The role of surface ionisation in the hydration-induced swelling of graphene oxide membranes

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Graphene Oxide (GO) membrane are hydrophilic materials that swell in the presence of water either in humid environment or when in contact with liquid water and the magnitude and mechanism of the swelling is dependent on the degree of ionisation of the functional groups present on the surface of GO flakes. In this work, using Grand Canonical Monte Carlo and Molecular Dynamics simulations we investigate the effect that surface charge, resulting from the ionisation **[1]** process, has on both the amount of water **[2]** adsorbed in the membranes at various humidity conditions and the swelling of the membranes in contact with liquid water **(Figure 1)**. Three models with increasing surface charge from -63 mC/m^2 to -177 mC/m^2 and a neutral one is used **[3]**. We show that by incorporating ionised functional groups, the onset of adsorption **(Figure 2)** is shifted to a lower chemical potential and the internal membrane pressure **(Figure 3)** increases due to the repulsive interactions between the graphene flakes. We suggest that for a fairly ordered membrane as the ones modelled here a surface charge of -120 mC/m^2 is the upper limit before membrane delaminate. Our simulations also show that the presence of ions in the channel reduced the swelling due to screening effect but also increases the amount of water adsorbed when the membrane is immersed in liquid water. At low chemical potential, instead, the amount of water adsorbed is determined by the number of ionised groups. The charged model is able to qualitatively reproduce experimental data showcasing the importance of including surface charge in GO model to predict hydration and swelling mechanism. These findings are crucial in underpinning the future development of GO membranes in simulation and experimental study for aqueous separations since hydration-induced swelling is widely known to lead to significant deterioration in performances.

FIGURES

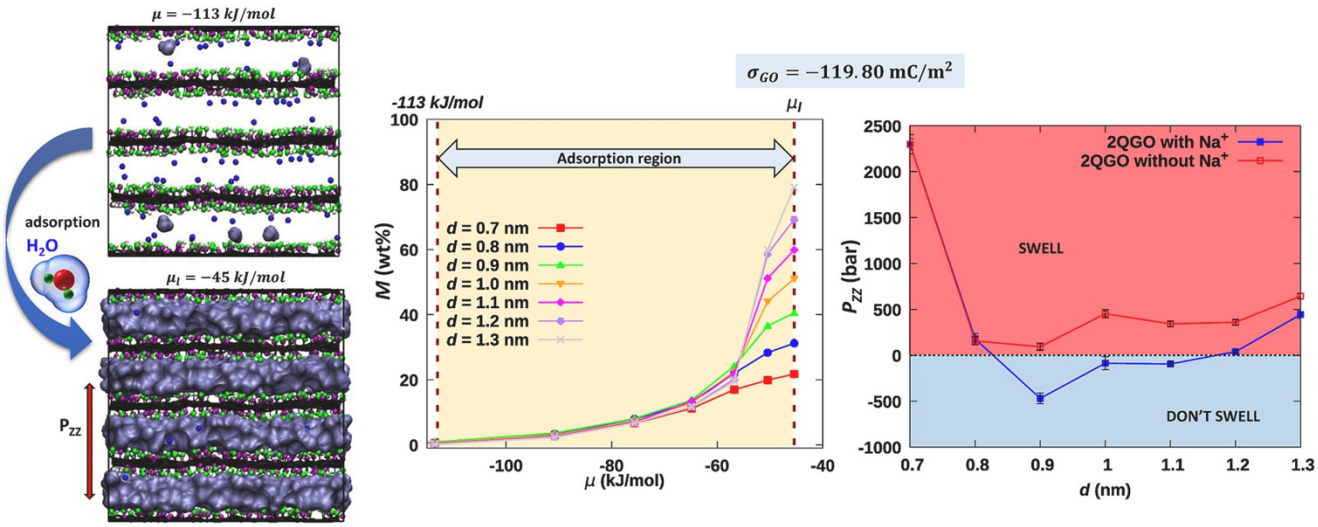

Figure 1: (a) Adsorption of water in a rigid charged GO membrane from low chemical potential to bulk liquid water chemical potential using Grand Canonical Monte Carlo simulation. (b) Amount of water adsorbed in GO membrane at different interlayer spacing (example on 2QGO model). (c) Pressure normal to plane of GO membrane, P_{zz} to check for swelling of GO membrane in liquid water (example on 2QGO model).

