Appendix A
Polarizability Effects in Molecular Dynamics Simulations of the Graphene/Water Interface

A.1 Abstract

The importance of including the polarizability of both water and graphene in molecular dynamics simulations of the water/graphene system was quantified. A thin film of rigid SPC/E and polarizable SWM4_DP water on non-polarizable and polarizable graphene surfaces were simulated. The graphene surface was either maintained neutral or charged, positively and negatively. The results suggest that SPC/E and SWM4_DP water models yield very similar predictions for the water structural properties on neutral non-polarizable graphene, although they yield slightly different dynamical properties of interfacial water on neutral non-polarizable graphene.

More pronounced were the differences obtained when graphene was modeled with a polarizable force field. In particular, the polarizability of graphene was found to enhance the number of interfacial SWM4_DP water molecules pointing one of their OH bonds towards the neutral surface. Despite this structural difference, the dynamical properties predicted for the interfacial SWM4_DP water were found to be independent on polarizability as long as the polarizability of a carbon atom is smaller than $\alpha = 0.878$ Å. On charged graphene surfaces, the effect of polarizability of graphene on structural properties and some dynamical properties of SWM4_DP water is negligible because electrostatic forces due to surface charge dominate polarization forces, as expected. For all cases, my results suggest that the hydrogen bond network is insensitive to the polarizability of both water and graphene. Understanding how these effects will determine the accumulation of ions near neutral or charged graphene could have important implications for applications in the fields of energy storage and water desalination.

A.2 Introduction

Many groups have discussed the importance of including the polarizable term in molecular dynamics (MD) simulations, especially in those simulations conducted for ions at the water/air interface [1–7]. Levin argued that the ability of adjusting the
charge distribution of an ion, i.e., its polarizability, is necessary to capture the right physic of ions at interfaces [8]. Berkowitz and Perera found significant differences in both energy and geometry for Na⁺(H₂O)ₙ and Cl⁻(H₂O)ₙ clusters depending on whether or not polarizable force fields were implemented [9]. Dang and Smith found that the properties predicted by simulations for water-ion clusters depend on the magnitude of the ion polarizability [10]. Jungwirth and Tobias [11] demonstrated that heavier halogen anions have a propensity to accumulate at the water/air interface, proportional to their polarizability. Recent interesting results by Caleman et al. explain the surface preference of halides using MD simulations that implemented polarizable force fields [12].

The work briefly summarized above suggests the need of implementing polarizable force fields in simulating aqueous electrolytes at the water/air interfaces. As other interfaces are of practical interest, one wonders whether polarizable effects are important to describe every interface. For example, it is still unclear whether it is important to implement polarizable force fields to simulate solid/water interfaces. In this work I are concerned with the graphene/water interface. Graphene is an exceptional material possessing a unique combination of high surface area, extraordinary mechanical, thermal, and chemical stability, and remarkable electronic and optical properties [13, 14]. It is being used in many applications, ranging from materials sciences [15, 16] to the energy field (batteries and electric double layer capacitors) [17–20], from sensing devices [21] to catalysis [22]. Because some of these applications take place in aqueous environments, it is important to understand at the molecular level the structure of interfacial water on graphene under different conditions. Simulations are often conducted for such purposes. Most of the simulations for water on graphene reported in the literature were obtained implementing non-polarizable force fields [23–25]. One exception is the work of Sala et al. [26] These authors studied aqueous electrolyte solutions confined within a graphene slit-shaped pore. Two sets of potential models were implemented: (a) the rigid non-polarizable SPC/E potential for water with non-polarizable ions, and (b) the rigid polarizable RPOL model for water with polarizable ions. Graphene was in both cases treated as non-polarizable. The results indicated that polarizable force fields favor the accumulation of ionic species near the solid/liquid interface. To secure progress, I believe it is necessary to quantify the effect of polarizability of both water and graphene on the water properties, as predicted by simulations. When synergistically coupled to experimental data, this quantification will allow accurate prediction of the properties of aqueous electrolyte solutions at the graphene interface, necessary for the development of energy storage (e.g., electric double layer capacitors) and water desalination devices, among others. The performance of these devices depends in fact on the accumulation of ions near graphene, which, as suggested by the results obtained at the water/air interface, might be affected by polarization effects.
A.3 Simulation Methods

