Molecular simulations of hydrated inorganic nanopores

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Fluid transport in porous media is of interest in fields as diverse as aquifers, oil reservoirs, cement hydration, plant-water hydraulics and human physiology. Nuclear magnetic resonance (NMR) experiments have considerably improved the understanding of the dynamics of proton-bearing fluids in porous media[1] by measuring the spin-lattice and spin-spin relaxation times, denoted as T_1 and T_2 respectively, which arise as a result of magnetic dipole coupling between diffusing spins.

In nanoscale pores, surface effects can be very prominent because, for example, paramagnetic impurities may reside in the solid surface and the transition between 'surface' and 'bulk' fluid is often blurred. Molecular simulations can play a vital role in complementing NMR experiments in terms of understanding the chemical morphology of the solid surface and the atomistic details of liquid diffusion.

We have carried out classical molecular dynamics (MD) simulations of water confined between SiO_2 and tobermorite surfaces. NMR relaxation rates are determined by taking the Fourier transform of the time-dependent dipolar spin-spin correlation function, $G^*(t)$, which captures the details of the angular and the relative translational motion of spins[2,3,4].

We have calculated the water density profile, diffusion coefficients and NMR relaxation rates as a function of slit-pore thickness in cement analogues. We find that the diffusion of water on the surface is slow, in agreement with experiments on cements, but that it may take place predominantly in one-dimensional channels rather than in two dimensions as supposed by analytical models of NMR relaxation. Surface-bulk exchange rates are estimated and interpreted in terms of these current models. The impact of aqueous calcium ions on water mobility is found to be significant and to play a critical role in the interpretation of experimental relaxation rates.

These results help us understand cement nanostructure, which is vital in creating durable and eco-friendly cements for the future.

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[1] McDonald, P.J., Korb, J.-P., Mitchell, J., Monteilhet, L., *Phys. Rev. E* 72:011409, 2005.
[2] Sholl, C.A., *J. Phys. C: Solid State Phys.* 14:447-464, 1981.
[3] Faux, D.A., Ross, D.K., Sholl, C.A., *J. Phys. C: Solid State Phys.* 19:4115-4133, 1986.
[4] Faux, D.A., McDonald, P.J., Howlett, N.C., Bhatt, J.S., Churakov, S.V., *Phys. Rev. E*, accepted.