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Structural and dynamical characterization of water on the Au (100) and graphene surfaces: A molecular dynamics simulation approach

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The positioning, adsorption, and movement of water on substrates is dependent upon the chemical nature and arrangement of the atoms of the surface. Therefore the behavior of water molecules on a substrate is a reflection of properties of the surface. Based on this premise, graphene and gold substrates were chosen to study this subject from a molecular perspective. In this work, the structural and dynamical behaviors of a water nanodroplet on Au (100) and the graphene interfaces have been studied by molecular dynamics simulation. The results have shown how the structural and dynamical behaviors of water molecules at the interface reflect the characteristics of these surfaces. The results have demonstrated that residence time and hydrogen bonds' lifetime at the water-Au (100) interface are bigger than at the water-graphene interface. Energy contour map analysis indicates a more uniform surface energy on graphene than on the gold surface. The obtained results illustrate that water clusters on gold and graphene form tetramer and hexamer structures, respectively. Furthermore, the water molecules are more ordered on the gold surface than on graphene. The study of hydrogen bonds showed that the order, stability, and the number of hydrogen bonds is higher on the gold surface. The positioning pattern of water molecules is also similar to the arrangement of gold atoms while no regularity was observed on graphene. The study of dynamical behavior of water molecules revealed that the movement of water on gold is much less than on graphene which is in agreement with the strong water-gold interaction in comparison to the water-graphene interaction.

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I. INTRODUCTION

The interaction of water with solid substrates plays an important role in various natural phenomena such as catalysis [1], electrochemistry [2], motion of water [3], and corrosion [4] while having important applications in the production of hydrogen, fuel cells, and biological sensors [5]. Understanding the interaction of water and solid surfaces can help in comprehension and control of reactivity of water and surfaces [6,7]. In the last two decades, water adsorption on single crystalline metallic surfaces has been studied as a result of great progress in laboratory techniques [8] which along with quantum computations and molecular dynamics simulations, can improve our understanding of water-substrate interfaces and reveal valuable information regarding these interfaces [9]. Recent studies on the structure of water on surfaces indicate that as result of experimental conditions and amount of covered surface, water can form various structures such as segregated monomers, hydrated clusters, one-dimensional chains, and two-dimensional ordered multilayers [10–12]. Stability and structure of adsorbed water on the metallic surfaces are affected by two important aspects of water-metal interfaces; (i) water-surface interaction which generally occurs at the interfacial layer of the water-metal system, and (ii) the nature and strength of hydrogen bonds in the water which can be affected by the substrate. These two interactions compete with one another on almost any metallic surface [13]. Recent experiments uncovered two-dimensional and ordered structures of water using low energy electron diffraction [14]. The scanning tunneling microscope (STM) has helped in revealing single clusters of water as well [15]. For example, monomer, dimer, and hexamers of water on Ag (111) [16], Al(111) and Rh(111) [17],Cu (111) [18], Pd (111) [19], and a one-dimensional water chain on Pd (111) have recently been discovered using STM devices [20]. A network of hydrogen bonds is formed as more surface becomes covered with water molecules [21]. These networks have been studied in detail on Au (111), Rh (111), and Pt (111) surfaces [22–24]. STM analysis along with simulation methods present useful techniques to determine the structure of water molecules on substrates [25]. Recent experiments have been carried out in high vacuum conditions and cryogenic temperatures which revealed that water forms various networks from dimers to oligomer on metal surfaces [26]. Theoretical analyses have shown a relative stability of water hexamer on special surfaces [27]. However, empirical data are not always in line with such low energy calculations. For example, hexamer structures were observed via STM on the Cu (111) surface even though curved structures are expected to be more stable [28]. Limitations in using STM could have also caused this contradiction [29]. Low energy electron diffraction, IR reflection-adsorption spectroscopy, and density functional theory (DFT) analyses were used to study planar hexamer water on the Ru (0001) surface which revealed that Ru-water interactions dominate the hydrogen bonding among water molecules and the result is the hexamer structure [30]. The structure of water on the Pt (111) surface has been carefully studied using various experimental techniques [31]. The two-layer structure of water was reported on this surface for the first time in Ref. [32]. This two-layer structure is interesting since it provides initial conditions to form a network of hydrogen bonds on the surface. A similar structure has been discovered on other metallic surfaces such as Rh (111) and Au (111) [33,34]. Meng *et al.* have reported the adsorption of water on metal surfaces such as Ru, Rh, Pd, Pt, and Au (100) using DFT which indicated that water-substrate bonding

