Supporting information for:

Doping-Driven Wettability of Two-Dimensional Materials: a Multiscale Theory

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Figures

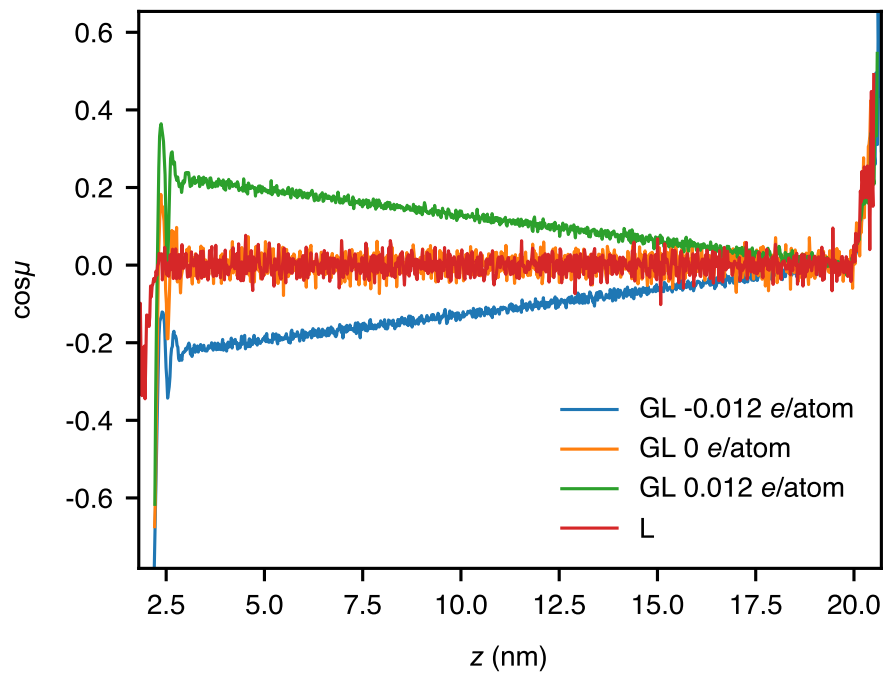## Dipole Orientation Profiles of MD Simulations

Figure S1: Dipole orientation $\cos\mu$ as a function of z in MD simulations of different systems (L, and GL with varied graphene doping densities). The orientation at the water-vacuum interface ($z = 20$ nm) is invariable in all cases, indicating a minimal effect of the long range Coulombic interaction on the selected interface.