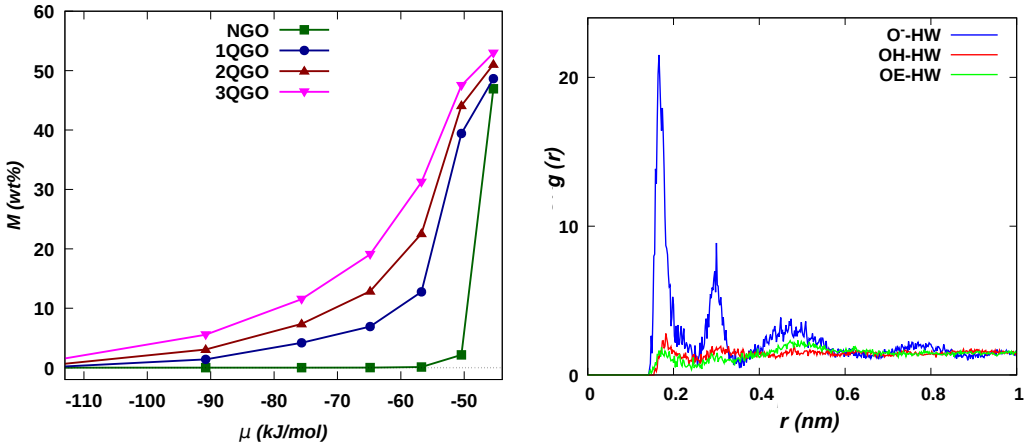

Figure 2: (a) Water adsorbed in GO membrane model NGO, 1QGO, 2QGO, 3QGO (d = 1.0 nm). (b) RDF between oxygen atom of ionised hydroxyl (O-), hydroxyl (OH) and epoxide (OE) with hydrogen of water molecules (HW).

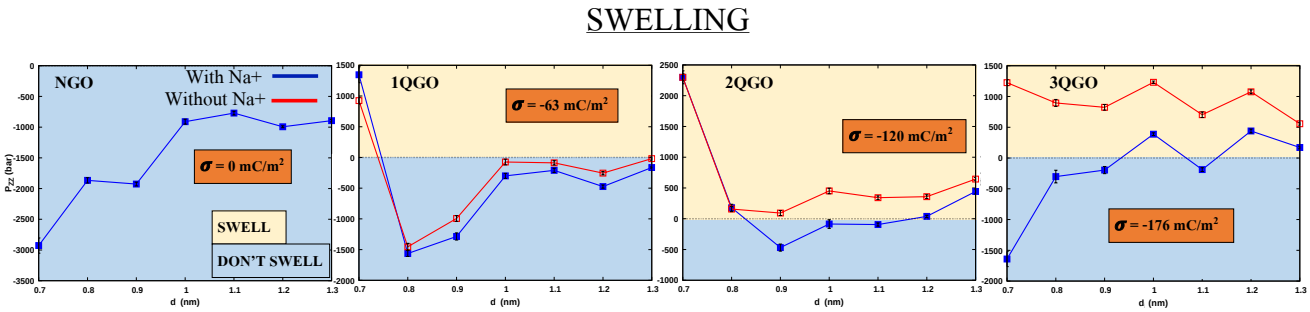

Figure 3: Pressure (P_{ZZ}) in (a) NGO, (b) 1QGO, (c) 2QGO, and (c) 3QGO. $P_{ZZ} > 0$ = swelling of GO membrane.

REFERENCES

[1] Mouhat, F., Coudert, F. and Bocquet, M., Nature Communications 11 (2020), 1566.
[2] Price, D. and Brooks, C., The Journal of Chemical Physics 121 (2004), 10096-10103.
[3] Williams, C., Carbone, P. and Siperstein, F., Nanoscale 10 (2018), 1946-1956.