Water Mediated Interactions Between Calcium Carbonate Surfaces at Nanoconfinement Conditions

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Calcium carbonate (CaCO₃) polymorphs such as calcite and aragonite are cementing materials used by many oceanic organisms to create protective exoskeletons. The material is abundant in the earth's crust and has been used for centuries as a construction material (cement). Crystal growth and dissolution in solution is initiated at the molecular level, hence, structural forces arising from the ordering of water in solvation layers are important [1]. The ordering of the solvent leads to solvation forces at short crystal interfacial separations [2]. A better understanding of solvation forces is essential to develop models to describe the mechanisms determining particle suspensions relevant in cementing materials. We have performed grand canonical molecular dynamics simulations of water in CaCO₃ nanoconfinements of calcite (1014) and aragonite (001) surfaces which have hexagonal and orthorhombic symmetries, respectively. The topology of the surface induces strong epitaxial effects in the structure of the layers adsorbed on the mineral surfaces. We find that the calcium ions impose a specific adsorption pattern of the water molecules with the oxygen atoms in the water molecule bridging the Ca²⁺ ions in the surface. The checkerboard pattern on the (1014) surface of calcite imposes more ordering than the (001) surface of aragonite. We also investigate the impact of surface-to-surface epitaxy. We show that, in the case of calcite, the solvation forces on the (1014) surface are weakly dependent on epitaxy perpendicular to the (010) surface, and in the case of aragonite, the solvation forces on the (001) surface of aragonite is strongly dependent on epitaxy shifting the surface out of registry perpendicular to the (010) surface.

References:

[1] Y. Diao and R. Espinosa-Marzal (2016), Proc. Natl. Acad. Sci. U.S.A. 113(43), 12047-12052, "Molecular insight into the nanoconfined calcite–solution interface"

[2] J. Israelachvili (1987), Acc. Chem. Res. 20(11), 415-421, "Solvation forces and liquid structure, as probed by direct force measurements"