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Ion Distributions in Water/Graphene Interface: A Molecular Dynamics Study

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Abstract: Classical Molecular Dynamics (MD) with a non-polarizable force field is used to quantify the ion size effect on structure and dynamics of the confined electrolyte solution by considering the series of sodium halides (NaX with X = = F, Cl, Br, and I). Ions and water transport were simulated through a rigid and neutral atomistic carbon wall (graphene). The results showed that the solid surface has a major effect on the ion distribution in nano-aqueous solutions near interfaces. Cl, Br, and I tend to be repelled from the regions where the density of water is high, while F was found to be significantly solvated by water. Due to confinement, the dynamical properties of the electrolyte solution were also observed on the anions and cations pairing through determining the self-diffusion coefficient.

Key words: surface effect, ions size, graphene wall, molecular dynamics

I. INTRODUCTION

In various scientific fields including chemistry, geology, nanotechnology, and biology, the structure and dynamic properties of water and ions in a confined medium are essential. Recent advances in nano-material fabrication [1–4] raise fundamental questions on how the solid surface affect ion transportation. This effect plays a crucial role in understanding ion selectivity, assists in predicting properties of nano-porous membranes and gives a designing guide to synthetic membranes used in several applications such as nanofiltration. The classical electrostatic theory predicts that ions are repelled from water/hydrophobic (e.g., air/water) interfaces. Computer simulations along with experiments show that chaotropic ions exhibit enhanced concentrations at an air/water interface. Despite the development of mechanistic pictures in order to explain this counterintuitive observation, their general applicability remains unclear, particularly in the presence of material substrates. This study goes beyond the theoretical approach by performing classical Molecular Dynamics (MD) that are particularly well adapted for studying this phenomenon at the nanoscale. During the past two decades, many MD studies have been performed with atomistic models of ion transport [5–15]. The researchers have focused on the study of structures of ion channels and their contents dynamics, which consist of explicit water molecules and a few ions in the channel. Netz and coworkers [16] have performed a study on MD computer simulations which was used to examine ion distribution on a water/hydrophobic-assembled monolayer interface. They

have asserted the similarities between their obtained results for a solid wall and those of Tobias and co-workers [17] on a water/vapor interface. Recently, Debra L. McCaffrey and co-workers [18] have studied the mechanism of ion adsorption on aqueous interfaces: (graphene/water vs. air/water). They focused on the influence of a simulated graphene substrate on two factors previously emphasized in the context of air-water interfaces. The first is the entropic cost associated with capillary wave pinning and the second is the enthalpy gain associated with repartitioning under coordinated water molecules at the bulk interface. This paper reports a molecular simulation study of an ion structure at the water/graphene interface. It addresses the effect of neutral atomic surface that is expected to play a crucial role on the behavior of the alkali-halide aqueous electrolytes (NaX with X = F, Cl, Br, and I). The size effect of the ions on the structure and dynamics of the confined electrolyte solution was quantified. Behavior of the ions at the interface was characterized by determining the density distribution and the pair correlation functions. The dynamical properties of the system are then determined by calculating mean square displacements and self-diffusion coefficients. Moreover, the simulation's details, including the models description and the interaction potentials, were provided as well as discussion of the attained results.

II. SIMULATIONS DETAILS

The molecular dynamics simulations were performed using the NAMD program package [19]. The model consists of a 3 nm thin film containing 864 water molecules placed between two graphene layers by adding 18 pairs of sodium/halide ions NaX (X = F, Cl, Br, and I). The sodium/halide concentration was equal to 1.2 M. The system was situated into a $30 \times 30 \times 100$ A^3 rectangular box and periodic boundary conditions were applied in three dimensions (see Fig. 1).

