Supporting Information: Influence of Surface Hydrophilicity and Hydration on the Rotational Relaxation of Supercooled Water on Graphene Oxide Surfaces

Rajasekaran M,^a and K. Ganapathy Ayappa*^{a,b}

1 Simulation Details

Figure S1 illustrates the simulation setup for all three surfaces used for MD simulations. We have chosen hydration levels from previous grand canonical Monte Carlo (GCMC) simulations using the SPC water model on the GO surface¹. We used the water loadings from GCMC simulations to provide a realistic estimate of the water densities for our studies on supercooled water. GCMC simulations were carried out using the standard Metropolis acceptance criterion for insertion, deletion, rotational and displacement moves². From the adsorption isotherms obtained from the GCMC simulations, we used the water loading corresponding to a relative pressure (P/P_0) of 0.9, where P_0 is the saturated vapor pressure for the interfacial water dynamics. Loadings at low hydration corresponding to a relative pressure of 0.6 was used for the surface water MD simulations.

The atomic coordinates of the graphene surfaces were obtained from previous density functional theory (DFT) computations and charges were evaluated using the CHarges from ELectrostatic Potentials using a Grid-based method scheme (CHELPG). These are similar to the coordinates and charges used in our earlier work^{3,4} where the atomic co-ordinates and charges for the different surfaces have been tabulated in the Supplementary Information³. Due to the natural asymmetry across the graphene surface that arises in the relaxed structures obtained from DFT computations, the water densities on both surfaces obtained from the GCMC simulations are not identical. As a check, when symmetric surfaces were used by reflecting one of the surfaces, we obtained symmetric density profiles from the GCMC simulations. The asymmetric loading of water observed on the GO surface during the GCMC simulations was used in MD simulations for all three different surfaces. The number of water molecules observed for the z > 0region and z < 0 regions were 4572 and 3501, respectively corresponding to a P/P_0 of 0.9. This was the water loading used for the interfacial water MD simulations reported in this study. For the surface water corresponding to a P/P_0 of 0.6 the number of water molecules on each surface was 1135.

2 Hydrogen bond analysis

We evaluated the number of hydrogen bonds between water molecules and water molecules and the surface functional groups

Table S1 M	/lodel param	eters obt	ain	ed from	fitt	ing C _{HB}	for interfacial	water
molecules	on the GO,	O, and	G :	surfaces	at	various	temperatures	The
C_{HB} is fitte	ed to Eq. 2.							

Surface	T(K)	а	β	τ _{HB} (ps)
GO	210	0.9108	0.8991	7400
	230	0.9349	0.8131	1034
	250	0.9333	0.6943	193
	270	0.9612	0.725	47.37
	298	0.9277	0.7603	16.69
0	210	0.9352	0.7789	8461
	230	0.9545	0.6627	4108
	250	0.9125	0.5505	108.2
	270	0.8294	0.6693	76.22
	298	0.9949	0.3524	25.52
G	210	0 9032	1.0	783.2
0	230	0.0002	0.752	124.8
	250	0.8884	0.752	28.1
	270	0.0004	0.6868	10 10
	298	0.9228	0.7525	7.131

using standard geometric criteria⁵. The hydrogen bond between two water molecules occurs when the distance between oxygens of both water molecules are less than 3.5 Å and the distance between the oxygen of the acceptor and hydrogen of the donor is less than 2.4 Å and the angle between oxygen-oxygen direction and donor molecule oxygen-hydrogen direction is less than 30⁵. The hydrogen bond between water and epoxy as well as hydroxyl functional group in the GO surface is described only by the distance criteria, $R_{OH} \leq 2.4$ Å ⁶.

We also investigated hydrogen bond dynamics by analyzing the intermittent hydrogen-bond correlation function (C_{HB}) using⁷,

$$C_{HB}(t) = \frac{\langle h(t)h(0)\rangle}{\langle h(0)h(0)\rangle} \tag{1}$$

where h(t) the hydrogen-bond population descriptor, is 1 if a tagged water pair is hydrogen-bonded at time t and zero otherwise. The hydrogen-bond autocorrelation function, $C_{HB}(t)$, is computed only for molecules that continuously reside in the layer up to time t, and only hydrogen bonds among water molecules are considered for the time correlation function. We extract the hydrogen-bond relaxation time by fitting $C_{HB}(t)$ to a stretched exponential function (Eq, 2).

$$C_{HB}(t) = a \exp\left[-(t/\tau_{HB})^{\beta}\right],$$
(2)

The model parameters for C_{HB} of interfacial and surface water are provided in Table S1 and S2.

^a Department of Chemical Engineering, Indian Institute of Science, Bangalore, India 560012. Fax: +91-80-2360-8121; Tel: +91-80-2293 2769; E-mail: ayappa@iisc.ac.in

^b Centre for Biosystems Science and Engineering, Indian Institute of Science, Bangalore, India 560012



Fig. S1 Simulation box dimensions used in MD simulations: (a) Side view of the simulation box illustrated for the striped GO surface (b) top view of the GO surface, (c) top view of the O surface, and (d) top view of the G surface. The GO surface used in MD simulations contains 3456 carbon atoms, 288 epoxy groups, and 576 hydroxyl groups. The O surface is comprised of 3456 carbon atoms, 504 epoxy groups, and 1152 hydroxyl groups. Color scheme: carbon-cyan, oxygen-red, and hydrogen-white.



Fig. S2 Unit cell used in DFT calculations: (a) Optimized structure of the graphene oxide surface (GO) made up of strips of functionalized and non-functionalized regions, and (b) optimizd structure of the fully functionalized graphene oxide surface (O). The GO surface used in DFT calculation contains 96 carbon atoms, 8 epoxy(-O-) groups and 16 hydroxyl(-OH) groups. whereas, the O surface consists of 96 carbon atoms, 14 epoxy groups and 32 hydroxyl groups. The epoxy and hydroxyl functional groups are located on the surface. Color scheme : carbon - silver, oxygen of epoxy group - red, oxygen of hydroxyl group - blue, hydrogen - orange

Table S2 Model parameters obtained from fitting of C_{HB} for surface molecules on the GO, and O surfaces at various temperatures. The C_{HB} is fitted to Eq. 2.

Surface	T(K)	а	β	τ _{HB} (ps)
GO	210	0.9261	0.714	2622
	230	0.9406	0.6089	460.9
	250	1.0	0.5993	114.2
	270	0.9326	0.6527	43.23
	298	1.0	0.5863	12.98
0	210	0.9327	0.7075	4865
	230	0.9382	0.6536	2168
	250	0.9851	0.4789	476.4
	270	0.9224	0.6991	160.4
	298	0.8136	0.7416	40.1

Notes and references

- 1 R. Manokaran, *Exploring water dynamics and gas separations in graphene oxide surfaces and nanopores. Ph.D. Dissertation, Indian Institute of Science, Bangalore, India, 2020.*
- 2 M. P. Allen and D. J. Tildesley, *Computer simulation of liquids*, Clarendon Press, New York, USA, 1989.
- 3 R. Manokaran and K. G. Ayappa, J. Phys. Chem. B, 2019, **123**, 2978–2993.
- 4 R. Manokaran and K. G. Ayappa, J. Phys. Chem. B, 2020.
- 5 J. Marti, J. Chem. Phys., 1999, 110, 6876-6886.
- 6 A. Malani, K. Ayappa and S. Murad, *The Journal of Physical Chemistry B*, 2009, **113**, 13825–13839.
- 7 A. Luzar and D. Chandler, Phys. Rev. Lett., 1996, 76, 928.