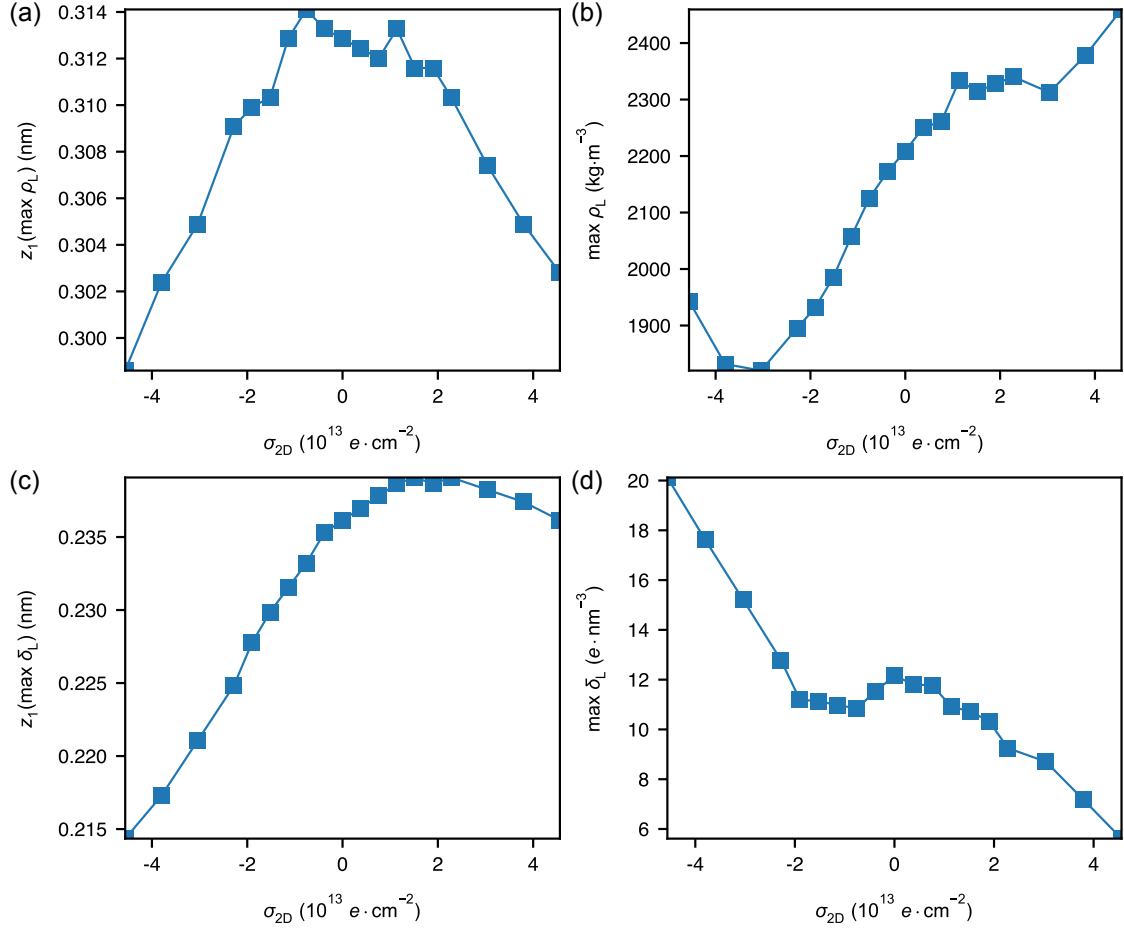# Properties of First Water Layer Adjacent to Charged Graphene Surface

Figure S2: Properties of the first water layer adjacent to the charged graphene surface. The following quantities are plotted as a function of σ_{2D}: (a) z-position of the first water layer with maximal value of ρ_L. (b) maximal ρ_L of the first water layer. (c) z-position of the first water layer with maximal value of δ_L. and (d) maximal δ_L of the first water layer.
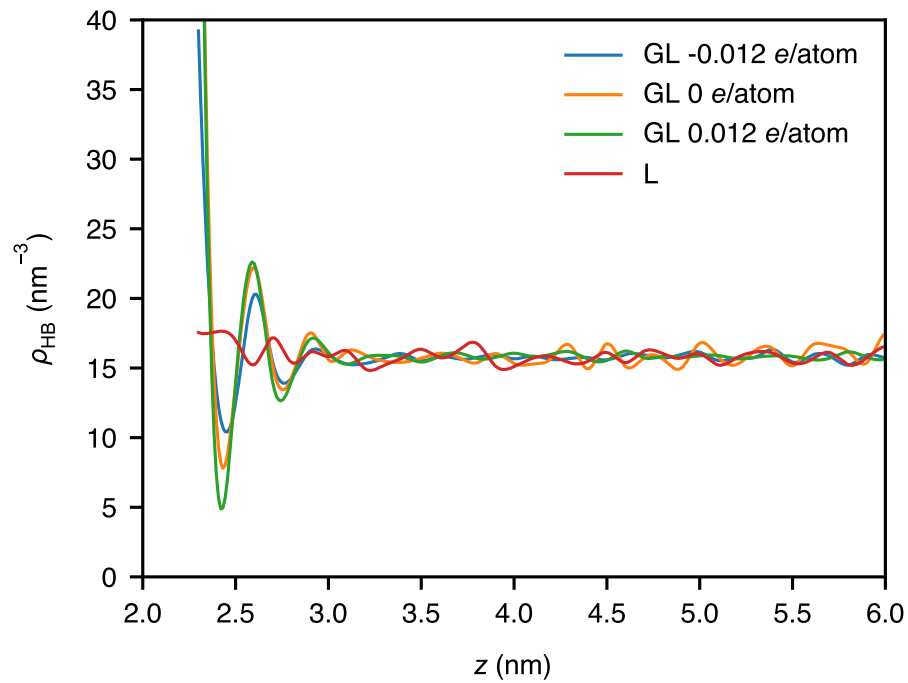
Hydrogen Bond Profiles of MD Simulations

Figure S3: Hydrogen bond density (ρ_{HB}) as a function of z in MD simulations of various conditions (L, GL with graphene doping densities of -0.012, 0 and 0.012 e/atom).