In this work, three simulation sets were conducted. In the first set, I considered a thin film of either SPC/E [27] or SWM4_DP [28] water on neutral, non-polarizable graphene. These simulations were conducted to verify the importance of implementing a polarizable water model when the water/graphene system is of interest. Within the SPC/E model water is described as rigid with three point charges: two hydrogen sites and one oxygen site. The oxygen site also corresponds to the center of Lennard-Jones (LJ) interactions. This model has been extensively used by many, and it is known to satisfactorily reproduce structure and diffusion of bulk liquid water at ambient conditions. In my simulations one SPC/E water molecule was kept rigid by applying the SHAKE algorithm [29] to constrain the two OH bonds and the fictitious H–H bond length. The polarizable water model SWM4_DP was chosen because it reproduces well vaporization enthalpy, dielectric constant, self-diffusion coefficient, and air/water interfacial tension. In the SWM4_DP model, the permanent charge distribution of a water molecule is represented by three point charges: two hydrogen sites and one site positioned along the HOH bisector. The electronic induction is represented by a classical charged Drude particle [30, 31], bound to the oxygen site by a harmonic spring. The oxygen site carries a charge equal and opposite to the one of the Drude particle. The oxygen site is also the center of intermolecular LJ interactions. In neutral non-polarizable graphene, all carbon atoms were maintained rigid and modeled as LJ spheres employing literature parameters [32].

In the second simulation set, a thin film of polarizable SWM4_DP water [28] (polarizability $\alpha \approx 1.042 \, \text{Å}^3$) on neutral polarizable graphene surfaces was simulated to study the effect of graphene polarizability on water properties. To simulate the polarizability of carbon atoms, I implemented the Drude-particle method [30, 31], inspired by the SWM4_DP water model (described in the paragraph above). Each carbon atom was represented by a fixed charged LJ carbon atom and a Drude particle carrying a charge opposite in sign to that fixed on the center. The fixed carbon atom and the Drude particle were connected by a spring. Manipulating the spring constant and the charge on the Drude particle results in different polarizability. The LJ parameters for the fixed carbon atoms were identical to those used in the first simulation set. The polarizability of a carbon atom in graphene is expected to be around $\alpha \approx 0.878 \, \text{Å}^3$, which is the polarizability of the carbon atom in CCl$_4$ as simulated by Chang and Dang [33]. Because I excluded the interactions among the carbon atoms in the graphene sheet, the polarizability of carbon atoms used in my simulations should reflect the out-of-plane value. According to Langlet et al. [34], the out-of-plane polarizability of a carbon atom varies from 0.5 to 1.5 Å$^3$. They used 0.86 Å$^3$, close to the value $\alpha \approx 0.878 \, \text{Å}^3$ I expect to be reasonable. Karapetian and Jordan [35] implemented out-of-plane $\alpha \approx 0.57 \, \text{Å}^3$ to study the properties of a water cluster on graphite. They concluded that using an anisotropic polarizability on the carbon atoms gave the similar structures and binding energies to those obtained using an isotropic polarizability. To fully understand the effect of
I conducted additional simulations, varying the polarizability $\alpha$ of a carbon atom from 0 (no polarizability) to 1.1 Å$^3$ (i.e., $\alpha = 0$, $\alpha = 0.578$, $\alpha = 0.878$ and $\alpha = 1.1$ Å$^3$).

In the third and last simulation set, a thin film of polarizable water SWM4_DP was simulated on charged polarizable graphene and on charged non-polarizable graphene surfaces to understand the role of the polarizability of graphene on the water properties when the graphene surfaces are charged, negatively or positively. The water/charged graphene interface is encountered in many practical applications such as electric double layer capacitor (EDLC) or capacitive desalination (CD) [36]. In the present contribution I considered two representative surface charge densities (i.e., $-8$ and $+8$ μC/cm$^2$). The non-polarizable graphene was simulated as discussed in the first simulation set. The polarizable graphene was simulated using the approach described in the second simulation set, with polarizability $\alpha = 0.878$ Å$^3$. When the graphene surface was charged, all the fixed carbon atoms belonging to the graphene sheet on top of the graphitic slab (shown below) carried the same partial charge.

