Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

Water dynamics at electrified graphene interfaces: a jump model perspective

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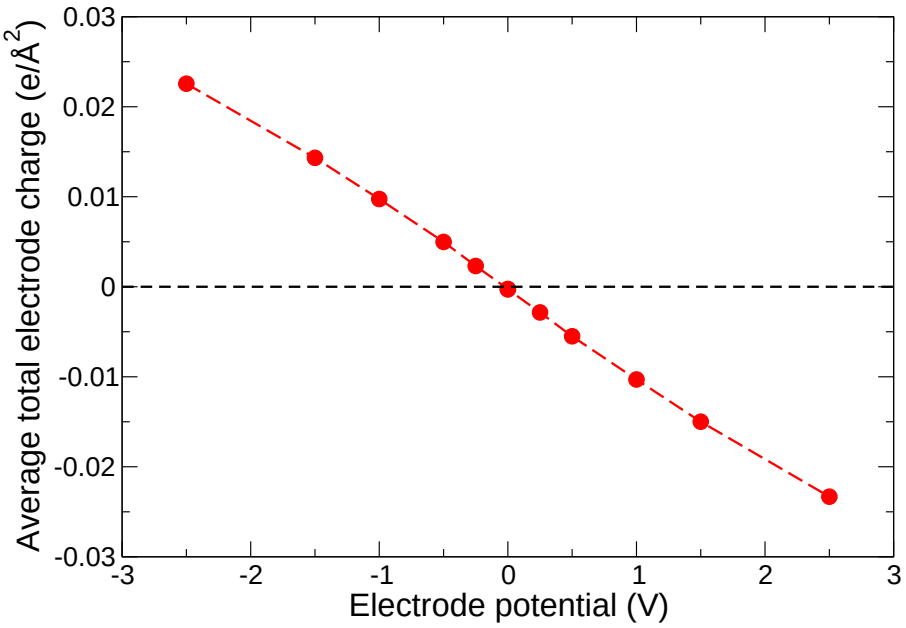

Figure S1: Total electrode charge variations with electrode potential. The potential at the point of zero charge is approximately -0.02 V.

Table S1: Parameters of extended jump model for water molecules at the negatively charged graphene interface (see eqn 2). $p^{\mathbf{S,W}}$ are the fractions of OH groups in each population, and $p^{\mathrm{W}\to\mathrm{S}}$ the probability to jump to state S when starting from state W. The jump times at the negative electrode consider all H-bond jumps from the specified initial state to any new acceptor in the S, W and bulk states (jump times at the positive electrode in fig 4 do not consider the S state which is unstable at these potentials). The jump angles are taken to be $\Delta\theta^{\mathbf{WW}}$=68° [1] and $\Delta\theta^{\mathbf{SW}}$=90° based on figure 2; no frame reorientation is considered in state S because the graphene interface is fixed. The extended jump model average reorientation time in the interfacial water layer is determined as $\langle\tau^{\mathrm{EJM}}_{\mathrm{reor}}\rangle = p^{\mathbf{S}}\tau^{\mathbf{S}}_{\mathrm{reor}} + p^{\mathbf{W}}\tau^{\mathbf{W}}_{\mathrm{reor}}$. The EJM eqn 2 is applied to the W and S states to obtain $\tau^{\mathbf{S,W}}_{\mathrm{reor}}$, as described in eqn S1, where the two possible jump types starting from an initial W state are considered.

