Universal dipole correlation in homogeneous bulk and interfacial water

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Understanding electrostatic interactions near surfaces and interfaces is of critical importance in various fields of science. The interplay of electrostatic interactions through the symmetry-breaking boundaries plays the major role in thermodynamic and dynamic behavior of the system. Recent advances in surface specific spectroscopic techniques have greatly enhanced our understanding on these interfacial phenomena, although precise molecular understanding of these complex systems is still challenging. Strong confinement induced by two of such dielectric interfaces provide unique environment for novel materials synthesis and manipulation.

This study investigates the anomalous behavior observed in strongly confined water, specifically the significant reduction in its dielectric constant that has been confirmed through experimental and simulation studies. Using molecular dynamics simulations that fully incorporate the dielectric response of confining walls, we aimed to identify the molecular mechanisms governing the dielectric reduction. Our simulations revealed that the reduction in dielectric constant occurs independently of the electronic polarization at the surface, which contradicts previously proposed mechanisms. We also found that the local fluctuation in the dipole of a water slab does not vary significantly from the locally aligned interfacial region to the homogeneous bulk region. Instead, we discovered that a small, positive dipolar correlation between a set of water slabs plays a critical role in determining the total dielectric response of the confined water. We found that the long-range correlation is independent of the confinement size and the interfacial structure, resulting in a linear correspondence between the confinement length and the total dielectric constant in the direction orthogonal to the confining wall surface. Furthermore, our simulation suggests that allowing capillary fluctuation on the interfacial water structure mitigates the dielectric reduction. Our findings provide novel insights into the nature of the observed anomalous behavior and have important implications for controlling and designing interfacial electrochemical systems.