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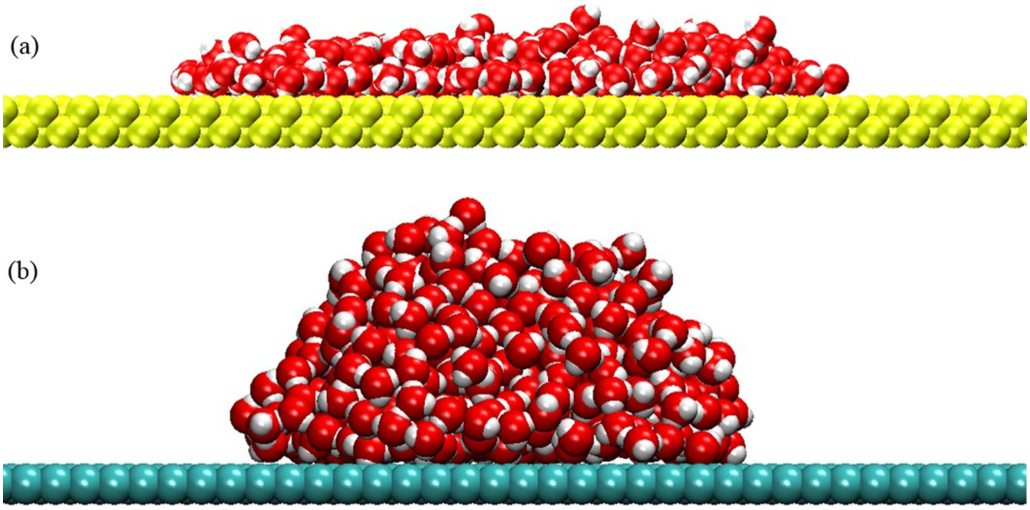

FIG. 1. The final snapshots of the water nanodroplet on (a) Au (100), and (b) graphene surfaces. Red, white, yellow, and green represent oxygen, hydrogen, gold, and carbon, respectively.

is focused on contact regions. Furthermore, the wettability of these metals was classified as Au < Pt < Pd < Rh < Ru which is affected by chemical activity of the substrate and coupling of electrons between water and the substrate [13]. Aside from the two-layer structures, very little is known about other nanostructures of water on surfaces such as monomers, clusters, and one-dimensional chains. Identification and characterization of water on surfaces are difficult tasks even though STM is capable of taking images of these water clusters. This is mainly due to rapid movement of water molecules even at temperatures as low as 10 K [12]. Molecular dynamics simulation is a helpful tool in studying water-metal interactions as well as the movement of water molecules on such surfaces. In this study, water-gold and water-graphene were chosen and the interaction of water-substrate along with the dynamic structure of water were analyzed in both systems. Furthermore, the relation between structural and dynamical behavior of water and surface properties was studied.

II. SIMULATION DETAILS

Molecular dynamics (MD) simulations were performed using LAMMPS [35] and structures were visualized using the VMD package [36]. All simulations were carried out in an *NVT* ensemble. A Nosé-Hoover thermostat [37] was applied to maintain temperature at 300 K, with a damping coefficient of 0.1 ps^{-1}. Time integration of Newton's equation of motion was achieved using a velocity Verlet algorithm with a time step of 1.0 fs. Nonbonded van der Waals interactions were modeled in terms of a 12-6 Lennard-Jones potential [38]. The particle-particle particle-mesh (PPPM) method was applied to minimize error in long range terms in Columbic interactions. Lennard-Jones and Columbic cutoff radii were set as 10 and 12 Å, respectively. Each MD simulation was carried out for 4.0 ns. The TIP4P model was utilized for the water molecules [39]. The SHAKE algorithm was used to keep the O-H distance fixed at 0.9572 Å and the H-O-H angle at 104.52° [40]. The adaptive intermolecular reactive empirical bond order potential was used to define interaction of carbon atoms [41]. The embedded-atom method (EAM) potential was used to define interaction between Au (100) atoms [42]. A water cubic box was initially placed on the top of the surfaces. We used an armchair configuration of a graphene sheet with dimensions of $(200 \times 200)\,\text{Å}^2$ and two layers Au substrate with dimensions of $200 \times 200\,\text{Å}^2$. The size of the water cubic box was $(25 \times 25 \times 25)\,\text{Å}^3$ and the number of water molecules was 500 in both the Au and graphene systems. During the simulations, atoms of the substrates were fixed. Nonperiodic boundary conditions were applied along the *Z* direction of the simulation box while periodic boundary conditions were considered in the other two directions. The mirror boundary condition was defined at the top surfaces along the *Z* axis, i.e., the vertical direction. Figure 1 shows the final snapshots of the water nanodroplet on Au (100) and graphene surfaces.

III. RESULTS AND DISCUSSION

In this section, the acquired results based on the structural and dynamical behavior of water on gold and graphene are presented in Secs. III A and III B, respectively. Based on this premise, the wetting behavior of the substrates, density fluctuations, adsorption energy of the water molecules, interaction energy distributions, arrangement of water molecules near the surface, and droplet displacement are studied.

A. Structural behavior of water nanodroplet

Density of water on gold and graphene surfaces was analyzed to study the structural behavior and layer formation of water molecules. Figure 2 illustrates the density profiles with respect to the distance of oxygen molecules from the surface. The number of oxygen atoms was counted in 1-Å intervals along the *Z* axis to plot these diagrams and the mass of the water molecules was divided by the unit volume of each interval.

