Dielectric water properties, which significantly change in confinement, determine electrostatic interactions and thereby influence all molecular forces and chemical reactions. Furthermore, many vital processes taking place in electrolytes, such as nanoparticle self-assembly, water purification, and the operation of aqueous supercapacitors, rely on the precise electrostatic many-body interactions between surfaces and ions in water.

But how to derive meaningful effective dielectric quantities from simulations or experiments and how to calculate ion−ion interactions at interfaces or in confinement in the presence of tensorial dielectric constants are far from settled. We use atomistic molecular dynamics simulations in conjunction with effective medium theory to investigate dielectric effects at aqueous interfaces, in planar and cylindrical nanoconfinement. Together with the solution of Poisson's equation for anisotropic dielectric media we are able to predict electrostatic self energies at interfaces and ion−ion interactions in confinement. These analytic predictions are on a level of linear dielectrics in good agreement with ion free energies obtained from simulations.