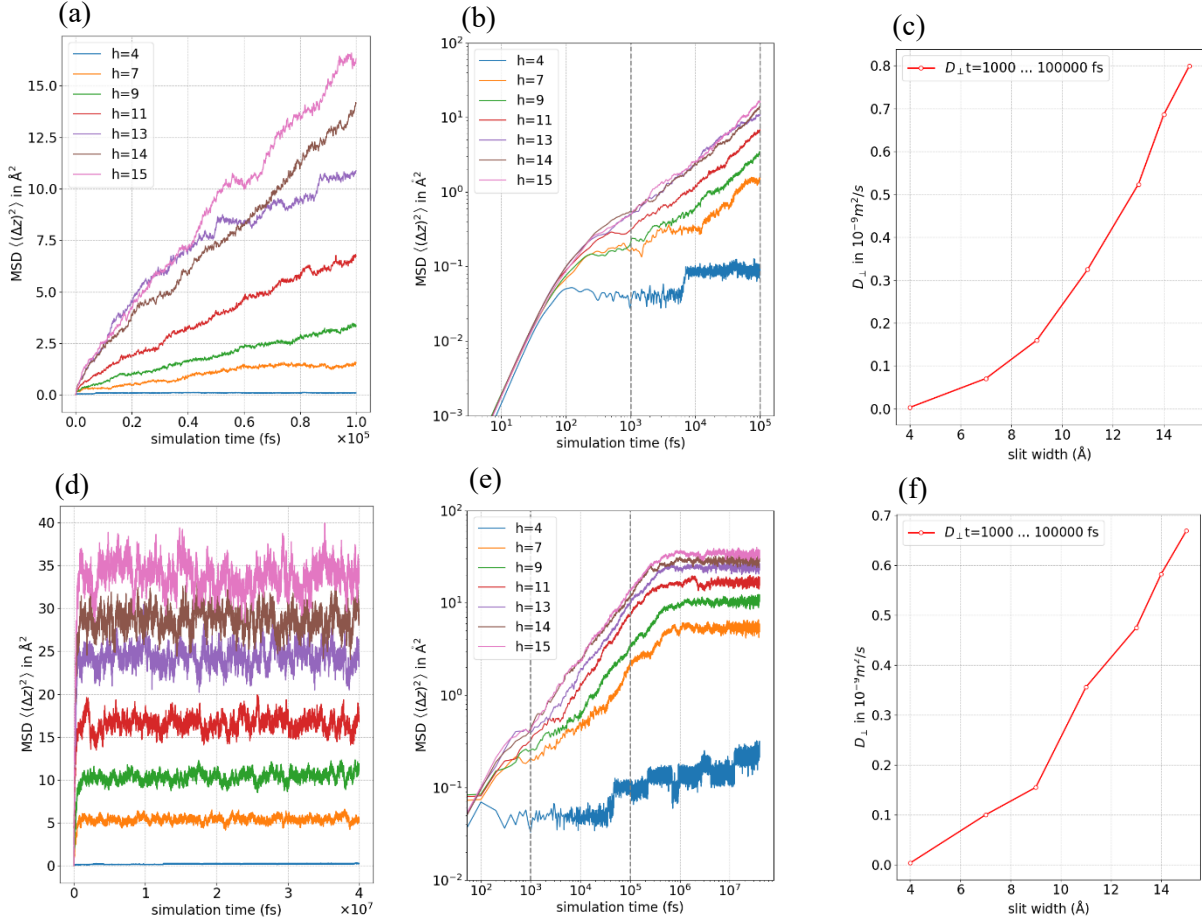


Fig. 8. Mean square displacement $MSD = \langle (\Delta z)^2 \rangle$ for different slit widths h (a: linear scale, b: logarithmic scale) and c: self-diffusion coefficients $D_{\perp}$ (normal direction) until simulation timestep $t = 10^5$ fs. For comparison, the values for extended simulation time (4×10^7 fs) are given in (d) to (f).

Conclusions

The results of our computer simulations confirm the assumption that the hysteresis of swelling and shrinkage of some microporous cementitious materials during water adsorption/desorption cycles can be caused by enormous forces occurring between pore walls of micropores. These forces give rise to anisotropy of pressure and self-diffusion of the adsorbed water. In this way, simulating water self-diffusion helps understand a key aspect of the behavior of water in interlayer pores, of cement hydration and draw conclusions about the behavior of building materials under atmospheric conditions as well.

References

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