In Fig. A.1 I represent a simulation domain containing SPC/E water molecules on a neutral non-polarizable graphite surface. Similar domains were employed for all other simulations. In my simulation box, a thin film composed by 829 water molecules was placed on a 27.0 × 29.8 Å$^2$ graphite surface. All simulations presented below were conducted using the GROMACS simulation package [37], version 4.0.7. During each simulation the number of particles (N) in the system, the volume (V), and the temperature (T) were maintained constant (i.e., I implemented the NVT ensemble). The system temperature was maintained at 300 K by applying the Nose-Hoover thermostat with the relaxation time of 100 fs. Periodic boundary conditions were applied in all three directions (note that the Z direction is the one perpendicular to the solid substrate). Long-range interactions were calculated by the particle mesh Ewald (PME) method [38]. Along the Z direction a large vacuum volume was added to eliminate unphysical interactions between periodic images of the simulated system. Similar approaches have been implemented in my prior work [39]. Alternatively, one can apply two-dimensional algorithms available for treating long-ranged electrostatic interactions [40]. The resultant lengths of the simulation box used herein along the X, Y, and Z directions were 2.70, 2.98, and 10.00 nm, respectively.

The equations of motion were integrated with a time step of 1 fs. After equilibration, the system coordinates were recorded every 200 time steps (i.e., 200 fs of simulation), and used for subsequent analysis. Each simulation lasted 3 ns. The results obtained during the first 1 ns were discarded (equilibration), while the trajectories recorded during the last 2 ns of the simulation were used to calculate the properties of interest. By monitoring temperature, density profiles, and orientation probability as a function of simulation time I confirmed that the reported results are obtained after equilibration is complete. The simulation trajectories were analyzed to extract detailed information regarding atomic density profiles, orientation, residence time, translation and rotational dynamics for interfacial water. Additional
details concerning the hydrogen bond network near the interface were extracted. The algorithms employed for such analysis have been described in previous publications from my group [39, 41–45].

A.4 Results and Discussions

A.4.1 Density Profiles

In Fig. A.2 I present the density profiles in the direction perpendicular to the surface for oxygen (left) and hydrogen (right) atoms of water molecules near graphite. The results are compared when different force fields are implemented.

On the top panels I compare the density profiles obtained for SPC/E and SWM4_DP water simulated on the neutral non-polarizable graphene surface. The comparison suggests a minimal difference due to the polarization. The oxygen density profile obtained for SPC/E water indicates that a first intense density peak forms at \( z = 3.25 \) Å and a second, less pronounced density peak forms at \( z = 6.05 \) Å. This is in agreement with results reported by other groups [23–25]. The oxygen density profile obtained for SWM4_DP water is different from that obtained.
for SPC/E water, but the differences are almost insignificant. For example, the peaks observed on the oxygen density profile for SWM4_DP are higher and narrower than those observed for SPC/E water. Quantitative calculations presented below indicate that water molecules are predicted to pack in the interfacial layer at a constant surface coverage (9.9 water molecules per nm²), independently on the water model implemented. The hydrogen density profiles (top right) also show negligible differences between results obtained implementing either the SPC/E or the SWM4_DP water models. The results presented on the top panels of Fig. A.2 demonstrate that the distribution of oxygen and hydrogen atoms of water molecules in the direction perpendicular to the surface are predicted to be comparable when either the rigid non-polarizable SPC/E or the polarizable SWM4_DP water models are implemented.

The next question I address is whether including the polarizability of carbon atoms of graphene and the polarizability of water molecules will affect the predicted structure of water. In the middle panels of Fig. A.2 I compare the results obtained using the polarizable SWM4_DP model of water, combined with a Drude-particle model to describe polarizable effects in the carbon atoms of graphene. The results suggest that including the polarizability of graphene negligibly affects the vertical distribution of oxygen atoms of interfacial water (left panel). However, the prediction for the density profiles of hydrogen atoms (right panel) is affected by the polarizability of carbon atoms. In particular, a small shoulder at \( z = 2.15 \) Å gradually forms when the polarizability increases. The shoulder found at \( z = 2.15 \) Å on the hydrogen density profile is 1 Å closer to the surface than the first oxygen peak observed on the oxygen density profile. This suggests that polarizability affects the orientation of interfacial water molecules. My results indicate that the number of water molecules in the first hydration layer projecting one of their hydrogen atoms toward the surface increases when the graphene polarizability increases. This observation is supported by additional results, discussed below, for the orientation of interfacial water molecules and by the estimation of the number of water molecules pointing one of their hydrogen atoms towards the surface. The results just discussed show that polarizability is important in predicting the orientation of interfacial water molecules near neutral graphene. The next question I address is whether or not the same observation holds when the graphene surface, instead of being neutral, is charged.