Explanation for Shift of $\Delta\Phi_{\text{Coul}}$ Maximum from Charge Neutral State

As can be seen in Figure 3(c) in the main text, the maximum of $\Delta\Phi_{\text{Coul}}$ as function of σ_{2D} shifts from charge neutral state ($\sigma_{2D} = 0$) to slightly n-doped region. This behavior can be explained by the contribution from the interfacial charge density to the Coulombic interactions (Figure S4(a)). Assuming that the interfacial charge density per unit area of the water layer σ_L is approximated by $\sigma_L = \delta_L \cdot t_1$, where t_1 is the thickness of the 1st water layer (~2.8 Å). The interfacial Coulombic potential caused by the 1st charged layer is then:

$$\begin{aligned}
\Phi_{\text{Coul}}^{\text{int}} &= \frac{\sigma_{2D}\sigma_L}{2C_{\text{int}}} \\
&= \frac{\sigma_{2D}\delta_L t_1 d_1}{2\epsilon_{\text{int}}}
\end{aligned} \tag{1}$$

where $C_{\text{int}} = \epsilon_{\text{int}}/d_1$ is the geometric capacitance of the interfacial void, ϵ_1 and d_1 are the permittivity and thickness of the interfacial void. We assume that the interfacial dielectric constant $\epsilon_{\text{int}} = 20\epsilon_0$,[S1] and take the value of d_1 from the value of the most probable charge distribution distance z_1 from Figure S2(c). The comparison between the $\Delta\Phi_{\text{Coul}}$ from MD results and the proposed model can be seen in Figure S4(b). The degree of Coulombic interactions from the model is close to that of the MD results, indicating that the decrease of interaction potential of the graphene-water system is mainly determined by the interfacial charge distribution. The result predicted by the model also shows a shifted maximum of $\Delta\Phi_{\text{Coul}}$, well corresponding with the MD results. Such asymmetric behavior is further ascribed to the decrease of δ_L when graphene is slightly n-doped (see Figure S2(d)), as a combined result of the Coulombic interaction and hydrogen bonding. Note that in the p-doped regime, the model-predicted $\Delta\Phi_{\text{Coul}}$ value differs from the MD results, suggesting that the contribution from the subsequent layers are important.
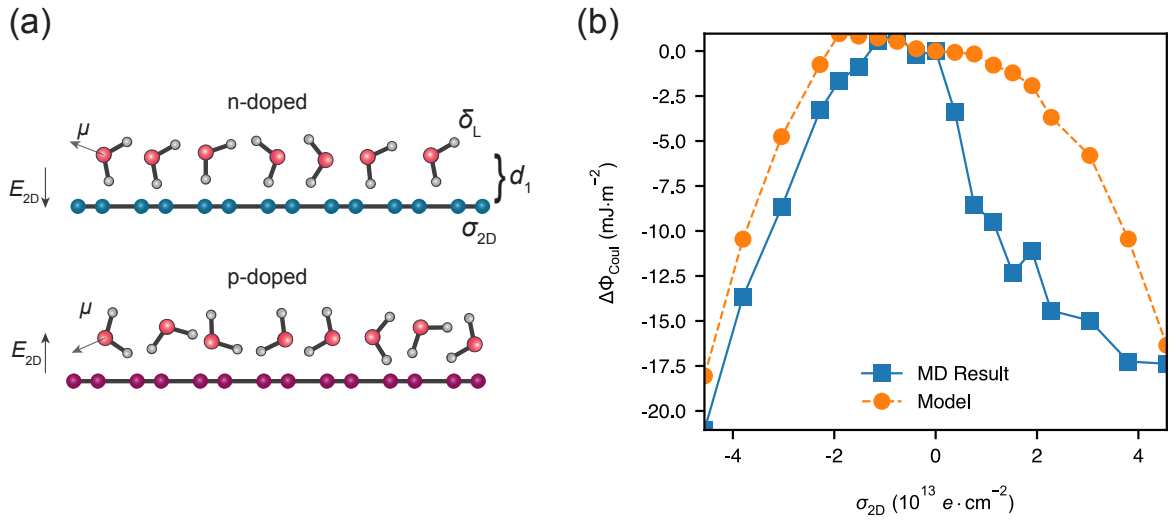
Figure S4: Simple model for the asymmetric behavior of $\Delta\Phi_{\text{Coul}}$ as a function of σ_{2D}. (a) Proposed orientation of first layer water molecules on n- and p-doped graphene surface. (b) Comparison between the $\Delta\Phi_{\text{Coul}}$ values calculated by MD simulation and the proposed model. The results obtained by the simple capacitance model shows similar shift of $\Delta\Phi_{\text{2D}}$ maximum.