The two highest peaks have heights of 4.61 and 2.43 and are placed at 2.8 and 3.2 Å for water-gold and water-graphene systems, respectively. Therefore the height of the first peak in

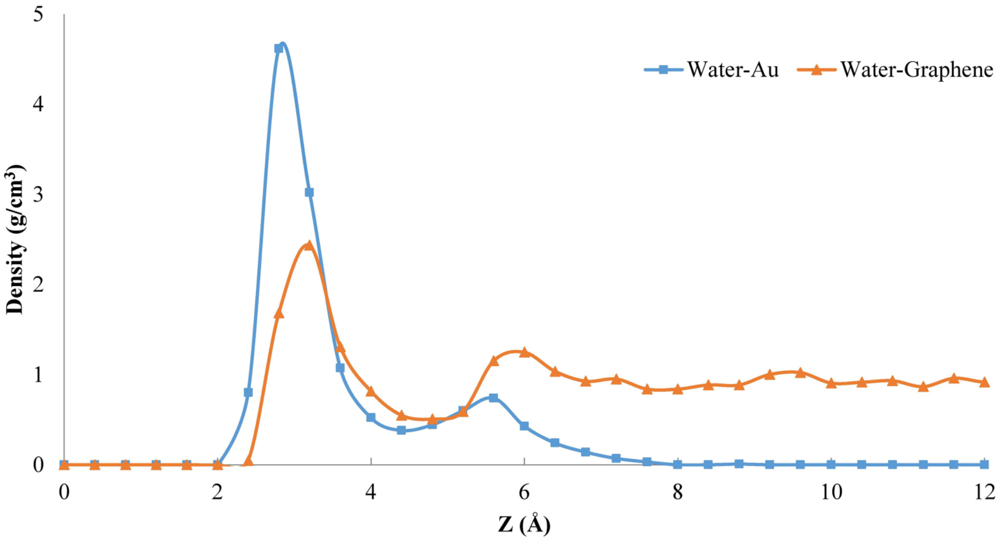

FIG. 2. Density profile of water molecules on Au (100) and graphene substrates.

water-gold has a higher value than the water-graphene system. The lower peaks occur at 5.6 and 6.1 Å for water-gold and water-graphene systems, respectively. Based on this premise, two regions can be defined in both systems denoted as *interface* and *adjacent*. Therefore the thicknesses of these layers are 2.8 and 5.6 Å on gold surfaces and 3.2 and 6.1 Å on graphene surfaces, respectively. The obtained results are in agreement with the quantum data [43,44]. Quantum studies indicate that a strong interaction can be observed on the Au (100) surface at a 2.8-Å distance from the surface while weaker interactions occur on graphene [45,46]. Based on the acquired data in the current work and quantum results, it can be concluded that stronger interaction with and nonuniformity of the Au surface can pin the nanodroplet on the gold surface. In the following sections, the position of the water molecules will be divided into two regions: interface and adjacent. The thicknesses of these layers are extracted from the density profiles; see Fig. 2.

The contact angle can describe the interaction of a fluid with a surface. The value of the contact angle for a liquid is different on different surfaces [47]. It was shown that the contact angle is related to the surface energy of solid-liquid, solid-vapor, and liquid-vapor. Two extreme cases of wetting take place at $\theta = 180^\circ$ where no wetting occurs and the droplet forms a spherical shape, and $\theta = 0^\circ$ where complete wetting occurs and the liquid uniformly spreads on the surface. In the current study, the contact angle of water was found to be 18° and 89° on gold and graphene surfaces, respectively. Figures 1(a) and 1(b) illustrate that water spreads on gold while it forms a droplet on graphene.

1. *Contour map and adsorption energy of water nanodroplet*

The geometry and structure of the surfaces should be introduced prior to analyzing the structural behavior of water molecules on gold and graphene. Based on this premise, the interaction energy of one water molecule with both substrates was studied. Figure 3 shows the interaction energy contour map of one water molecule with gold and graphene surfaces. The water molecule was scanned on the surfaces $Z = 2.5$ Å and $Z = 3.2$ Å, based on the first peak of the density profiles, and its interaction energy with each substrate atom along the XY plane was recorded.

It can be seen in Figs. 3(a) and 3(b) that the distributions of interaction energy on gold and graphene substrates are different, and the graphene surface possesses a more uniform surface energy than Au (100). The differences between energy peaks and troughs for water-gold and water-graphene systems are -2.099 and -0.146 K J mol^{-1}, respectively. Thus the water molecules require less energy to overcome the energy barrier on the graphene surface, while based on the maximum and minimum energy values, the interfacial water molecules are highly affected by the gold surface. Figure 3(c) illustrates the energy diagram of the interaction between a water molecule and both substrates and indicates that the potential well in the water-gold system is deeper than in the water-graphene system. Additionally, the adsorption energy per water molecule was calculated using the following equation:

$$E_{\mathrm{ads}} = (E_{[m/M]} - E_{[M]} - nE_{[m]})/n, \tag{1}$$

where $E_{[m/M]}$ is the total energy of the adsorption system, n is the number of water molecules, and $E_{[M]}$ and $E_{[m]}$ represent the energy of the isolated substrate and a water molecule, respectively. The adsorption energy per water molecule in graphene and gold systems are -0.001 and -0.041 kcal mol^{-1}, respectively. Higher adsorption energy of water molecules on the gold surface can result in a different behavior and less movement of water molecules, which will be discussed further in the following section.