In the bottom panels of Fig. A.2 I present the density profiles predicted when the SWM4_DP water is simulated on charged non-polarizable and charged polarizable graphene surfaces. Graphene was either positively or negatively charged. The density profiles for SWM4_DP water on neutral non-polarizable graphene (black line) are also shown for comparison. The results shown in the bottom panels of Fig. A.2 indicate that the surface charge density has a strong effect in determining the orientation of interfacial water. More importantly for the scopes of the present work, however, is that when graphene is charged, my results show that including the polarizability of graphene in the calculations has little effect. For instance, the oxygen density profile (left panel) for water on \(-8 \mu \text{C/cm}^2\) non-polarizable
graphene (solid red line) shows little difference compared to that obtained on polarizable graphene (green solid line). The same can be repeated for the hydrogen density profile (right panel) on +8 μC/cm² non-polarizable or polarizable graphene.

Fig. A.2 Top Oxygen (left) and hydrogen (right) density profiles of SPC/E and SWM4_DP water on neutral non-polarizable graphene surfaces. Middle Oxygen (left) and hydrogen (right) density profiles of SWM4_DP water on neutral polarizable graphene surfaces of different polarizability α. Bottom Oxygen (left) and hydrogen (right) density profiles of SWM4_DP water on charged non-polarizable and charged polarizable graphene surfaces.
A.4.2 Orientation

In the left panel of Fig. A.3 I present the orientation distribution of interfacial SPC/E (pink circles) and SWM4_DP (black circles) water on neutral non-polarizable graphene. In the left panel I also report the results obtained for SWM4_DP water on neutral polarizable graphene (red circles, green triangles, and yellow triangles). The angle $\Phi$ was defined as the angle between the OH bond of one water molecule and the normal vector of the surface. When $\cos(\Phi) = 1$, the OH bond points away from the surface. When $\cos(\Phi) = -1$, the OH bond points towards the surface. The probability $P[\cos(\Phi)]$ of observing the various angles $\Phi$ for the water molecules whose oxygen atom is found within 5 Å from the surface is reported. It should be remembered that Lee et al. [46] were the first to predict that water molecules within the first hydration layer near a hydrophobic surface point some of their OH groups towards the surface to minimize the number of hydrogen bonds lost because of the presence of the surface. Many subsequent simulations for water on graphite agree with such prediction [23–25]. Qualitatively, the results obtained here on the neutral graphene also show that some of the water molecules within the first hydration layer point one of their OH bonds towards the surface. Further, the results obtained for SPC/E (pink circles) and SWM4_DP (black circles, obtained for $\alpha = 0$) suggest that the polarizability of water insignificantly affects the orientation of interfacial water when graphene is neutral and not polarizable. However, my results show that the polarizability of graphene affects the orientation of interfacial water. The results obtained for interfacial SWM4_DP water on neutral polarizable graphene indicate that the probability $P[\cos(\Phi) \sim -1]$ increases when the polarizability increases, indicating that more interfacial water molecules point one of their OH bonds towards the surface when the surface polarizability increases.

In the right panel of Fig. A.3 I report the number of oxygen and hydrogen atoms found in the first peak on the density profiles obtained for SPC/E water on neutral non-polarizable graphene (pink circles), and for SWM4_DP water on neutral polarizable graphene. The number of oxygen and hydrogen atoms were counted up to 5 Å (the first minima on oxygen density profile) and 2.65 Å from the surface (the shoulder on the hydrogen density profile), respectively. On neutral non-polarizable graphene nearly 9 % of interfacial water molecules (either SPC/E or SWM4_DP) point one of their OH bonds toward the surface. On the most polarizable graphene considered ($\alpha = 1.1$), nearly 14 % of interfacial SWM4_DP water point one of their OH bonds toward the surface. At the expected polarizability of a carbon atom ($\alpha = 0.878$), approximately 12 % of interfacial water molecules point one OH bond towards the surface. Experimental results show that at water/air interface more than 20 % water molecules have ‘dangling’ OH bonds projecting into the air [47], suggesting that perhaps including polarizability is important for capturing the correct physics of the water/graphene interface as well. Experimental data necessary for validating my predictions are at present not available.