The simulations were run at a constant temperature of 300 K with NVT set. The smooth particle mesh Ewald method was used to calculate the electrostatic energies and the Van der Waals interactions. The real space part of the Ewald sum was truncated at 12 Å. A time step of 1 fs was used in the integration of the motion equations. The OH bond vibrations were frozen using the SHAKE algorithm. Each simulation consisted of 2 ns equilibration and 1 ns data collection. The system reached a stationary state after a 0.5 ns as was shown by the total energy. The initial configuration of the simulation was obtained by homogeneously distributing water molecules and ions in the film. The Verlet leap-frog algorithm was used to integrate the motion equations with a time step of 1 fs. The rigid water model (SPC) was used to describe the water-water interaction. A water molecule is represented as a sphere with the oxygen atom located in its center, whereas partial charges are found on the oxygen and on the hydrogen sites. The geometry of the SPC water molecule is shown in Fig. 2. The ions were described as a charged rigid sphere using the parameters proposed by Dang and coworkers [20] and the walls consisted of a neutral Lennard-Jones (LJ) sphere. The polarizability term (dipole-dipole interaction) is not included because we quantified the size effect only.

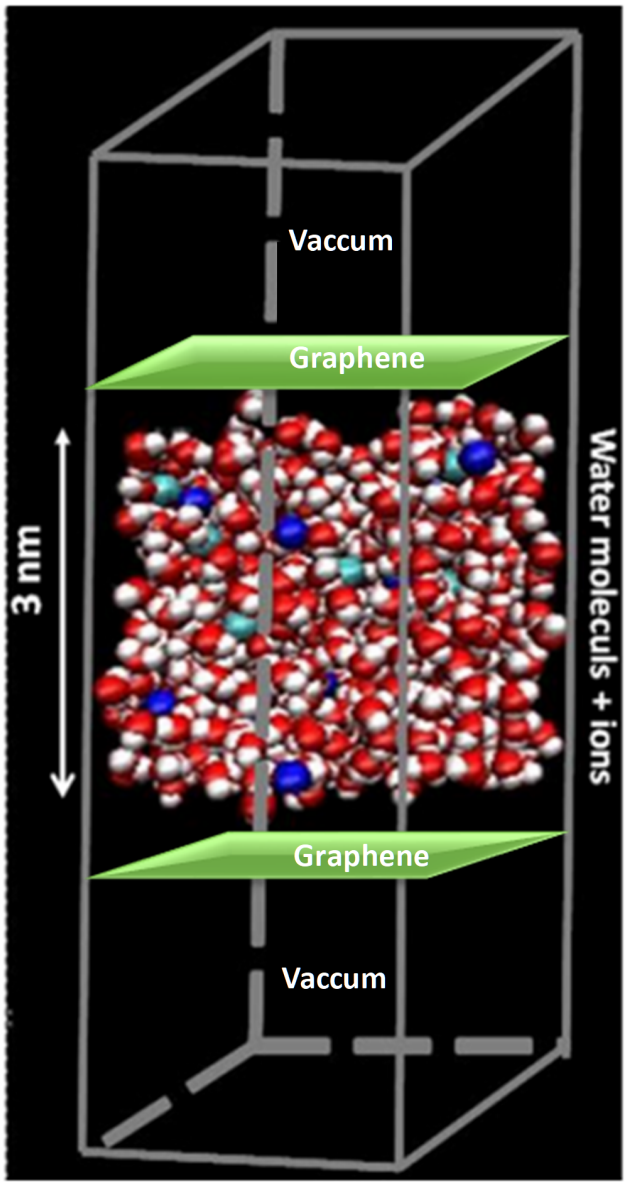

Fig. 1. Snapshot of the 1.2 M NaI in SPC water simulated system. Red and white spheres are oxygen and hydrogen atoms of the water molecules, respectively. Dark blue and light blue spheres are Iodide and sodium ions, respectively. The green surface is the graphene sheets. The square section of the film along x and y is 3×3 nm. The size of the parallelepiped box along the direction perpendicular to the film is 10 nm so that each face of the film is in contact with the graphene sheets

The interaction energy V_{pair} between the atom pairs is the sum of the coulombic interaction and the repulsion and dispersion terms modeled by LJ potential:

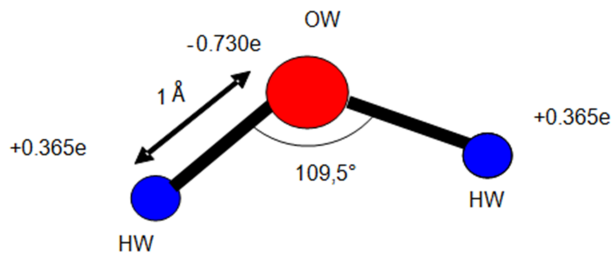

Fig. 2. The geometry of rigid water model "SPC" was used to describe the water-water interaction

$$V_{\text{pair}} = \sum_{i<j} \frac{q_i q_j}{r_{ij}} + \sum_{i<j} \varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - 2 \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right] \quad (1)$$

