ATOMISTIC MODELLING OF WATER TRANSPORT DYNAMICS IN CEMENTS

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Introduction

Molecular Dynamics (MD) and Monte Carlo (MC) modelling techniques are used to determine the pairwise dipolar correlation function, $G^*(t)$, and the exchange between different water populations in a series of model systems advancing in complexity and approaching that of a C-S-H (Calcium Silicate Hydrate) analogue shown in fig. 1. The correlation function is used to calculate the nuclear magnetic resonance (NMR) spin-lattice relaxation dispersion, $T_1(\omega)$ where ω is the Larmor frequency in the applied static field. Comparisons can then be made between the simulations and experimental data and also the Korb[1] model which is currently accepted as the best fit to experimental data.
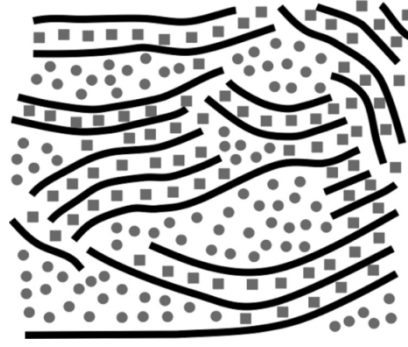

Figure 1: A schematic view of the calcium-silicate-hydrate gel nanostructure proposed for cements. The gel comprises of layers of calcium and oxygen atoms and silicate tetrahedra (solid lines) separated by sheets of water (filled square). Slightly larger gel pores circa 3–5 nm wide and filled with water (filled circle) separate regions of locally aggregated layers (from [2]).

NMR relaxometry is a powerful characterization tool of porous structures saturated with proton-rich fluids. In systems with bulk and surface-bound water, and in the limit of fast exchange between them, the NMR dispersion can be interpreted as a mixture of relaxation profiles modulated by an exchange time. Korb's model supposes water molecules undergo a 2D walk over porous surfaces and that the dominant relaxation mechanism is associated with Fe^{3+} impurities. The model introduces two adsorbed correlation times, one for the surface diffusion and one for the surface residency time. The overall observed relaxation rate is the weighted average of that from the surface and the bulk. The Korb model has been so far successful in fitting to experimental data but remains under investigation because the surface residency time of 13 μs derived from fit to experimental data is surprisingly long and is more than three orders of magnitude larger than observed in MD simulation.

MD is used to investigate the nanoscale dynamics of water in the vicinity of poor surfaces. It is also used to calibrate large-scale, longer time MC simulations.

Theory and methods

The spin-lattice (T_1) relaxation dispersion for a collection of spins of the same nuclear species diffusing in a space subject to a static magnetic field is given by the well-known equation [3]

$$\frac{1}{T_1(\omega)} = \frac{1}{5}\left(\frac{\mu_0}{4\pi}\right)^2 \gamma^4 \hbar^2 I(I+1)[J^*(\omega) + 4J^*(2\omega)], \tag{1}$$

where γ and I are the gyromagnetic ratio and spin of the spins and ω is the Larmor frequency in the static field. The powder-averaged spectral density function $J^*(\omega)$ is defined as the Fourier transform of the stationary pairwise dipolar correlation function, $G^*(t)$:

$$J^*(\omega) = \int_{-\infty}^{\infty} G^*(t)\, e^{i\omega t} dt, \tag{2}$$

$$G^*(t) = \left\langle \left| \frac{\frac{1}{2}(3\cos^2\psi - 1)}{r_0^3 r^3} \right| \right\rangle^1, \tag{3}$$

where r_0, r are the magnitudes of spin-pair vectors, $\boldsymbol{r_0}, \boldsymbol{r}$ at $t = 0$ and time t respectively. The angle ψ represents the angle between the vectors $\boldsymbol{r_0}, \boldsymbol{r}$. The angled brackets denote an ensemble average over all spins in the system. The powder average correlation function $G^*(t)$ may therefore be computed directly from either a MD or MC simulation using equation (3) regardless of the geometry of the system [5]. $G^*(t)$ contains all the information necessary for the computation of the spin-lattice relaxation dispersion.

