Interfacial Water Properties in the Presence of Surfactants

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Figure S1: Compressibility of water layers as a function of distance away from pristine graphite, 100% protonated HD (13.6 OH/nm^2), and 100% protonated LD (4.5 OH/nm^2) silica surfaces.

Even though the bulk compressiblity is 60×10^{-11} Pa^{-1}, the compressibility values when computed with the bin size of 0.1 A converge to ~24×10^{-10} Pa^{-1}. This value is similar to that reported in Reference [1].

Figure S2: Compressibility of water as a function of distance away from LD silica surfaces in the presence of $C_{12}E_6$ surfactants with 100%, 50% and 20% degrees of protonation.
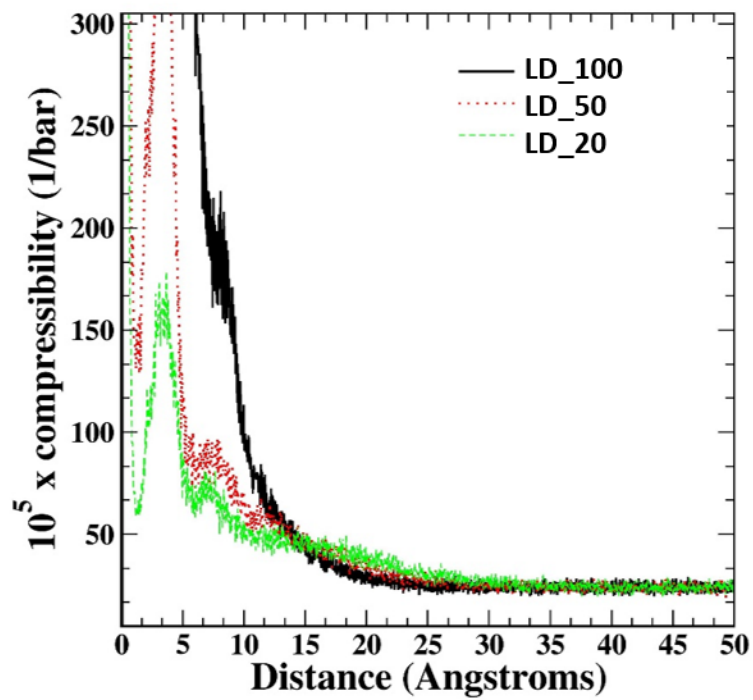
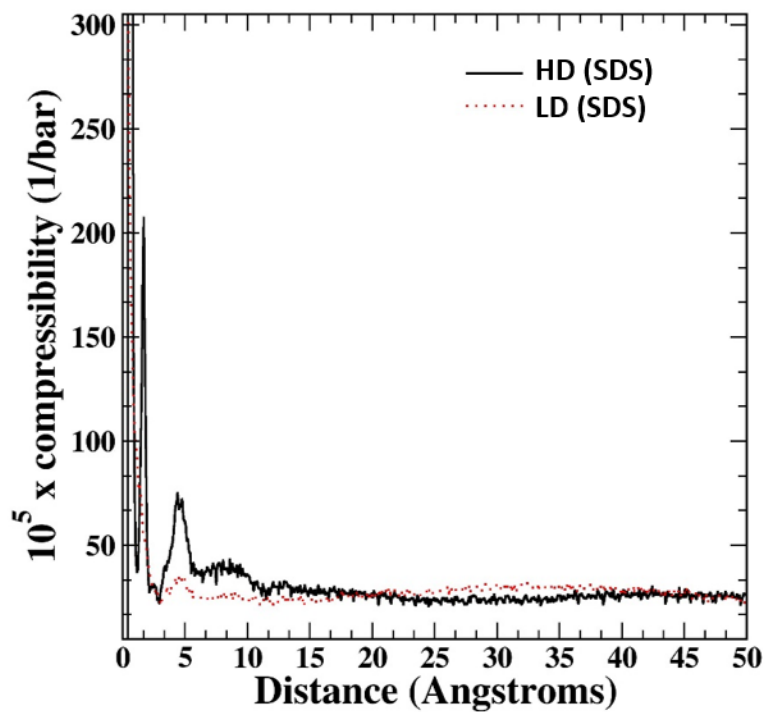**Figure S3**: Compressibility of water as a function of distance away from 100% protonated HD (13.6 OH/nm^2) and LD (4.5 OH/nm^2) surfaces in presence of SDS surfactant molecules.
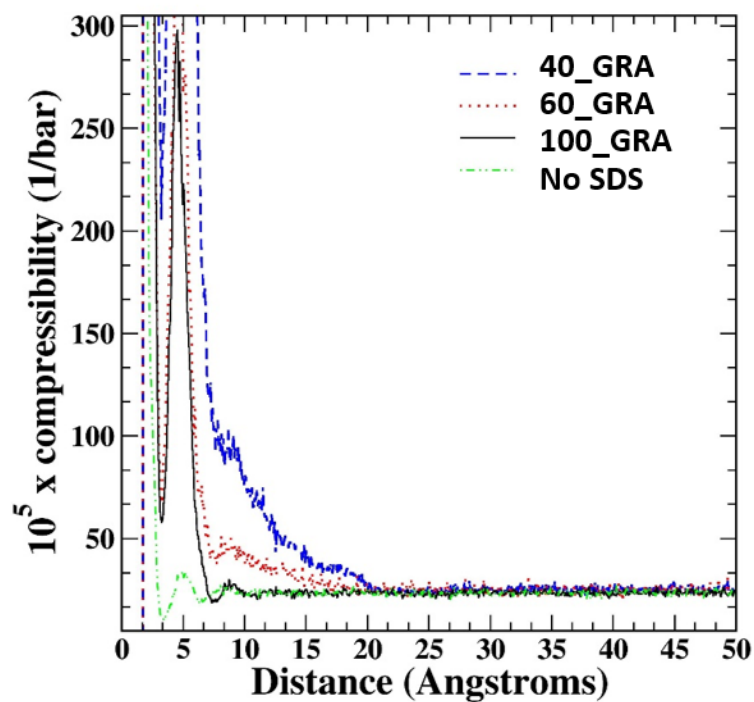
Figure S4: Compressibility of water layers at graphite interface in presence of SDS surfactant molecules with varying number of surfactant concentration. In "X_GRA" notation, X indicates the surface area available for each surfactant in $Å^2$.

Figure S5: Excess chemical potential computed using Widom particle insertion method as a function of distance from graphite surface for 2 different diameter, 0.30 nm (left) and 0.35 nm (right) for neutral, anionic, and cationic at pristine graphite:water interface and at graphite:water interface in the presence of SDS surfactants for 100_GRA system.

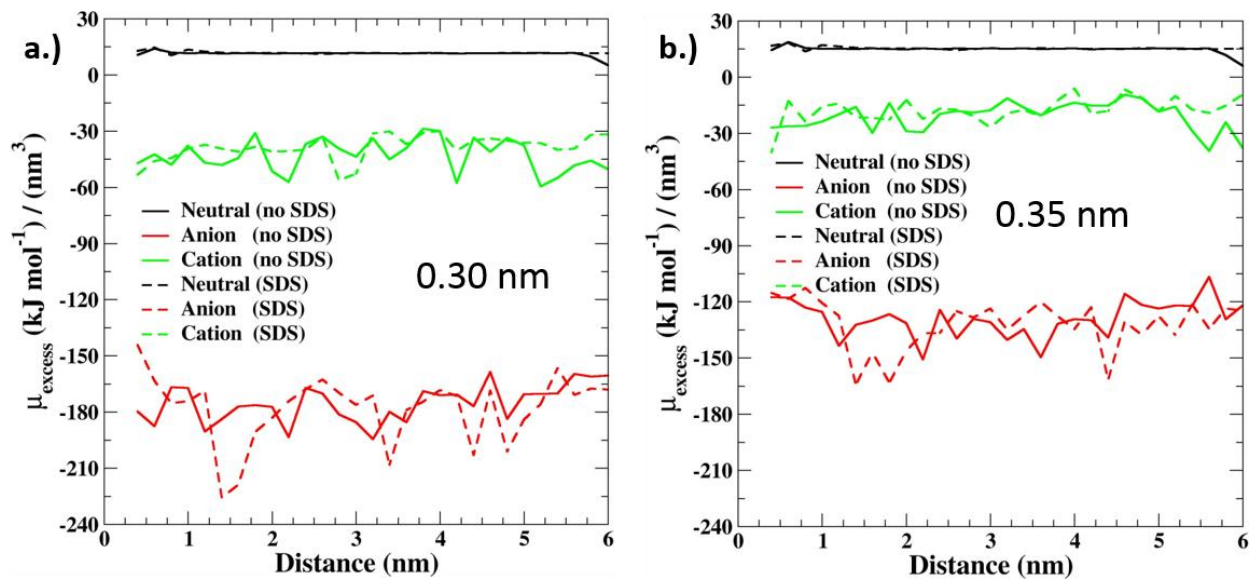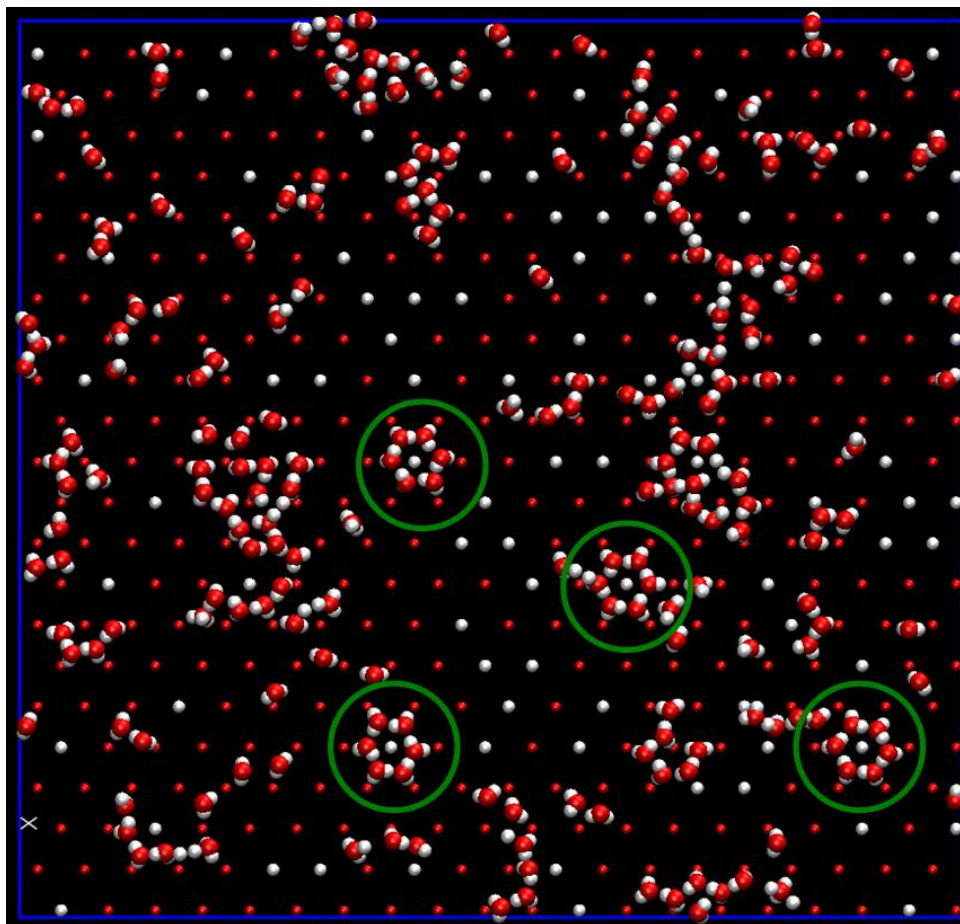**Figure S6:** Top view of water molecules within 3.3 Å from the non-bridging oxygen atom on LD_20 silica. Small red spheres are non-bridging oxygen atoms of silica, white spheres are surface hydrogen atoms, and large white and red spheres are hydrogen and oxygen atoms of water. Green circles highlight hydrogen bonded water molecules on top of surface hydrogen atom. We do not show $C_{12}E_6$ surfactants for clarity.

In Figure S6 we show a representative snapshot for water molecules on LD_20 in the presence of $C_{12}E_6$ within 3.3 Å from the non-bridging oxygen atoms. We observe the hexagonal clusters of hydrogen-bonded water molecules responsible for the slow decay of P for water molecules on LD_50 and LD_20 in the presence of $C_{12}E_6$. Within these hexagonal clusters, the oxygen atom of each water molecule is simultaneously hydrogen bonded to the surface hydrogen atom and to the hydrogen atoms of the adjacent water molecules. The hydrogen atoms of the water molecules

within this hexagonal cluster that are pointing away from the central surface hydrogen atom are hydrogen bonded to the non-bridging non-protonated oxygen atoms. We did not observe such hexagonal clusters on water molecules on LD_50 and LD_20 surfaces without surfactants or with SDS. We observe these hexagonal clusters only on LD_50 and LD_20 silica with $C_{12}E_6$ surfactants. The presence of surface hydrogen atoms surrounded by non-protonated non-bridging oxygen atoms of silica together with the tail-groups or coiled headgroups of $C_{12}E_6$ that do not strongly interact with adjacent water contribute to the formation of the hexagonal clusters of water molecules just discussed.
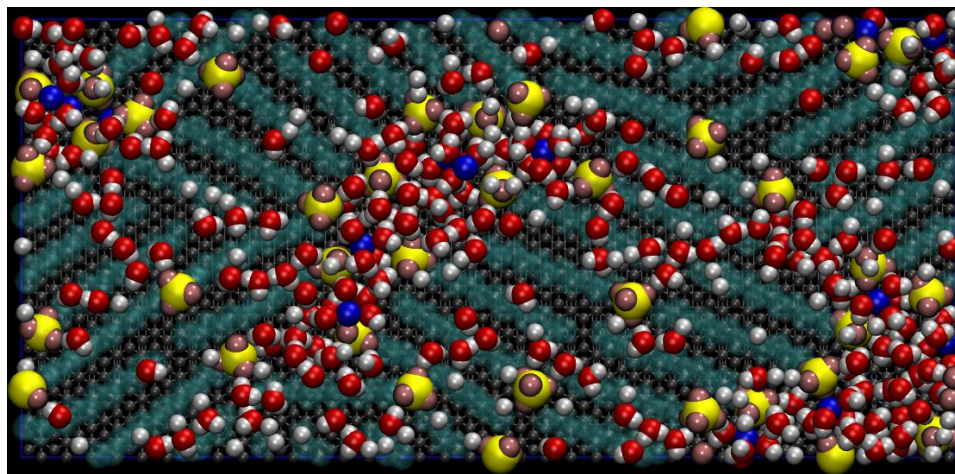

Figure S7: Representative snapshot for water molecules close to SDS headgroups on graphite. Yellow, pink, red, white, blue, grey, and transparent cyan spheres represent sulfur and oxygen atoms of SDS headgroups, oxygen and hydrogen atoms of water, sodium counterions, carbon atoms of graphite, and methyl groups of SDS surfactant molecule, respectively.
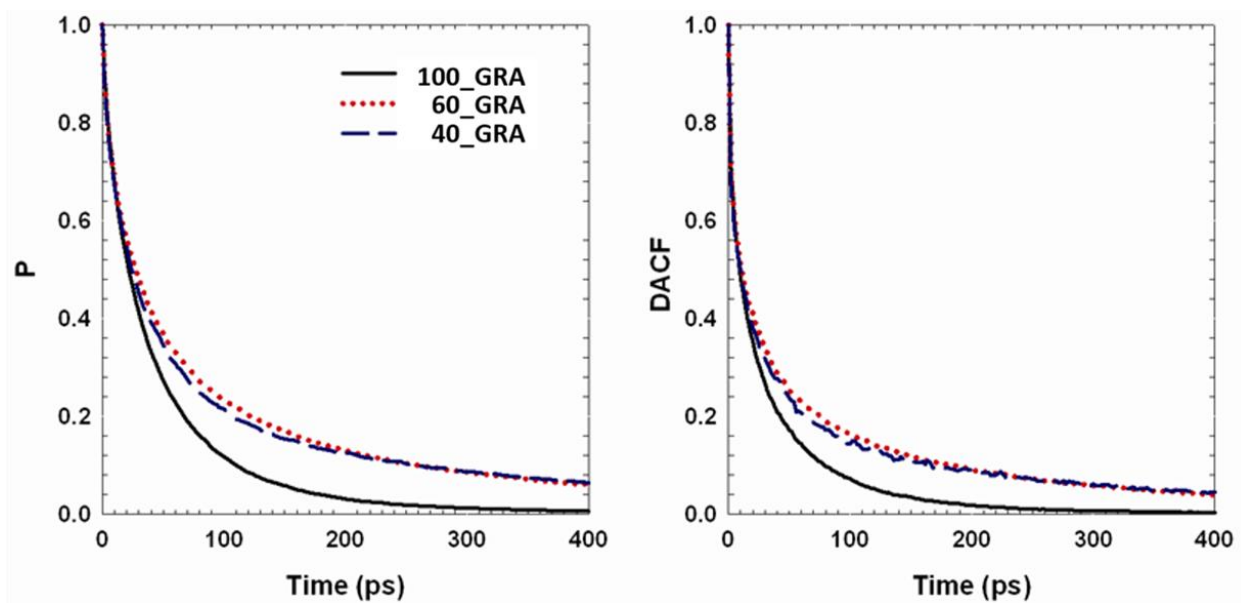
Figure S8: Left: Residence probability function (P) Right: Dipole-dipole auto-correlation functions for water molecules simultaneously present in the surfactant headgroup hydration shell and in the interfacial layer (within 5.1 Å from graphite).
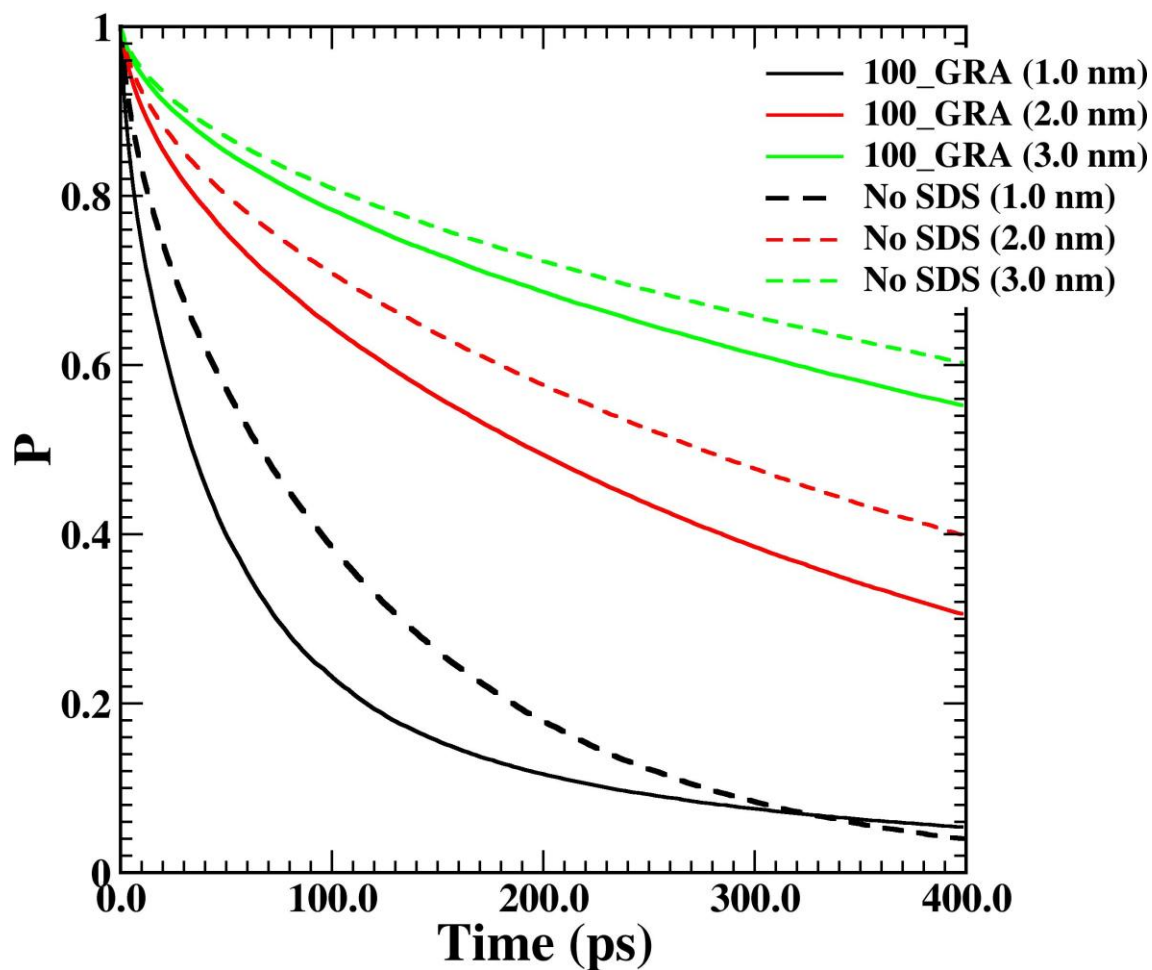
Figure S9: Residence probability function of 1.0, 2.0, and 3.0 nm thick water slabs away from the graphite surface in presence of SDS in 100_GRA system (solid lines) and pristine graphite surfaces (dashed lines).

References

1.   Sharma, S.; Debenedetti, P. G. Evaporation rate of water in hydrophobic confinement. *Proc. Natl. Acad. Sci. USA* **2012,** *109*, 4365-4370.