Where r_{ij} is the distance between the atoms i and j with q_i and q_j are the partial charges. σ and ε are the Lennard-Jones parameters for the repulsion and dispersion interactions. All the parameters used in the present work for the water molecules, the ions and the graphene are listed in Tab. 1.

Tab. 1. Potential parameters for the different ions, water molecule and graphene considered in this study [10, 14]

Element	weight (g/mol)	σ (Å)	ε (Kcal/mol)	Charge
Na	22.99	2.341	0.100	+1
F	19.00	3.173	0.100	−1
Cl	35.45	4.348	0.100	−1
Br	79.90	4.708	0.100	−1
I	126.9	5.160	0.100	−1
H	1.008	0.000	0.000	+0.365
O	16.00	3.210	0.156	−0.730
C	12.00	2.000	0.110	0

III. SIMULATION RESULTS AND DISCUSSION

Herein, the effect of the size of the anions on their behavior in aqueous electrolyte interfaces was studied by considering the following systems: water with NaX where X = = F, Cl, Br, and I. In this part, non-polarizable ions were considered. Fig. 3 shows the water's cation and anion concentration profiles as a function of the distance z normal to the interface, and illustrates the positions of the different species across the water/graphene interface. Water density exhibits a maximum at a well-defined position from the graphene surface and structured with a high concentration peak at $z = 87.3$ Å. Oscillations or perturbations due to the water molecule interactions with the wall surface atoms were observed. The maximal amplitude decreased as the distance from the wall surface increased. The density tended towards the bulk value as the water molecule recovered their bulk properties. The density oscillations revealed the significant layering of water in the vicinity of the nanochannel wall. Such a spatial ordering of confined water is characteristic of hydrophobic or hydrophilic spaces [21–25]. This result was confirmed by the fact that the density profiles were found to be almost identical to that obtained for pure water. The large anions such as iodide, bromide and chloride are strongly repelled from the interface and remain within the water film. Three layers of anions were observed at $z = 76.5$ Å, $z = 79.5$ Å, and $z = 82.5$ Å. The concentration started to increase toward the center of the slab, where their distributions were localized below the second peak of water molecules. The distributions became structured when the size of the anion increased from chloride to bromide and then to iodide. In this case the sodium cations did not follow the anions as they were also located within the water film. In fact, this configuration where sodium cations are sandwiched between water layers is favorable as it led to higher solvation of the cations while being compatible with the layering imposed by the graphene wall. Such a significant solvation of sodium cations observed, both for bulk and confined electrolyte solutions, is due to their small size which weakly perturbs the hydrogen bonding between water molecules. On the other hand, fluoride anions occupy the slab space within the carbon graphene in a more homogeneous way, though layering was also observed for this anion (i.e., smooth density oscillations were observed in the corresponding plots). The locations of the density peaks for fluoride seem to be correlated with those for sodium cations. This result suggests that, as in bulk NaF solutions, the fluoride anions tend to: (1) pair with the sodium cations and (2) be solvated by water molecules. These results, which depart from what was observed for the smallest anions, suggest that the system evolves towards another equilibrium configuration as the size of the anion increases. The results for the large anion confirmed this, since iodide was preferentially localized in the low water density zone. Three marked peaks were observed in the region where the water concentration tends to the bulk. Near the graphene surface water and ions are not the bulk properties, the structures and dynamics of water and ions were modified by the presence of wall surface. Therefore, the structure and dynamic properties of water and ions depend on the surface nature. For example, the results obtained from the air/water interface were different from the water/graphene interface. The origin of the ion size effect is the cost in free energy to solvate the ions as their presence may hinder hydrogen bonding [26]. For large ions such as iodide, the volume fraction occupied by the ions becomes significant and leads to high free energy penalties. In this case, the ions tend to move towards the less hydrophilic zone which cannot be solvated without drastically hindering hydrogen bonding between the water molecules.

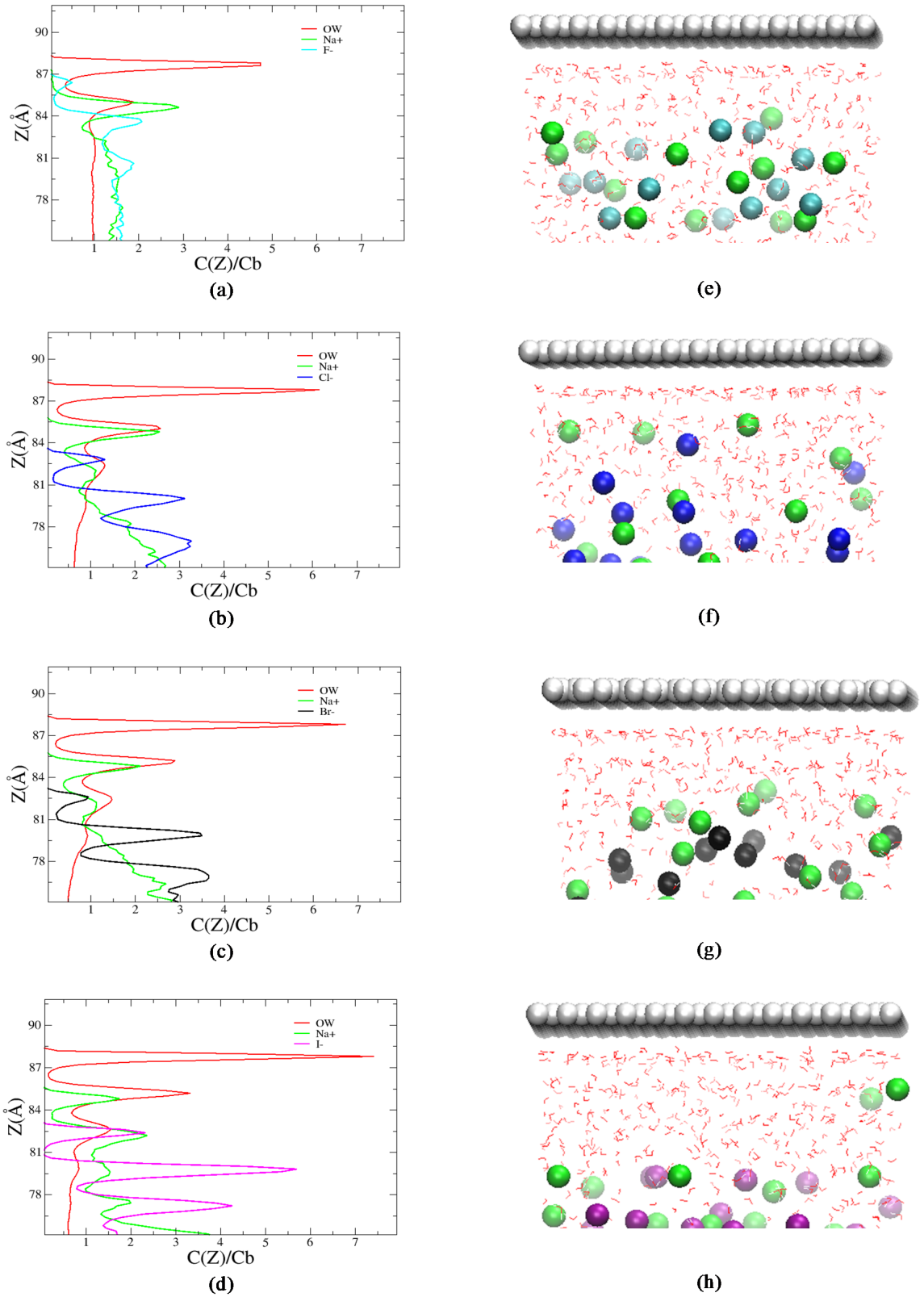

Fig. 3. (a), (b), (c) and (d) are the snapshots of the solution/graphene interfaces from the molecular dynamics simulations. Coloring scheme: water oxygen, red; sodium ions, green; Floride ions, turquoise; chloride ions, dark blue; bromide ions, black; iodide ions, magenta. (e), (f), (g) and (h) are the concentration $C(z)$, of water oxygen atoms and ions plotted vs. distance from the center of the slabs in the direction normal to the interface (z), normalized by the bulk concentration. The colors of the curves correspond to the coloring of the atoms in the snapshots

On the other hand, water molecules can easily solvate small solute sodium and fluoride without breaking the hydrogen bonding network so that no ion exclusion was observed. The volume fraction occupied by these ions is small and they remain in the zone; the cost in free energy to have these ions in water remains low so that no perturbation was observed.

Fig. 4 shows the pair correlation functions between the halide ion (X = F, Cl, Br, I) and the hydrogen atom of the water molecule. The anions and hydrogen atoms have peaks located at different positions. In particular, the distance from the nearest neighbor corresponding to the position of the first peak increases with the size of the anions. The fluoride anion behaves in a very different way from other anions (Cl, Br, I). The F anion tends to be completely solvated by water so that the pair correlation function between water and the anion shows a peak of a very large amplitude at $r = 1.5$ Å, corresponding to the distance from the nearest neighbor. Due to the steric and hydrophobic effect, the larger anions (Cl, Br, I) tend to be excluded from water so that the distance from the nearest neighbor to the water is much greater than that for F and increases with the anion size.

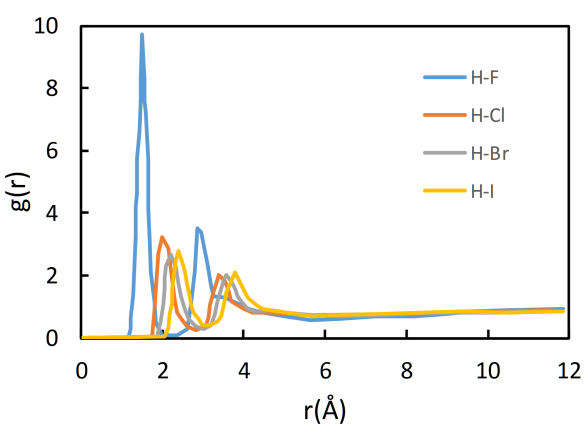

Fig. 4. Pair correlation functions $g(r)$ between the halide ions (X = = F, Cl, Br, I) and the hydrogen atoms (H) of water

The above work presented the structure of water and ions confined between two graphene monolayers. Now, we analyze the dynamical properties by calculating mean square displacements and self-diffusion coefficients. The mean square displacement (MSD) for all the species of the confined electrolyte solutions NaX (X = F, Cl, Br, I) was calculated. In fact, for such correlated systems, the time required to obtain reliable statistics (where events are uncorrelated so that normal diffusion is observed) increases drastically with the size of the system. Fig. 5(a) shows the MSD in two dimensions along x and y axis for the anions confined between two graphene monolayers. According to the classical diffusion law, MSD is proportional to time. The MSD in the direction parallel to the graphene increased very rapidly at short times intervals and then exhibited a defined direction at larger intervals. This finding is in agreement with previous studies on the dynamics of fluids of water atoms confined in nanopores [27–30]. No perpendicular diffusion to the graphene surface was observed. The MSD in two dimensions exhibited a linear behavior when plotted in a log- log scale, where the exponent was found to be 1 as expected for species obeying normal diffusion. To further characterize the dynamics of ions, their self-diffusion coefficients were calculated from the derivative of the MSD with respect to time

$$D_{xy} = \frac{1}{4t}\left\langle [x(t) - x(0)]^2 + [y(t) - y(0)]^2 \right\rangle \quad (2)$$

Fig. 5(b) shows the self-diffusion coefficients along x and y as a function of the parameter σ which corresponds to the ion size (σ is equal to the ion radius divided by 2). The calculation was done in the direction parallel to the wall for