The MD simulation technique involves evaluating all the inter-atomic forces present in the system using specified potentials. Femtosecond-interval constant-acceleration calculations enable the atomistic trajectories to be determined. This provides a unique insight into the dynamics of the system given well-chosen and calibrated potentials, but comes at great computational cost. The MC acts as a crude representation of the MD simulation. A lattice is created with a defined structure which represents the different states of water; bulk and surface bound. The crucial dynamics observed in the MD can be encoded into the MC via a parameterization of the concentrations and rates of motion for atoms moving in and exchanging between regions. The MC can then be used to map out a larger time domain for the correlation functions, allowing for relaxation times to be calculated in the frequency range of 1-10MHz, which is important for drawing comparisons with experiment. A snapshot of a MD system, and a schematic of the MC system can be seen in fig. 2.
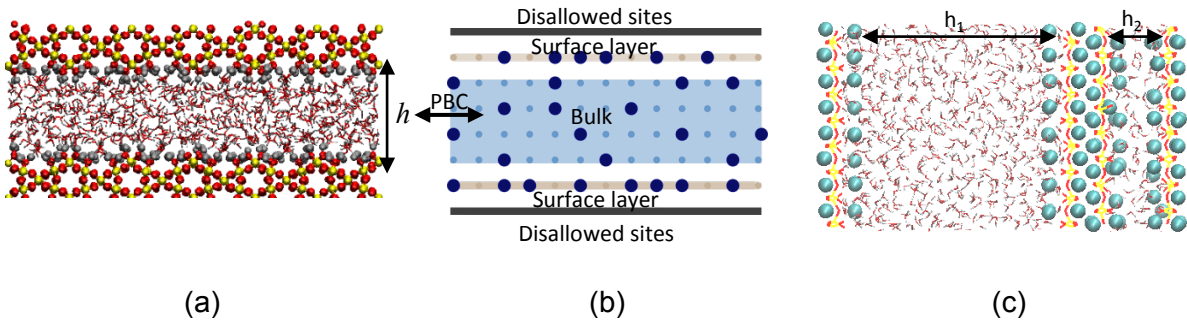

<p style="text-align:center">(a)   (b)   (c)</p>

Figure 2: (a) A snapshot from MD simulations of Q2D water confined between (100) facets of alpha-quartz with h = 1.0nm. The atoms of the crystal are large spheres, surface hydroxyls are small spheres, and water molecules are shown as sticks. (b) Schematic of a Q2D MC lattice, showing the structural regions and periodic boundaries. The spins move in discrete hops from site to site with probabilities parameterized from MD. PBC indicates periodic boundary conditions apply. (c) A snapshot from MD simulation of a two pore modified Tobermorite system with h_1=3.0nm and h_2=1.4nm. Yellow and red lines represent the crystal Silicate structure, blue balls are Calcium atoms and water molecules are shown as sticks.

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[1] Note the $G^*(t)$ given here is the reduced version obtained from performing a powder average over crystallite orientations.

Results

Fig. 3 shows the correlation functions $G^*(t)$ and resultant T_1 dispersions from MC and MD Q2D systems of varying pore thickness (1nm, 2nm, 3nm) with results from bulk water simulations included for comparison in Fig. 3(a).
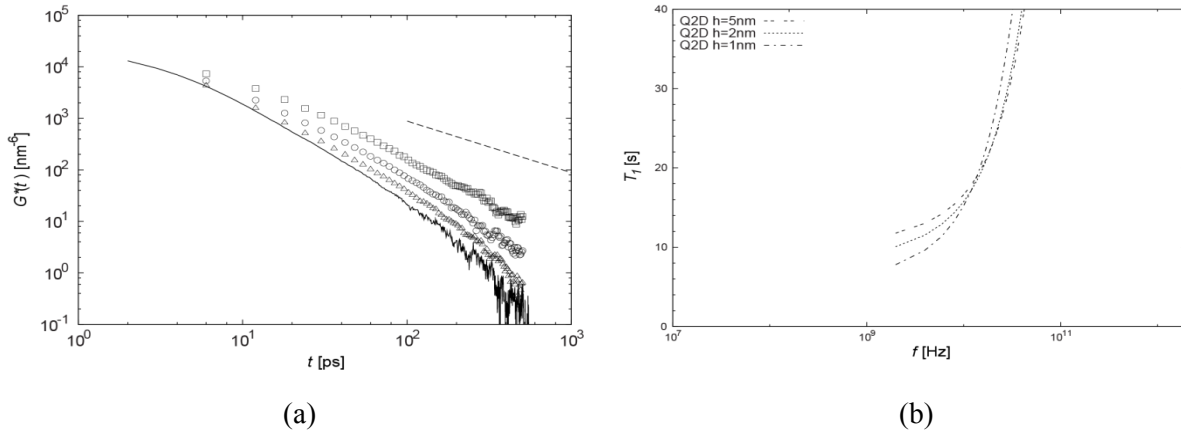

<center>(a)   (b)</center>

Figure 3 (a): $G^*(t)$ from MD simulations of water in a Q2D system with thickness approximately 1.0 nm (open square), 2.0 nm (open circle), and 5.0 nm (open triangle). The MD 3D data (solid line) and the analytic expression for $G^*_{2D(t\to\infty)}(t)$ (dashed line) are also presented for comparison. (b) T_1 dispersions for the MD Q2D correlation functions shown in (a).

Fig. 3 shows the progressive change in $G^*(t)$ moving from a 2D to a 3D system. Q2D systems are thought to be characteristic of cement pores. The dashed line represents an approximate analytical 2D result applicable for long times.

Not seen on the timescale of the MD simulations, but clearly seen in the longer MC Q2D simulations in Fig 4, is a later transition to 2D behaviour. This transition is clearly seen by a sharp departure from the 3D curve. The relaxation dispersions show a splitting as the frequency decreases, this is indicative of a linear relationship of T_1 with pore thickness, which is expected. It is noted that the $G^*(t)$ does not attain the standard A/t form at longer times until 0.1 μs for the thinnest slab pore and at longer times for thicker Q2D systems.

