Nonreciprocal interactions induced by water in confinement

Felipe Jimenez-Angeles, Katherine J. Harmon, Trung Dac Nguyen, Paul Fenter, and Monica Olvera de la Cruz

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The water polarization at the interface with graphene responds unsymmetrically to anions and cations and leads to non-equivalent interactions (upon position interchange) between two oppositely charged ions at the water graphene interface.

Electrostatic interactions between ions, molecules, and interfaces are crucial in ion adsorption and transport, molecular self-assembly, surface chemical reactions, to mention a few. At the water-graphene interface these physicochemical phenomena are employed for applications such as water desalination, electrochemical energy storage and harvesting, and characterization of biomolecules. Hence, it is of paramount importance understand how water mediates electrostatic interactions via the orientation of its dipoles. We investigate the effective interaction between two oppositely charged ions in different positions in water confined between two graphene surfaces. We find that the attraction between physisorbed ions is enhanced in the surface normal direction while the in-plane interaction is almost unaffected. The attraction in the surface normal direction is further enhanced by decreasing the confinement distance. Moreover, upon exchange of the ions' positions along the surface normal direction, the interaction energy changes by about $5k_BT$. Conversely, when one ion is intercalated into the graphene layers, the interaction becomes repulsive. The nonequivalent and directional properties found here, referred to as nonreciprocal interactions, cannot be explain by current water permittivity models in confinement. Our x-ray reflectivity experiments of the water structure near a graphene surface support our molecular dynamics simulation results.

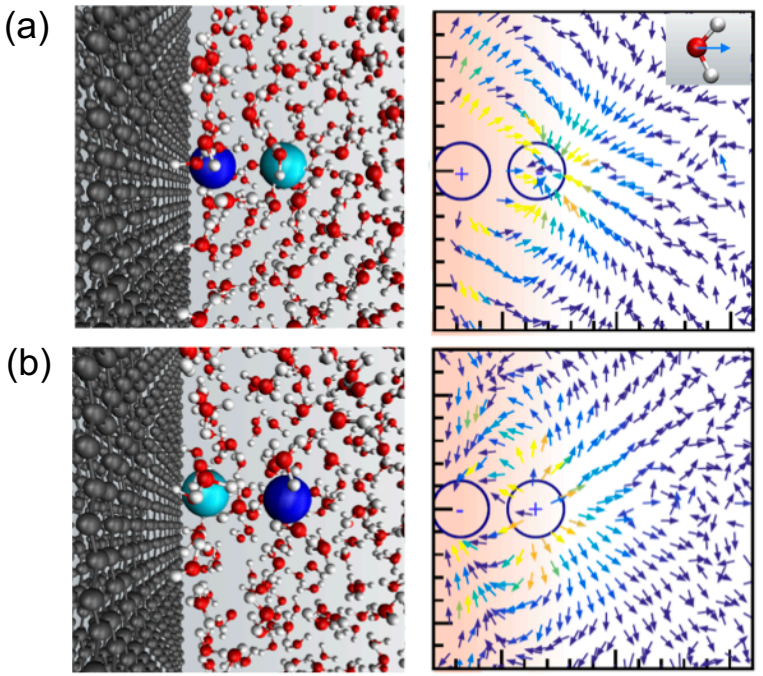

Figure 1: Snapshots from MD simulations (left) and polarization field (right) from water and two ions nearby a graphene surface. The ions are aligned in the surface normal direction as (a) cation (in) and anion (out) and (b) anion (in) and cation (out). The water polarization symmetry is broken by the interface.

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