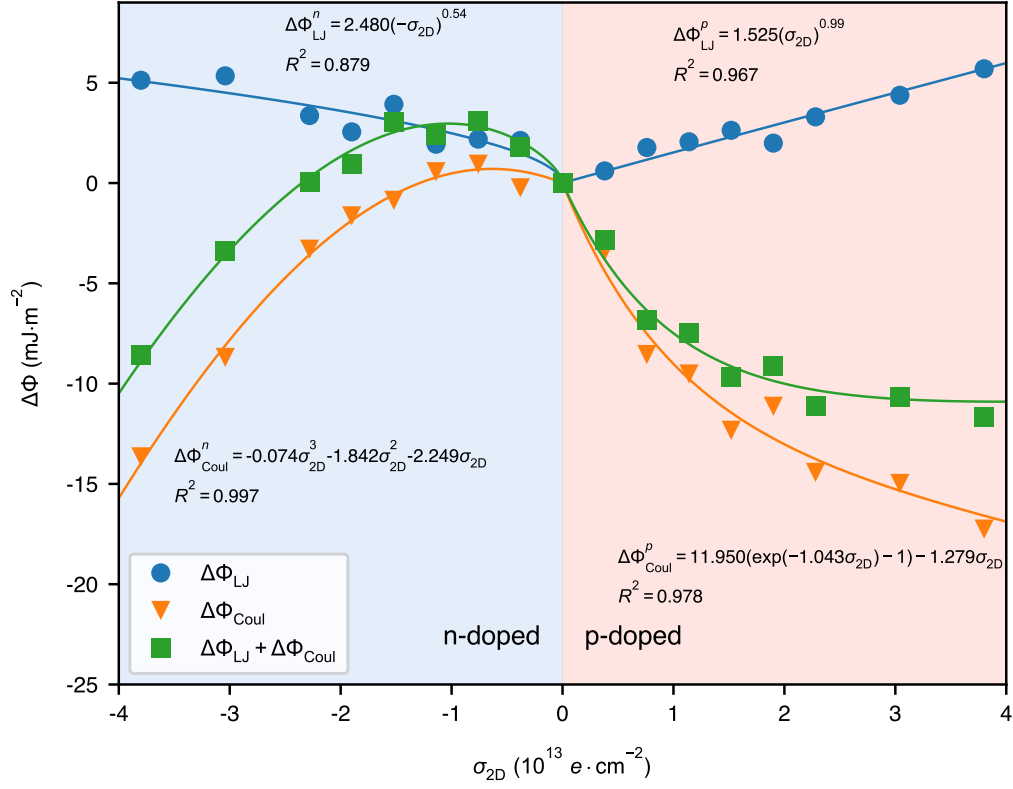# Fitting of the $\Delta\Phi$ - σ_{2D} Data in MD Simulations

Figure S5: Best fitting results of $\Delta\Phi_{LJ}$ and $\Delta\Phi_{Coul}$ as functions of σ_{2D} for n- and p-doped graphene-water systems. Total potential change $\Delta\Phi$ is fitted by combining the fitting results of LJ and Coulombic potentials

References

(S1) Conway, B. E.; Bockris, J.; Ammar, I. A. The dielectric constant of the solution in the diffuse and Helmholtz double layers at a charged interface in aqueous solution. *J. Chem. Soc. Faraday Trans.* **1951**, *47*, 756–766.