Finally, Fig. 5 presents the number of spins that are contained within the surface region of the Q2D pore at time t, given that they were in the surface region at $t=0$, as obtained from MD simulation. Curves are shown for a simple slab pore with silica walls and another with tobermorite walls containing terminating hydroxyl groups and calcium ions. The decay of the spin density is approximately exponential with time constants of 493 ps, 113 ps and 31 ps respectively, both significantly shorter than the 13 μs necessary for the Korb model to fit experimental data.
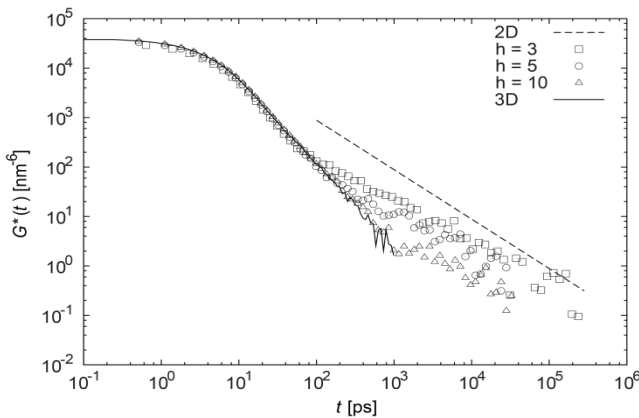

Figure 4: $G^*(t)$ is plotted as a function of time for MC simulations of water in a Q2D system with thickness 3 layers (0.7 nm) (open square), 5 layers (1.2 nm) (open circle), and 25 layers (6.0 nm) (open triangle). The MC 3D data (solid line) and the analytic expression for $G^*_{2D(t\to\infty)}(t)$ (dashed line) are also presented for comparison.

The conclusion drawn from this work is that the residency time obtained via the Korb model is not in agreement with any of the systems tested here. This implies that either the Korb model has shortcomings in its representation of the CSH system, or some fundamental structural/chemical component of the model is missing in the MD simulations.
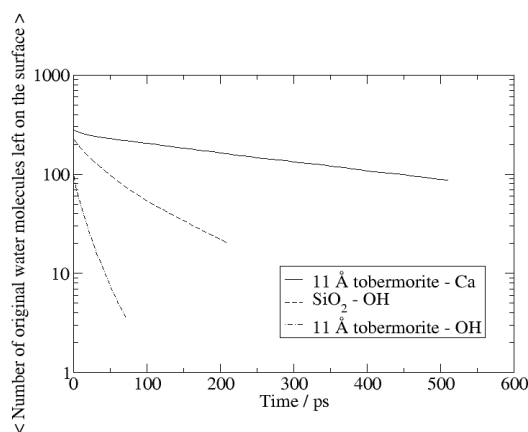
< Number of original water molecules left on the surface >

1000

100

10

1

— 11 Å tobermorite - Ca
--- SiO_2 - OH
-·- 11 Å tobermorite - OH

0   100   200   300   400   500   600
Time / ps

Figure 5: The number of molecules remaining absorbed to the surface, given they were at $t = 0$ is shown for different crystal nanostructures; SiO_2 and tobermorite with and without surface calcium ions. The calcium clearly increases the residency time, but remains more than four orders of magnitude below the 13µs value suggested by the Korb model [8].

REFERENCES:

[1] J.-P. Korb, M. Whaley-Hodges, and R. G. Bryant, Translational diffusion of liquids at surfaces of microporous materials: Theoretical analysis of field-cycling magnetic relaxation measurements, Phys. Rev. E 56, 1934 (1997).

[2]M. Zalzale, P.J. McDonald, Lattice Boltzmann simulations of the permeability and capillary adsorption of cement model microstructures, Cement and Concrete Res. 42 1601-1610 (2012).

[3] A. Abragam, The Principles of Nuclear Magnetism (Oxford University Press 1961).

[4] F. Barberon, J.-P. Korb, D. Petit, V. Morin, and E. Bermejo, Observation of exchange of micropore water in cement pastes by two-dimensional T2-T2 nuclear magnetic resonance relaxometry, Phys. Rev. Lett. 90, 116103 (2003).

[5] D. A. Faux, P. J McDonald, N. C. Howlett, J. S. Bhatt and S. V. Churakov, Nuclear magnetic resonance relaxometry of water in two- and quasi-two dimensions, Phys. Rev. E 87, 062309 (1013)

[6] R. T. Cygan, J.-J. Liang and A. G. Kalinichev, Molecular Models of Hydroxide, Oxyhydroxide, and Clay Phases and the Development of a General Force Field, J. Phys. Chem. B 2004, 108, 1255-1266.

[7] C. L. Freeman et al., New Forcefields for Modeling Biomineralization Processes, J. Phys. Chem. C 2007, 111 (32), 11943-11951.

[8] P.J. McDonald, J.-P. Korb, J. Mitchell and L. Monteilhet, Surface relaxation and chemical exchange in hydrating cement pastes: A two-dimensional NMR relaxation study, Phys. Rev. E 72, 011409 (2005)