Long-range dynamical correlations restrict water transport in smectite interlayers

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Swelling clay particles such as smectites may expand or contract by either including or excluding water from their interlayer spaces in response to external conditions. The dynamics of clay-trapped water differ from the bulk water, mostly due to the finite interlayer space (confinement)[1] and overlapping electrical double layers.[3] Because rate of many geochemical reactions involving clay systems is govern by reactants interlayer mobilities,[4] understanding of how these effects get entangled is critical.

Using molecular dynamics simulations we observed that rate of water diffusion increases with increasing smectite plate separation (Δl). However, we also detected a fascinating oscillation in water mobility as the number of water monolayers that separate clay plates incrementally increases (*i.e.*, in a layering transition: $1 \rightarrow 2 \rightarrow 3 \rightarrow \ldots \rightarrow n$). We observed that with increasing Δl water mobility in the middle of confinement approaches that of the bulk water, even though the of surface water remains dynamically restrained. More interestingly, we observed that the presence of water outside of the smectite plates decreases interlayered water mobility along the layering transition (molecular electrofriction), but has no effect on its structure.

Our findings suggest that the transport of all polarizable species within clay layers is affected by similar long-range interactions. For instance, the presence of other ions might diminish the interlayer water moblity by disrupting structure and collective dynamics of interfacial water.

[1] Burada P. S., et al. (2009) *ChemPhysChem* **10**, 45–54. [2] Dix J. A. and Verkman A. S. (2008) *Annu. Rev. Biophys.* **37**, 247–263. [3] Holmboe M. and Bourg I. C. (2014) *J. Phys. Chem. C* **118**, 1001–1013. [4] Churakov S. V. (2013) *Environ. Sci. Technol.* **47**, 9816–9823. [5] Demontis P., et al. (2013) *J. Phys. Chem. C* **117**, 15583–15592.