2. *Cluster of water molecules on Au and graphene*

Configuration of water molecules in the interface is dependent upon the configuration of surface atoms and can be analyzed. Such analyses can provide more information regarding the positioning and configuration of water molecules at the interface of gold and graphene. Water molecules can form clusters on the surface. Clusters are comprised of a number of water molecules that form circular structures through the formation of hydrogen bonds. In other words, interfacial water molecules

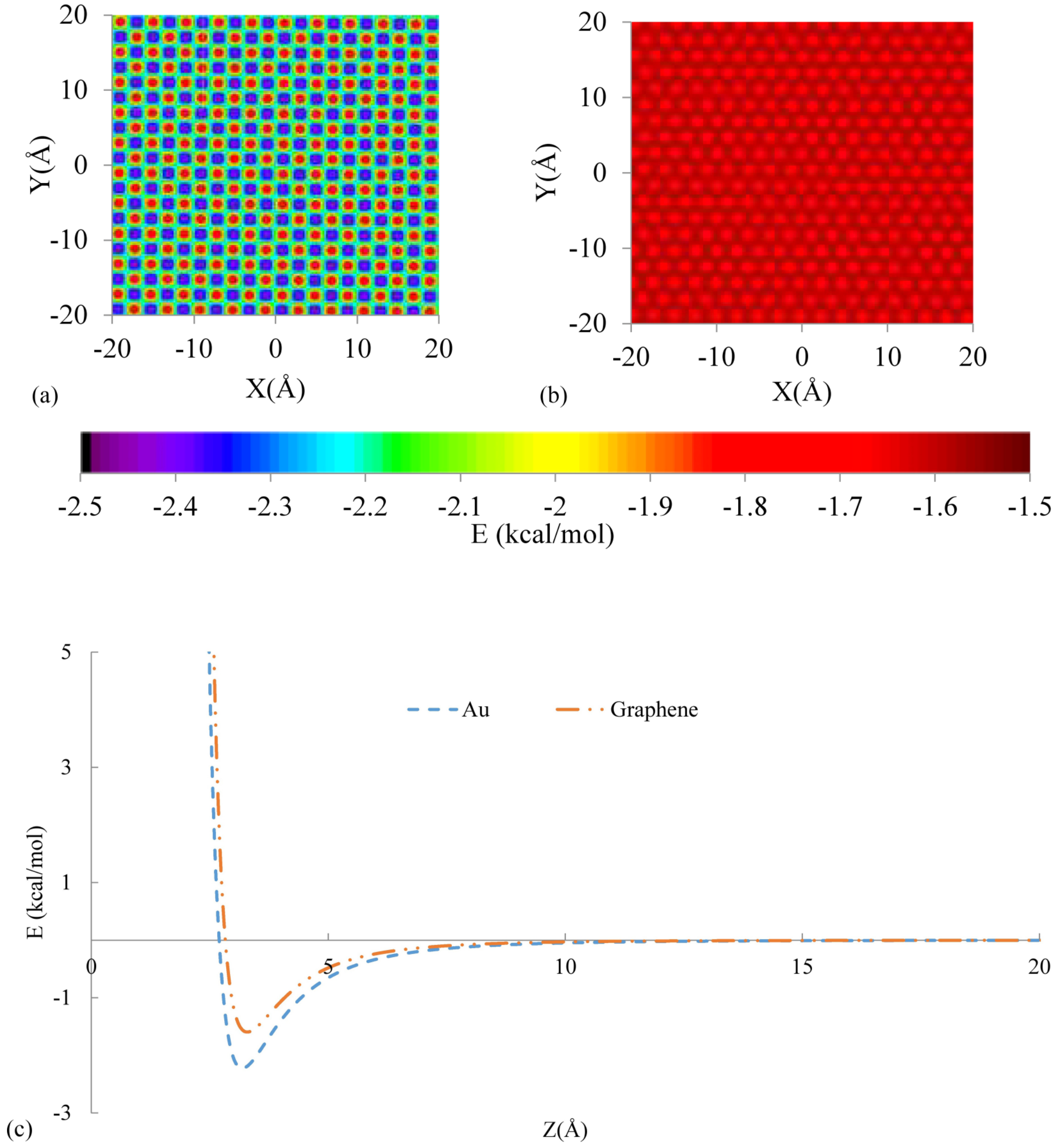

FIG. 3. Comparison of the contour map energy between one water molecule with (a) Au (100), and (b) graphene substrate. (c) Comparison of the interaction energy between a water molecule with Au (100) and graphene substrates along the Z axis.

can form hydrogen bonds which connect the molecules to one another. This is directly affected by the structure and formation of the substrate atoms. Based on this argument it is possible to define angles with different values among neighboring oxygen atoms which will be entitled *triple angles*. Figure 4 shows the triple angles among interfacial water molecules on gold and graphene.

Based on Fig. 4(a), two sharp peaks can be observed at 90° and 180° for interfacial water molecules on the gold surface which indicates squarelike formation for water molecules on this substrate. On the other hand, Fig. 4(b) illustrates a wider peak around 120° in the water-graphene system. This signifies a hexagonal formation for water molecules as the dominant configuration on the graphene substrate. These configurations of water molecules are formed under the influence of the gold and graphene surfaces, respectively. The wide peak in the water-graphene system indicates the contribution from other formations. In other words, the wide range of angles on the graphene surface illustrates how the arrangement of surface atoms has a lower impact on the configuration of interfacial water molecules.

The hexamer arrangement of water is a well-known structure in which all of the six molecules are donors and acceptors of hydrogen bonds [48]. This structure can be formed in both bent and planar arrangements. In the planar configuration each monomer connects to the surface from the same height while in the bent formation two different heights can be observed. In this work the number of molecular clusters of water at the interface of gold and graphene were calculated. Figure 5 shows the frequency distribution of water molecules in tetramer to hexamer clusters in both gold and graphene's interfaces.

In can be seen that the tetramer formation is the dominant arrangement for the water-gold system while no configuration is preferred to another according to Fig. 5(a). This result is in line with the argument presented regarding Fig. 4.

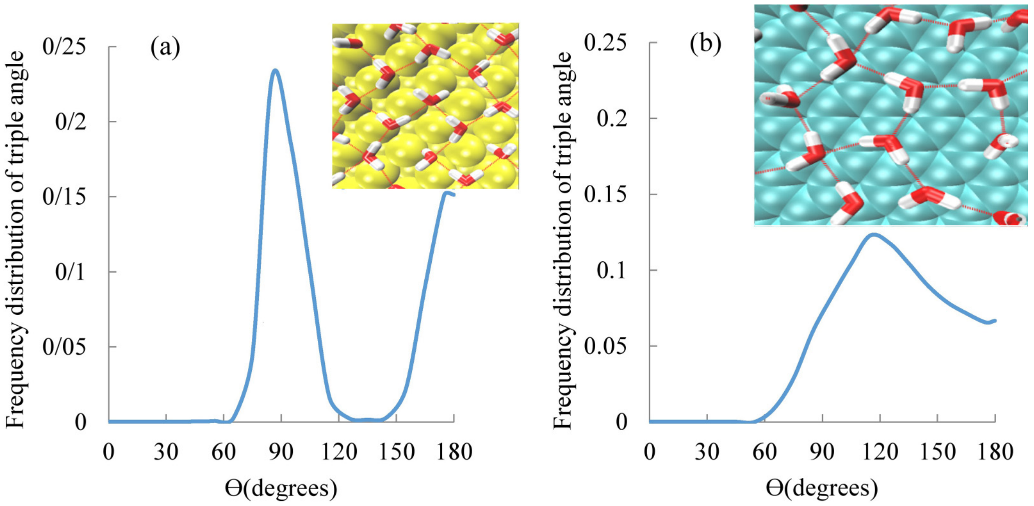

FIG. 4. Distribution of the triple angle between water molecules on the interface of (a) Au (100), and (b) graphene.

The order parameter with respect to the distance from the surface can be used to determine the influence of the substrates on the interfacial water molecules. The order parameter $S\o$ is defined as

$$S_{\o} = \frac{1}{2}\langle 3\cos^2 \o - 1\rangle, \qquad (2)$$

where ø is the angle between the dipole moment vector of water molecules and the normal to the surface. If the dipole moment vector of all water molecules was parallel to the surface, $S\o$ would be equal to -0.5. If the dipole moment vector was perpendicular to the surface, $S\o$ would be equal to 1. However, $S\o = 0$ for a random distribution of water molecules. Figure 6 illustrates the order parameter of water molecules along the direction perpendicular to the substrate, i.e., the Z axis.

Figure 6 shows that the nanodroplet has a trough and a peak at 2.8 and 5.6 Å for water-gold and 3.2 and 6.1 Å for water-graphene systems. It should be noted that these values are in agreement with the acquired data from the density profiles.

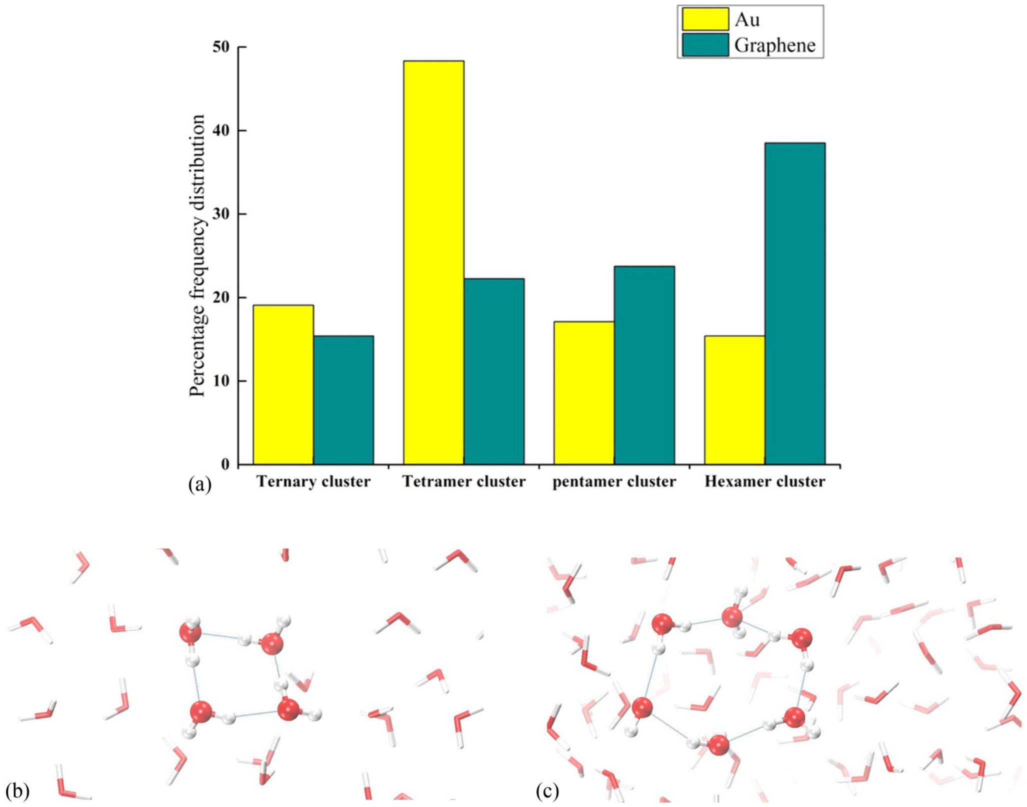

FIG. 5. (a) Frequency distribution of the ternary, tetramer, pentamer, and hexamer clusters at the interface of Au (100) and graphene; (b) Formation of the tetramer cluster at the interface of Au (100), and (c) the formation of the hexamer cluster at the interface of graphene.

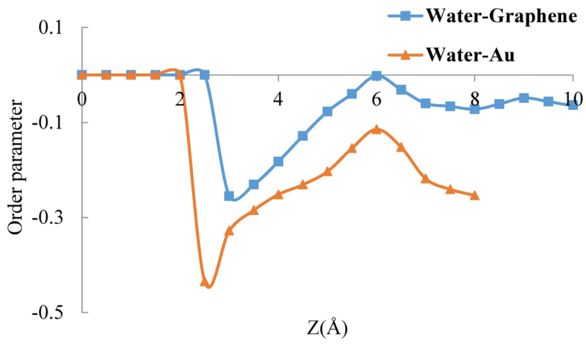

FIG. 6. Order parameter of water molecules along the *Z* axis.

The trough and the peak are a direct result of interface and adjacent regions. It can be observed that the order parameter has a more negative value for the Au surface which indicates a higher order for water molecules at the interface of the gold substrate. The interaction of water molecules residing in the interface and adjacent layers can be divided into intralayer and interlayer interactions. The intralayer interactions among water molecules result in their ordering and reorientation while interlayer interactions can cause disturbances to occur in the original layer. Figure 6 indicates that the interaction between interface and adjacent layers in gold is much weaker than in graphene. Therefore the interface layer in the water-gold system acts more independently of the bulk of the nanodroplet.

3. *Hydrogen bonding of water molecules*

The number of hydrogen bonds among water molecules and their stability can be used to characterize the strength of their interaction with the substrate. The extent to which hydrogen bonds form on gold and graphene surfaces and their order is affected by water-water and water-substrate interactions. Three parameters must be set to calculate the number of hydrogen bonds: (1) The distance between the oxygen of two water molecules *i* and *j* (ROO) must be less than 3.2 Å. (2) The distance between the oxygen of water molecule *j* and hydrogen of water molecule *i* (ROH) must be less than 2.5 Å. (3) The angle between ROO and ROH must remain less than 30°. Figure 7(a) illustrates the number of hydrogen bonds for each water molecule residing in the interface region for the last 500 ps of the simulation. Figures 7(b) and 7(c) show the snapshots of water molecules residing in the interface for the studied systems along with the intermolecular hydrogen bonds.

Figure 7(a) illustrates a higher number of interlayer hydrogen bonds per water molecule in the interface region of gold than graphene, which in turn shows a higher tendency for water molecules residing in the interface region of the water-graphene system to form hydrogen bonds with the upper layers. Figures 7(b) and 7(c) indicate a different hydrogen bonding arrangement for water molecules residing in the interface region of the substrates. Water molecules at the interface of gold are ordered and have a tetramer structure while the arrangement of the water molecules at the interface

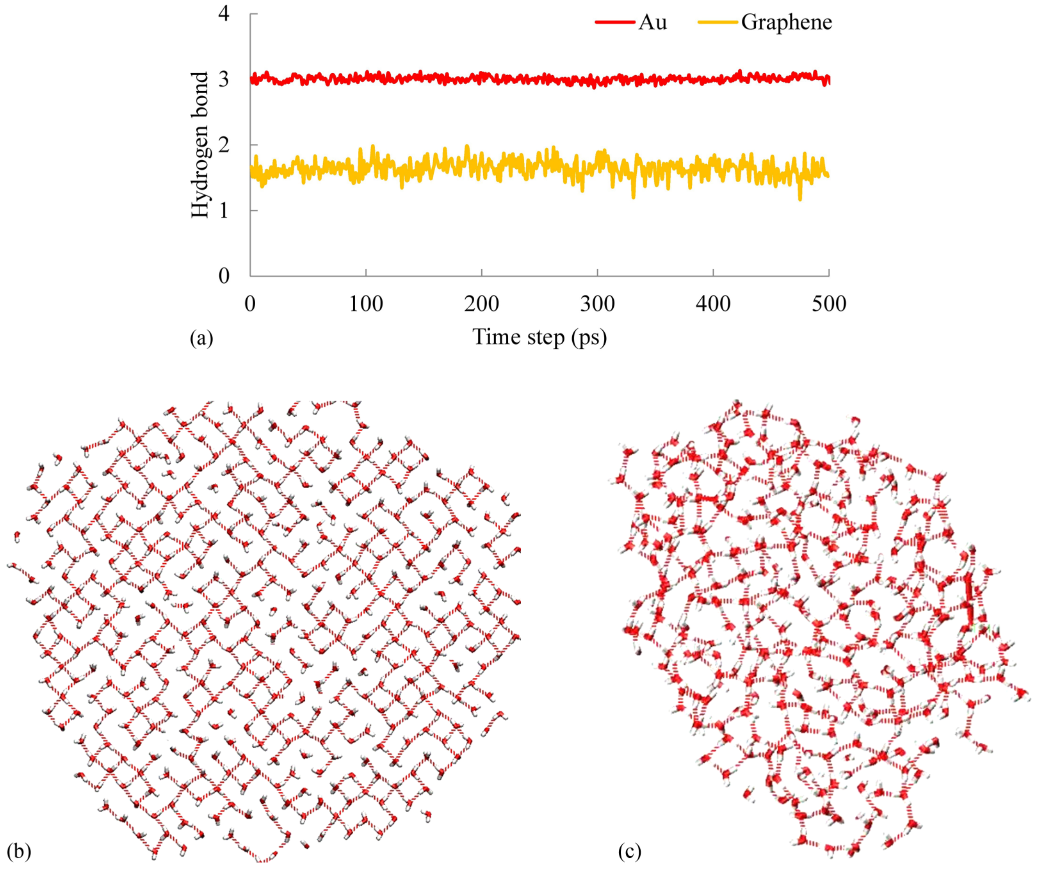

FIG. 7. (a) Number of hydrogen bonding at the interface of Au (100) and graphene in the last 500 ps of the simulation, Snapshots of water molecules at the interface of (b) Au (100), and (c) graphene.

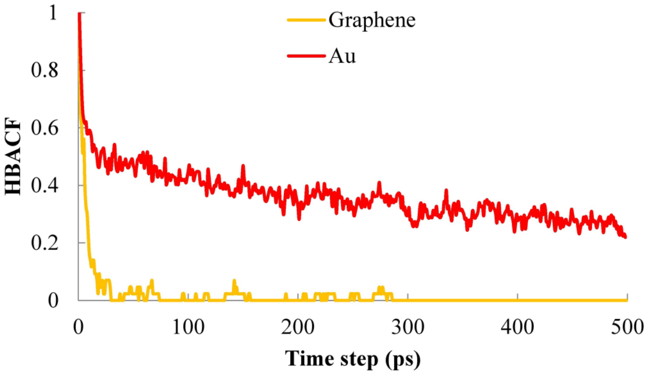

FIG. 8. Stability of hydrogen bonding at interface of Au (100) and graphene.

of graphene are less ordered. It can be observed that the arrangement of hydrogen bonds at the interface of Au is similar to the substrate atoms. However, this arrangement is fairly independent of surface atoms for the graphene substrate. On the gold substrate the water molecules arrange in a planar formation parallel to the surface. Conversely, on the graphene the water molecules arrange in such a way that it is possible for them to form additional bonds to other molecules that are residing in the upper layers. Hence the graphene atoms have a lower effect on the water molecules and the upper layers can directly influence them, which in turn facilitates their movements. Aside from the number of hydrogen bonds per molecule, the lifetime of the hydrogen bonds is also important and can be used to describe the mentioned conclusions. Figure 8 illustrates the stability of hydrogen bonds according to the hydrogen bond autocorrelation function (HBACF) for water molecules at the interface of gold and graphene.

The stability of the hydrogen bonds indicates the longevity of the hydrogen bonds among interfacial water molecules. Based on this premise, the number of hydrogen bonds among interfacial water molecules was estimated, and then the time evolution of the remaining hydrogen bonds was calculated. Based on the comparison of both systems from Fig. 8, it can be observed than for the water-gold system water molecules tend to retain their initial hydrogen bonds while the same diagram for the water-graphene system decreases dramatically, which reveals a low stability for hydrogen bonds among water molecules on the graphene substrate. It can be concluded from the stability and residence time of the hydrogen bonds that the water molecules tend to move much faster on graphene while in the water-gold system there is little tendency toward this much movement.

B. Dynamical behavior of water nanodroplet on the surface

The subject of the movement of a nanodroplet and its manipulation is of great interest. The movement of the nanodroplet can be used in characterization of many properties of the droplet. If the drop rests on top of the surface structure, the substrate can be denoted hydrophobic and if the drop surrounds the structure, it can be denoted hydrophilic [49]. In the former case the droplet can attach to the surface more intensely and retain a high contact angle while in the latter the droplet has a low contact angle which increases its movement. These properties have special applications in surface science [50]. Following the observed differences between graphene and gold in the previous sections dynamical properties of water molecules near the substrate will be discussed further.

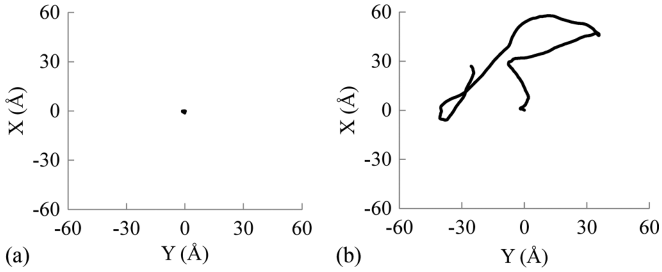

FIG. 9. Variations of center of mass of water molecules on (a) gold, and (b) graphene surfaces.

1. Analysis of the center of mass of a water nanodroplet

The spontaneous movement of a water nanodroplet on such surfaces as graphene and the possibility of its manipulation using electric field has been reported [51]. Ma and co-workers have shown that for a water droplet with less than 1000 molecules, fast diffusion can be observed which will exponentially increase as the number of water molecules is reduced even further [52]. Therefore information regarding the movement of nanodroplets can be acquired by studying the cause of droplet motion and stillness on different substrates and its effect on dynamical properties of the nanodroplet. Figures 9(a) and 9(b) show the variation of center of mass for water molecules on gold and graphene surfaces, respectively.

