

# **Role of dynamic polarization interactions in the electrical double layer structure at calcite (104) interfaces with aqueous solutions**

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Reactivity and dynamics at mineral interfaces with aqueous electrolytes control many geochemical and biogeochemical processes in the Earth's critical zone. Fundamental understanding of reaction mechanisms continues to improve due to the increasing fidelity of laboratory instrumentation and computational approaches. However, important techniques such as molecular simulation suffer from limited reach into relevant scales of time, length, and system complexity. To address this challenge, a novel hybrid approach that couples first principle plane-wave density functional theory (DFT) with classical DFT (cDFT) is demonstrated. In this approach, a region of interest described using DFT interacts with the surrounding medium described using cDFT to arrive at a self-consistent ground state. Benchmarking against experimental observations and entirely first principle DFT simulations demonstrates that this hybrid model efficiently encompasses the key short-range and collective interactions in the electrical double layer. The model is applied to reveal the role of static and dynamic polarization interactions in structuring of interfacial electrolyte at the calcite (104) interface. Our simulations predict that ion hydration interactions have the strongest effect on the depth of the first minimum in the density distribution of counterions at the surface, and that the position and width of the first peak is largely determined by the strength of ion-correlation forces. Mutual polarization of the calcite surface and interfacial electrolyte affects the fine details of ion distributions and is expected to modulate interfacial reactivity.