The orientation distribution of SWM4_DP water on neutral graphene surfaces, presented in the left panel of Fig. A.3, clearly indicates the effect of graphene
polarizability on the orientation of interfacial water. Will the polarizability of graphene affect the orientation of water on graphene when the graphene, instead of being neutral, is charged? The orientation distributions of interfacial SWM4_DP water on charged non-polarizable and charged polarizable graphene are presented in Fig. A.4. The results obtained for SWM4_DP water molecules on neutral non-polarizable graphene are also shown in this figure for comparison (black). Changing the surface charge density from negative to positive has the expected effect on the orientation of interfacial water. Briefly, water preferentially points more OH bonds towards the negatively charged surface (red triangles, note the high $P[\cos(\Phi) \sim -1]$ in

**Fig. A.3** Left The orientation distribution of SWM4_DP water molecules on polarizable graphene surfaces. Only the water molecules in the first hydration layer are considered in this calculation. Right The number of hydrogen and oxygen atoms of SWM4_DP water molecules within the first peaks observed on the atomic density profiles (see Fig. A.2). On both left and right panels, the results obtained for SPC/E water on non-polarizable graphene were also reported (pink circle) to compare with the results obtained for SWM4_DP (black) water on neutral non-polarizable graphene

**Fig. A.4** The orientation distribution of SWM4_DP interfacial water on charged non-polarizable and charged polarizable graphene surfaces. The results obtained for SWM4_DP water molecules (black circle) on neutral non-polarizable graphene are also shown for comparison. Only water molecules in the first hydration layer are used for this analysis
On the contrary, water points no OH bonds towards the positively charged surface (yellow diamonds, note the low $P[\cos(\Phi) \sim -1]$ in Fig. A.4). I focus here on the effect of graphene polarizability on the orientation distribution of interfacial SWM4_DP water on charged graphene. My results show that such effect is negligible. For instance, the orientation distribution of interfacial water on $-8 \mu C/cm^2$ non-polarizable (red) and $-8 \mu C/cm^2$ polarizable graphene (green), or the orientation distribution of interfacial water on $+8 \mu C/cm^2$ non-polarizable (yellow) and $+8 \mu C/cm^2$ polarizable (blue) graphene are identical. The electrostatic forces clearly dominate the effect of polarizable forces.

A.4.3 Hydrogen-Bond Network

In Fig. A.5 I present the number of hydrogen bonds per water molecule (left) and the hydrogen bond density profiles (right) obtained for SPC/E and SWM4_DP water on neutral non-polarizable graphene (top), for SWM4_DP water on neutral polarizable graphene surfaces (middle), and for SWM4_DP water on charged non-polarizable and charged polarizable graphene (bottom). One hydrogen bond was identified using the geometric criterion proposed by Marti [48]. The position of each hydrogen bond was considered as the middle point between the hydrogen of the donor and the oxygen of the acceptor molecules. The results presented in the top and middle panels indicate that the polarizability of either water or graphene have an insignificant effect on the hydrogen bond network. The water molecules in the first hydration layer (up to 5 Å from the surface) form fewer hydrogen bonds than the molecules in the bulk region do because of the asymmetry of the system (left panels). However, the hydrogen bond network is very dense in the contact layer as observed on the hydrogen density profiles (right panels) because the density of water molecules in the first hydration layer is high (see density profiles in Fig. A.2). These observations are in agreement with the results reported by Marti et al. [49] and Gordillo et al. [23]. The results obtained on charged graphene surfaces (bottom panels) also indicate that at the same surface charge density, the non-polarizable and polarizable graphene substrates do not affect the hydrogen bond network differently from each other.

A.4.4 Dynamical Properties

In Fig. A.6 I present several dynamical properties computed for interfacial water on various graphene surfaces. Only water molecules within the first hydration layer were considered for these calculations. I computed the residence auto-correlation function (left panels), the mean square displacement as a function of time (middle panels), and the reorientation correlation function (right panels). The results are compared when different force fields were implemented.
The residence auto-correlation function was defined as: 

\[ C_R(t) = \frac{\langle P(t) P(0) \rangle}{P(0) P(0)} \].

At time \( t = 0 \), \( P(0) = 1 \) for all the water molecules whose oxygen atom is found within the first peak on the oxygen density profile (see Fig. A.2). If the water molecules continuously stay in the first hydration layer when the time \( t \) progresses, then \( P(t) = 1 \), otherwise, \( P(t) = 0 \). The auto-correlation function decays from 1 to 0 when the system evolves because the interfacial water molecules leave the hydration layer as time progresses [50]. By studying the residence auto-correlation function it is possible to estimate the average residence time for water molecules at

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**Fig. A.5** Number of hydrogen bonds per water molecule (left panels) and hydrogen bond density profiles (right panels) as a function of vertical distance \( z \) from the surface. The results obtained for SPC/E and SWM4_DP water on neutral non-polarizable graphene, for SWM4_DP water on neutral polarizable graphene, and for SWM4_DP water on charged non-polarizable and charged polarizable graphene are shown in the top, middle, and bottom panels, respectively.
contact with the graphene (e.g., the time required for the auto-correlation function to decay from 1 to 1/e).

The in-plane MSD was quantified as: 

$$\langle (x(t) - x(0))^2 + (y(t) - y(0))^2 \rangle > \frac{N(t)}{N(t)}$$

where $N(t)$ is the number of water molecules remaining in the hydration layer at time $t$. Note that as time progresses, $N(t)$ decreases. Once a water molecule leaves the hydration layer, it does not contribute any more to the mean square displacement, even if it returns after some time. The slope of the in-plane MSD as a function of time could be used to estimate the self-diffusion coefficient for water molecules in the direction parallel to the surface, although the correlation should last for infinite times, which is not possible as water molecules eventually leave the hydration layer. Qualitatively, I estimate the mobility of interfacial water from the initial slope of the MSD data. The larger of the slope, the faster interfacial water molecules diffuse [50].

The reorientation correlation function was obtained as: 

$$C_{DM}(t) = \frac{\langle M(t)M(0) \rangle}{\langle M(0)M(0) \rangle}$$

where $M(0)$ is the dipole moment of water molecule vector at time $t = 0$, $M(t)$ is the dipole moment of water molecules vector at time $t$. Only water molecules continuously staying within the first hydration layer were considered for this calculation. The slower the reorientation correlation function decays from 1 to 0, the slower the water molecules rotate [50]. The rotational diffusion can be estimated, qualitatively, from the time required by the reorientation correlation function to decay from 1 to 1/e.

The comparison of the dynamical properties obtained for SPC/E and SWM4_DP water on neutral non-polarizable graphene surface is shown in the top panels of Fig. A.6. The results for the residence correlation function (top left) demonstrate that the SPC/E water molecules stay in the contact layer on average shorter than SWM4_DP water molecules do. However, the MSD results (top middle) suggest that SPC/E and SWM4_DP water molecules have similar mobility in the direction parallel to the substrate. The reorientation correlation function data (top right) indicate that the SPC/E water molecules rotate more slowly than SWM4_DP water molecules do. This appears to be counter-intuitive, since SPC/E water was found to reside in the first hydration layer for shorter times than the SWM4_DP water. However, I note that the differences are rather small.

The dynamical properties predicted for SWM4_DP water on neutral graphene as a function of graphene polarizability (middle panels from the top) show differences only when the polarizability of a carbon atom is larger than $\alpha = 0.878$ Å. Because on neutral polarizable graphene the orientation of SWM4_DP water was found different compared to that on non-polarizable graphene, it is surprising that the dynamical properties of water are not affected by the surface polarizability when $\alpha < 0.878$ Å. It is possible that the dynamics of interfacial water molecules depend more strongly on the presence of ions, whose predicted behaviour (i.e., surface adsorption) might depend on polarizability [26]. This possibility will be explored in the future.
The structural properties of water on charged graphene were found not to depend on graphene polarizability. However, the dynamical properties predicted for interfacial water on charged graphene appear to depend, to some extent, on the graphene polarizability (bottom panels of Fig. A.6). Note that these results were obtained when the polarizability $\alpha$ of carbon atoms of graphene was either 0 or equal to the expected value of 0.878 Å$^3$. The residence auto-correlation function data (bottom left) show no difference, as a function of surface polarizability, when graphene is charged. However, the MSD data (bottom middle) show that water molecules on charged polarizable graphene have faster mobility along the direction parallel to the substrate compared to water on charged non-polarizable graphene. For example, water molecules on the $-8 \mu C/cm^2$ non-polarizable graphene (dash red) diffuse more slowly than on the polarizable surface with the same surface charge density (dash green). The same can be repeated for the positively charged graphene. Experimental data such as those obtained from NMR or neutron scattering are needed to determine which of these predictions better reproduces reality. The reorientation correlation function data (bottom right) indicate that the effect of polarizability of graphene on the rotation of water on charged graphene is negligible.
A.5 Conclusions

The importance of including the polarizability of water and graphene in molecular dynamics simulation of the water/graphene system was explored. A thin film of rigid SPC/E and polarizable SWM4_DP water on non-polarizable and polarizable graphene surfaces was simulated. The graphene surface was either maintained neutral or charged. The obtained results suggest that the SPC/E and SWM4_DP yield very similar structural properties of water on neutral non-polarizable graphene, while the dynamical properties of SPC/E and SWM4_DP on neutral non-polarizable graphene are slightly different. More importantly, I found that including explicitly in the calculations the polarizability of graphene enhances the number of interfacial SWM4_DP water molecules pointing one of their OH bonds toward the surface, although it insignificantly affects the dynamical properties of interfacial SWM4_DP water if the polarizability of carbon is smaller than $\alpha = 0.878$ Å. On charged graphene surfaces, the effect of polarizability of graphene on the structural properties and some of the dynamical properties of SWM4_DP water is negligible because the electrostatic forces dominate the polarization forces, as expected. For all cases, the hydrogen bond network is insensitive to the polarizability of both water and graphene. These results, when accompanied by experimental data, will provide a comprehensive picture of water properties and insight into the importance of polarization at graphene/water interface. Applications that will benefit from this fundamental understanding include the design of energy storage devices as well as water desalination processes.

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**Appendix B**

Integration of the Poisson Equation

The Poisson equation reads (the symbols are explained in the Chap. 4):

\[
\frac{d^2 \psi}{dz^2} = -\frac{1}{\varepsilon_o} \rho(z) \tag{B.1}
\]

The first and second integrations with respect to the variable \( z \), the distance from the charged surface, yield:

\[
\frac{d\psi}{dz}(z) = -\frac{1}{\varepsilon_o} \int_0^z \rho(u) du + C_1 \tag{B.2}
\]

\[
\psi_z = -\frac{1}{\varepsilon_o} \int_0^s \rho(u) du + C_1 z + C_2 \tag{B.3}
\]

In Eqs. (B.2) and (B.3) \( u \) and \( s \) are dummy variables, \( C_1 \) and \( C_2 \) are constants of integration that are defined by imposing appropriate boundary conditions.

As the first boundary condition, I impose that

\[
\frac{d\psi}{dz} = 0 \text{ at } z = R/2
\]

(i.e., the electric field at the pore centre is zero), which yields.

\[
C_1 = \frac{1}{\varepsilon_o} \int_0^{R/2} \rho(u) du.
\]

As the second boundary condition I impose \( \psi(z) = 0 \text{ at } z = 0 \).
(i.e., the potential is chosen to be zero at \( z = 0 \)), which for all electrochemical cells yields.

\[ C_2 = 0. \]

The last equality implies that all electrical potentials shown in this work as expressed relative to the potential of the electrode at \( z = 0 \).

Using the relations just derived for \( C_1 \) and \( C_2 \), Eq. (B.3) becomes

\[
\psi_z = -\frac{1}{\varepsilon_o} \int_0^z \rho(u)du ds + \left[ \frac{1}{\varepsilon_o} \int_0^{R/2} \rho(u)du \right] z \tag{B.4}
\]

From Eq. (B.4) I switch the order of integration within the double integrals to obtain

\[
\psi_z = -\frac{1}{\varepsilon_o} \left[ \int_0^z \int_0^z \rho(u)du du - \left( \int_0^{R/2} \rho(u)du \right) z \right] \tag{B.5}
\]

and subsequently

\[
\psi_z = -\frac{1}{\varepsilon_o} \left[ \int_0^z (z - u)\rho(u)du - \left( \int_0^{R/2} \rho(u)du \right) z \right] \tag{B.6}
\]

The results presented in Figs. 4.4 and 4.6 are obtained by numerical integration of Eq. (B.6) using the respective charge density profiles as input.