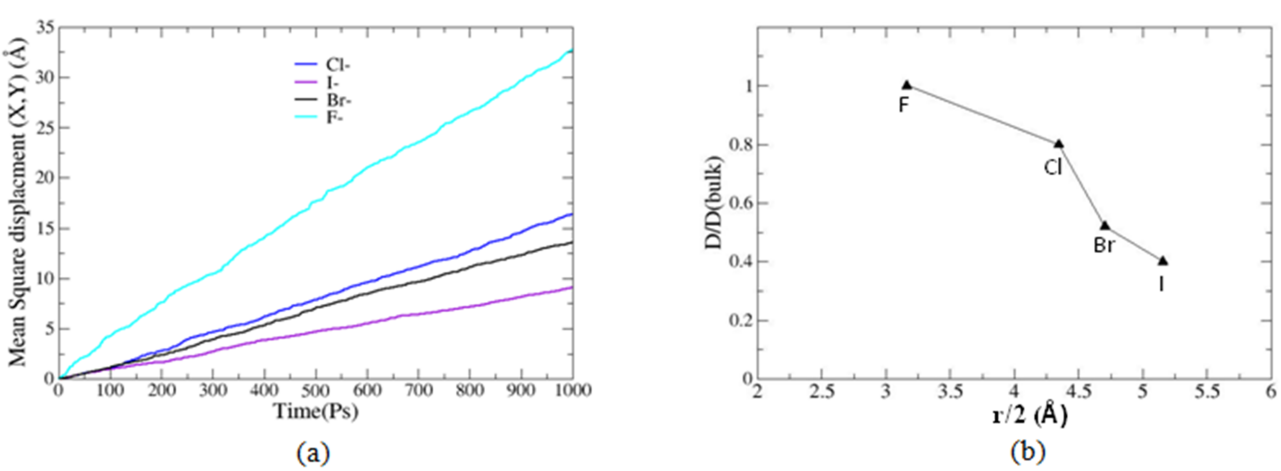

Fig. 5. (a) Mean square displacement of different ions for electrolyte solutions NaX (X = F, Cl, Br, I). (b) Ratio between the self-diffusion coefficient defined above and its bulk counterpart for the same electrolyte solutions and at the same concentration 1 mol/l versus the radius of ions divided by two

the different ionic species mentioned above. The result was normalized by the bulk counterpart for the same electrolyte solutions and at the same concentration 1 mol/l. It was observed that the self-diffusion coefficient for ionic species is smaller than the bulk. The presented simulation results showed that the ion self-diffusivities decreased when changing the ion size from fluoride to iodide. This result is due to the fact that the ions became structured forming layers with high density (especially for iodide) and diffuse slower when the size of the ion increases. This result is in good agreement with that found in literature for ions confined in a less hydrophilic system [31–34]. The ionic species diffuse faster in weakly hydrophilic wall materials because of the lack of strong adsorption sites. The predominant confinement effect at the nanoscale tends to decrease the diffusion of species compared by the results observed for the bulk electrolyte solutions.

IV. CONCLUSION

This study describes the molecular dynamics simulation of non-polarizable ions at the water/graphene interface. The obtained results from these simulations underlined the vital role played by the ion size effect on the phase behavior of electrolyte solutions in contact with a graphene monolayer wall. The following alkali-halide aqueous electrolyte NaX where X = F, Cl, Br, and I were considered in this study. The obtained results showed that water molecules are well structured in a weakly hydrophilic surface (graphene); therefore, water structures in confinement media play a crucial role in ion location in the system. The cations and anions were found to behave differently in the system depending on whether they were located within the center region or adsorbed at the interface. The results indicated that the surface effects changed the water structure and consequently the ion distribution in the system. However, it was clearly demonstrated that the structure of the interface can be altered drastically by the particular choice of the dissolved salt. The interfacial region became increasingly populated by ions upon moving from fluoride to larger halides specifically for the series of sodium halides. Ultimately, for bromide and iodide, there is an enhancement of the anionic concentration at the interface relative to the bulk.

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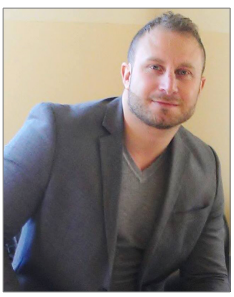

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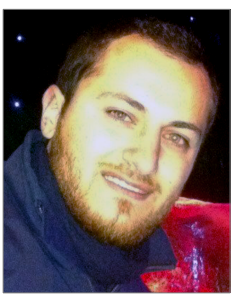

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