Potential (V)	$\tau^{\mathbf{S}}_{\mathrm{jump}}$ (ps)	$\tau^{\mathbf{W}}_{\mathrm{jump}}$ (ps)	$\tau^{\mathbf{W}}_{\mathrm{frame}}$ (ps)	$p^{\mathbf{S}}$	$p^{\mathbf{W}}$	$p^{\mathrm{W}\to\mathrm{S}}$	$\langle\tau^{\mathrm{EJM}}_{\mathrm{reor}}\rangle$ (ps)
0	1.1	3.82	8.7	0.08	0.92	0.3	3.64
-0.25	1.5	3.78	7.5	0.11	0.89	0.3	3.34
-0.5	1.7	3.57	6.7	0.13	0.87	0.3	3.07
-1	2.3	3.58	6.0	0.17	0.83	0.3	2.92
-1.5	2.9	3.62	6.1	0.20	0.80	0.3	3.01
-2.5	3.7	3.7	6.7	0.23	0.77	0.3	3.28

$$
\begin{aligned}
\frac{1}{\tau^{\mathbf{S}}_{\mathrm{reor}}} &= \frac{1}{\tau^{\mathbf{S}}_{\mathrm{jump}}}\left[1-\frac{1}{5}\frac{\sin\left(5\Delta\theta^{\mathbf{SW}}/2\right)}{\sin\left(\Delta\theta^{\mathbf{SW}}/2\right)}\right] \\
\frac{1}{\tau^{\mathbf{W}}_{\mathrm{reor}}} &= \frac{1-p^{W\to S}}{\tau^{\mathbf{W}}_{\mathrm{jump}}}\left[1-\frac{1}{5}\frac{\sin\left(5\Delta\theta^{\mathbf{WW}}/2\right)}{\sin\left(\Delta\theta^{\mathbf{WW}}/2\right)}\right] \\
&\quad + \frac{p^{W\to S}}{\tau^{\mathbf{W}}_{\mathrm{jump}}}\left[1-\frac{1}{5}\frac{\sin\left(5\Delta\theta^{\mathbf{SW}}/2\right)}{\sin\left(\Delta\theta^{\mathbf{SW}}/2\right)}\right] + \frac{1}{\tau^{\mathbf{W}}_{\mathrm{frame}}}
\end{aligned}
\tag{S1}
$$

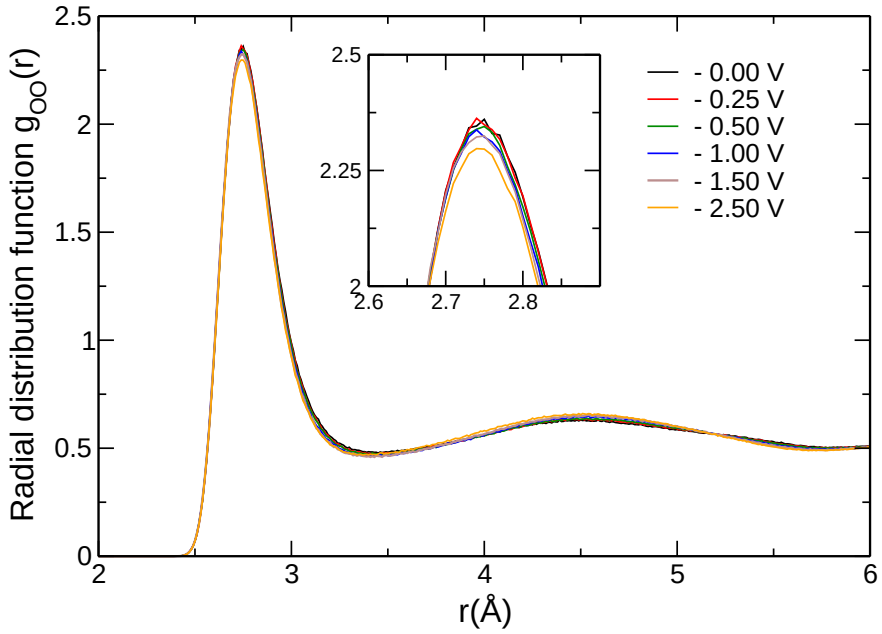

Figure S2: Oxygen radial distribution function around water oxygen atoms within the negative interface first hydration layer.

References

(1) Laage, D.; Hynes, J. T. On the Molecular Mechanism of Water Reorientation. *J Phys Chem B* **2008**, *112*, 14230–14242.