The extent of confinement effects on water is a subject of considerable research. While some properties are affected only within a few nanometers from the wall surface, others are affected over long length scales, but the range is debatable. In this work, we have examined the dielectric response of confined water under the influence of external electric fields along with the dipolar fluctuations at equilibrium. The confinement induces a strong anisotropic effect evident up to 100 nm channel width, and may even extend to macroscopic dimensions [1]. The root-mean-square fluctuations of the total orientational dipole moment in the direction perpendicular to the surfaces is one order of magnitude smaller than the value attained in the parallel direction and is independent of the channel width. Consequently, the isotropic condition is unlikely to be recovered until the channel width reaches macroscopic dimensions. Consistent with dipole moment fluctuations, the effect of confinement on the dielectric response also persists up to channel widths considerably beyond 100 nm. When an electric field is applied in the perpendicular direction, the orientational relaxation is 3 orders of magnitude faster than the dipolar relaxation in the parallel direction and independent of temperature. We suggest that spatial confinement induces a preferential path on the hydrogen bond network for the dipole moments to collectively align with a perpendicular electric field, without having to overcome any significant energy barrier. The perpendicular component of the net dipole moment relaxes toward the new equilibrium state in a few femtoseconds, even for mesoscale channel sizes.

References: