Supporting Information:

Comparison of the interfacial dynamics of water sandwiched between static and free standing fully-flexible graphene sheets

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Supporting Figures:

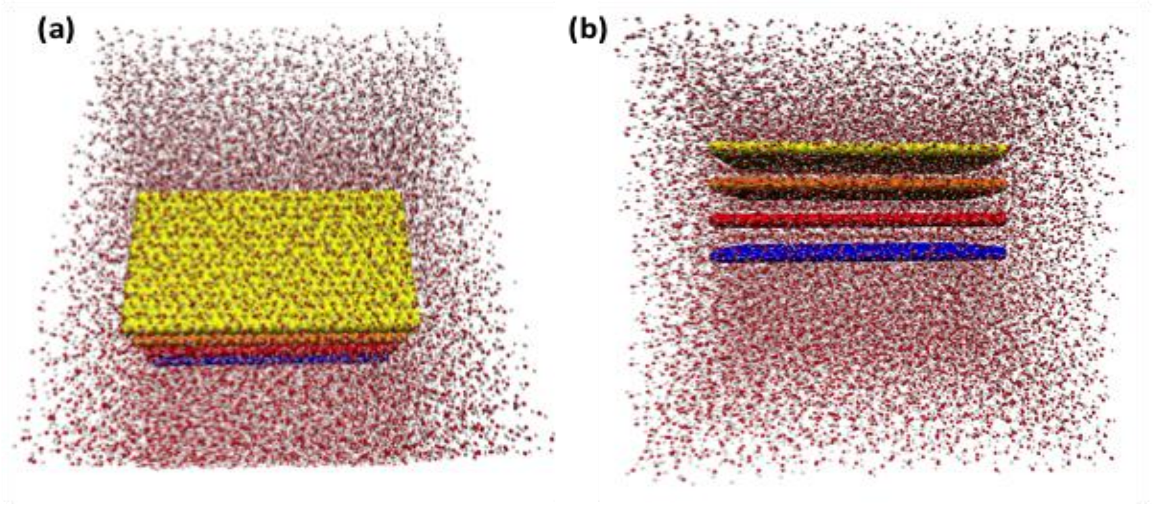

Figure S1: Snapshot showing the initial configuration of the simulation system studied in this work. (a) top view (b) side view.

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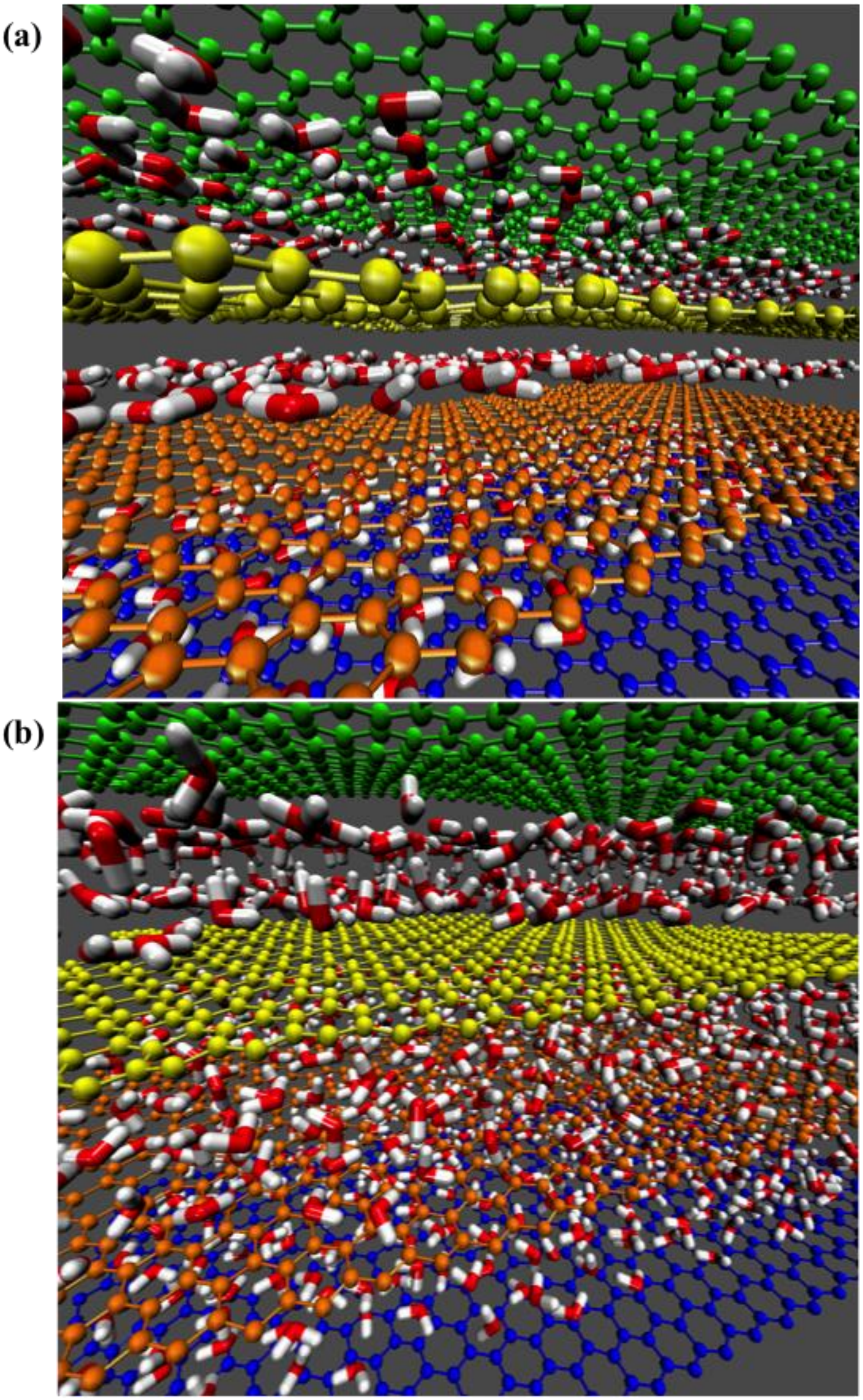
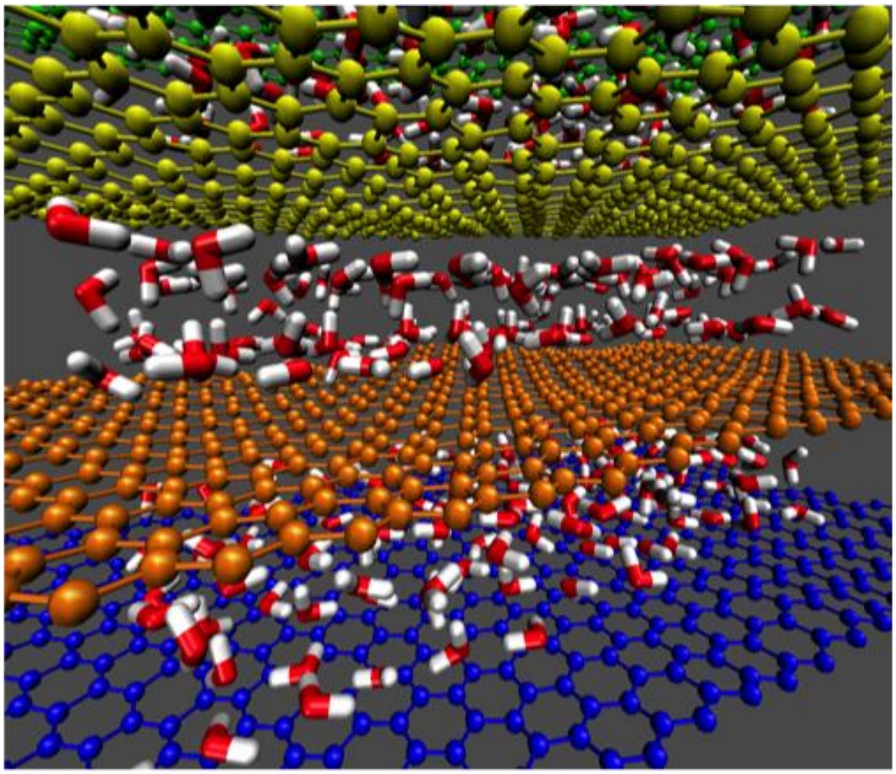
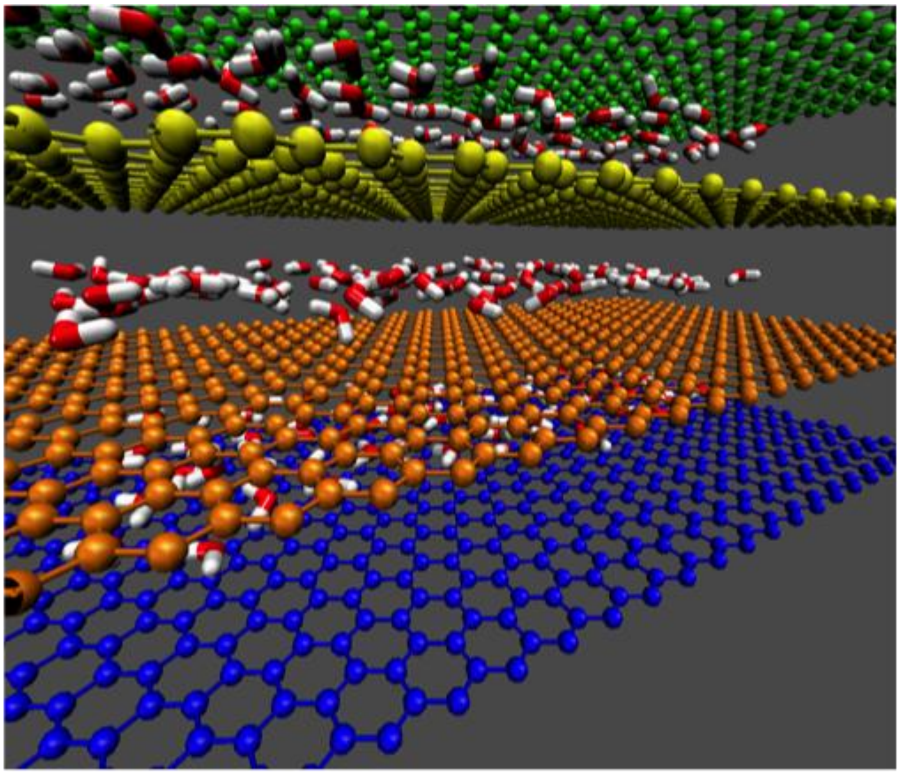

(a)
(b)

(c)



(d)



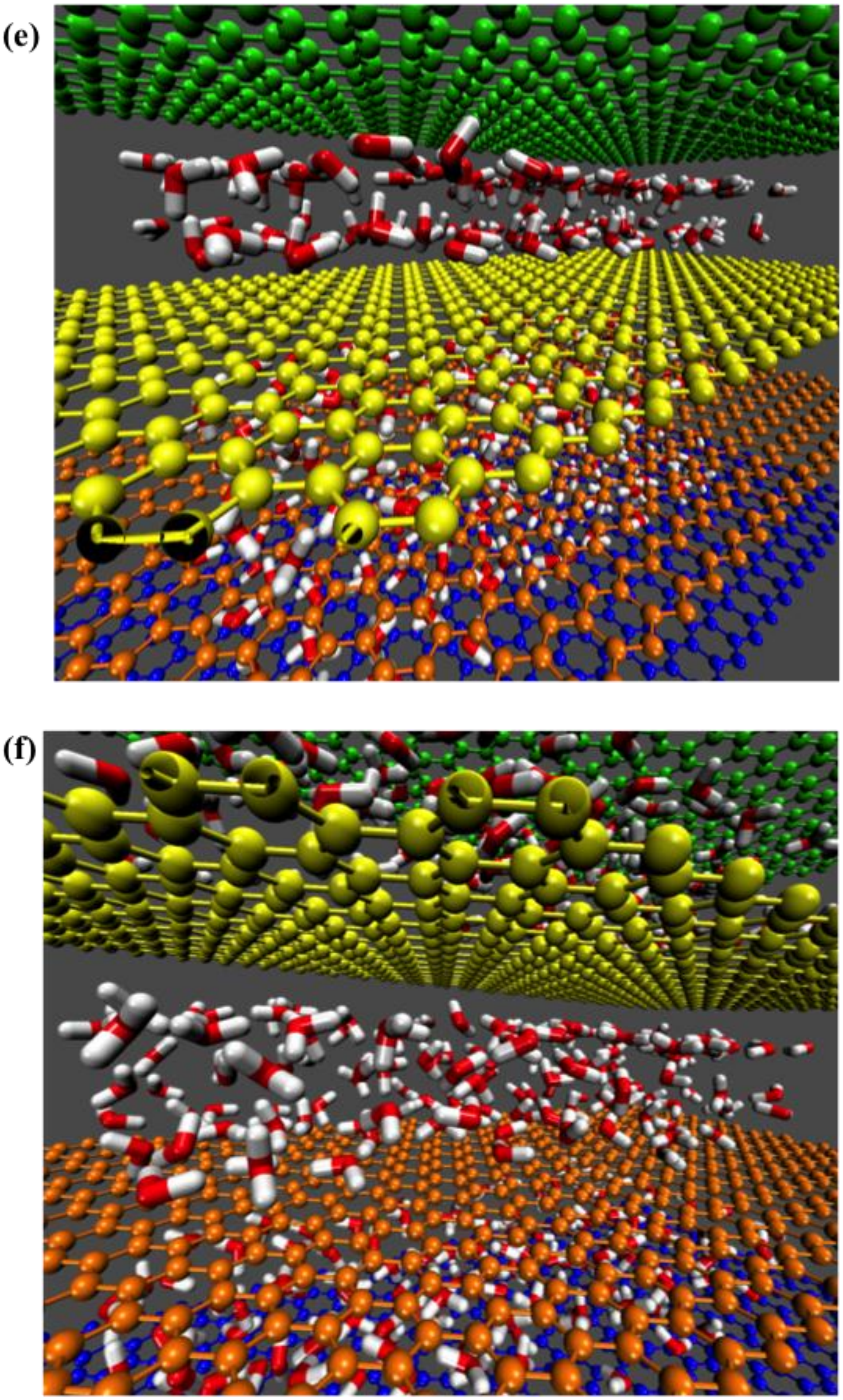


Figure S2: Zoomed in snapshots of water molecules sandwiched between fully-flexible sheets with (a) 8 Å, (b) 10 Å, and (c) 12 Å slit-width and static sheets (d) 8 Å, (e) 10 Å, and (f) 12 Å slit-width.

Comparison between TIP3P and SPC/Fw water model:

We have conducted simulations of a representative system consisting of four fully-flexible graphene sheets, placed at a distance of 8 Å from each other, with dimensions 30 Å x 13 Å in presence of SPC/Fw water model[1]. System size and simulations conditions in this study were similar to those we studied for a system with TIP3P water model.

At the end of simulation run of ~10 ns, the configurational energy of a system with TIP3P and SPC/Fw water model was -1.0768E+05 Kcal/mol and -7.6378E+04 Kcal/mol, respectively. This suggests that graphene sheets modeled using CHARMM force field and water modeled using TIP3P model is more stable energetically in comparison to graphene sheets modeled using CHARMM force field and water using SPC/Fw model. This bears certain resemblance with the previous calculations of Mark and Nilsson[2] who showed that the computed intermolecular energy for water molecule modeled using modified TIP3P was –9.98 kcal/mol was in closer agreement to experimental value of –9.92 kcal/mol in comparison to the intermolecular energy for water molecule modeled using SPC/E (–10.08 kcal/mol). Unlike the case of single water molecule, no experimental values exist for the case of graphene + water systems for comparison.

Additionally, we have also compared the diffusivities of water confined between the slabs for the two water models. In the case of TIP3P, the observed diffusivities of the water molecules confined between the slabs in the above case are ~ 3 x 10^{-7} cm^2/s. On the other hand, the diffusivities of confined water in the case of SPC/Fw model is ~3.5 x 10^{-7} cm^2/s, which is reasonably close to the predicted value for TIP3P water.

We have also evaluated the extent of tetrahedral and orientational order of the confined water in the two cases. For the TIP3P water model, the *q* parameter which is a measure of tetrahedral order is ~0.46 for a slit-width (8 Å) and is in very good agreement with the predicted tetrahedral order of 0.46 by SPC/Fw model. Furthermore, the orientational order parameter (Q_6) for the TIP3P water model is ~0.32. The corresponding (Q_6) for the SPC/Fw water model is ~0.34, which is again in good agreement with the predicted value for TIP3P.

Table S1: Comparison of configurational energy, diffusion coefficient and order parameters between SPC/Fw and TIP3P water model. Comparison is for water in a system consisting of four fully-flexible graphene sheets, placed at a distance of 8 Å from each other, with dimensions 30 Å x 13 Å.

Metric	**TIP3P**	**SPC/Fw**
Average configurational energy (graphene-water)	-1.0768×10^5 Kcal/mol	-7.6378×10^4 Kcal/mol
Diffusivity	3×10^{-7} cm^2/s	3.5×10^{-7} cm^2/s
Tetrahedral order	0.46	0.46
Orientational order	0.32	0.34

Table S2: Comparison of vibrational density of states for SPC/Fw and TIP3P water models. Comparison is between bulk water and confined water in a system consisting of four fully-flexible graphene sheets, placed at a distance of 8 Å from each other, with dimensions 30 Å x 13 Å.

Vibrational density of states	**Peak positions for TIP3P**		**Peak positions for SPC/Fw**	
	Confined water	**Bulk**	**Confined water**	**Bulk**
Libration	456 cm^{-1}	521 cm^{-1}	460 cm^{-1}	520 cm^{-1}
Bending	1800 cm^{-1}	1825 cm^{-1}	1430 cm^{-1}	1460 cm^{-1}
Stretching	3340 cm^{-1}	3360 cm^{-1}	3590 cm^{-1}	3600 cm^{-1}

We further explored the choice of water model and its effects on the vibrational density of states. Table S2 shows the peak positions in the various vibrational bands for TIP3P and SPC/Fw water molecules confined between fully-flexible graphene sheets with slit-width of 8 Å as well as for bulk water, respectively.

We find that the nature of the shift (confined vs. bulk) in the various modes (libration, bending, and stretching) predicted by the two water modes are in very good qualitative agreement. In the case of TIP3P water model libration, bending, and stretching band for confined water molecules can be found at ~456, ~1800, and ~3340 cm^{-1}, respectively. In the case of TIP3P bulk water libration, bending, and stretching band for confined water molecules can be found at ~521, ~1825, and ~3360 cm^{-1}, respectively. In the case of SPC/Fw water model libration, bending, and stretching band for confined water molecules can be found at ~460, ~1430, and ~3590 cm^{-1}, respectively. In the case of SPC/Fw bulk water libration, bending, and stretching band for confined water molecules can be found at ~520, ~1460, and ~3600 cm^{-1}, respectively. The shift in libration, bending and stretching bands of vibrational spectra shown by SPC/Fw water model under confinement is in good qualitative agreement with TIP3P water model.

References:

[1] Y. Wu, H. L. Tepper, and G. A. Voth, The Journal of Chemical Physics **124**, 024503 (2006).

[2] P. Mark and L. Nilsson, Journal of Computational Chemistry **23**, 1211 (2002).