Figure 9 indicates that the water nanodroplet moves on the graphene surface while on the gold substrate it stands still. The pinning of water on the gold surface and the movement of water on graphene can illustrate different aspects of their properties.

2. Analysis of mean-squared displacement of a water nanodroplet

Strong interaction of atoms usually results in less movement. A mean-squared displacement (MSD) diagram can present valuable information regarding the movement of interfacial water molecules. Figure 10 shows the variation of MSD with respect to time of the simulation for oxygen and hydrogen atoms of water molecules which are residing in the interface of gold and graphene. Additionally, MSD of interfacial water molecules is compared with the adjacent layer for both systems.

Figures 10(a) and 10(b) show that the value of MSD and its fluctuations for hydrogen and oxygen, in the water-graphene system, is larger than in the water-gold system. This indicates a stronger interaction between water and the gold substrate which results in less movement of the interfacial water molecules; see Fig. 2. The same figures also reveal that the MSD value of oxygen is much less than the MSD value of hydrogen atoms, while no such difference is observed for the water-graphene system. The reason behind this difference is the strong interaction of oxygen atoms with the gold surface which results in a decrease of MSD value. Furthermore, the MSD value of hydrogen also decreases since the oxygen and

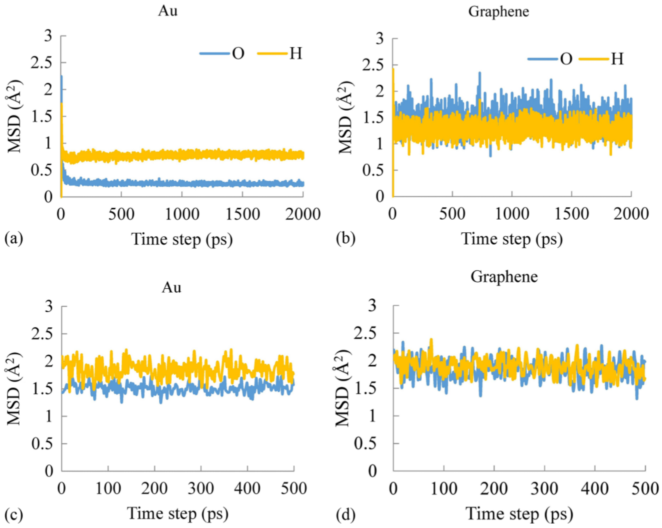

FIG. 10. Variation of MSD of hydrogen and oxygen atoms of water molecules at the interface of (a) Au (100) and (b) graphene. Variation of MSD of water molecules at the interface (blue) and adjacent layer (orange) of (c) Au (100) and (d) graphene systems.

hydrogen atoms are bonded together. Figures 10(c) and 10(d) illustrate the comparison of the MSD value of water molecules in the interface region with the adjacent layer. It can be observed that the MSD of the interface is considerably lower than the adjacent layer in the water-gold system, while both MSDs present similar values for the water-graphene system. This observation indicates that the interface and adjacent layers act more independently in the water-gold system than in the water-graphene system. Another major conclusion is the cause of the decrease in the movement in the water-gold system which can be attributed to the decrease in the motion of the interface layer. A comparison of Figs. 10(c) and 10(d) reveals that the MSD value for water molecules in the adjacent layer on both graphene and gold is almost similar while the MSD value of the interface is different. The MSD data can also be explained with the above-mentioned results with which they actually are in good agreement. The strong interaction of water molecules with the substrate for the water-gold system was discussed in the prior sections. It can be observed that the oxygen atoms of the interfacial water molecules do not move easily on the gold surface. Hence the water nanodroplet moves around the small region about which the oxygen atoms move. This is the main reason behind the stillness of the water nanodroplet on the gold surface.

3. *Residence time of water molecules at the interface*

Important information regarding the interaction of interfacial water molecules with the substrate and upper layers can be acquired from the calculation of the residence time of interfacial water molecules. Here, residence time is the estimation of the fraction of a time interval that water molecules spend in the interface layer. Stronger interaction between the water molecules and the substrate increases the residence time while stronger interaction with the upper layers of water molecules reduces this time. Figure 11 illustrates the residence time of water molecules in the interface of both graphene and gold substrates.

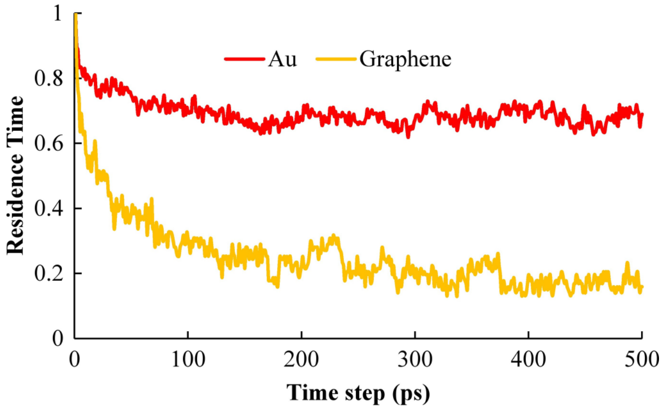

FIG. 11. Residence time of water molecules at the interface of Au (100) and graphene.

The diagrams presented in Fig. 11 show that water molecules residing in the interface of gold tend to stay in this layer and not move to upper layers while the decrease in time evolution of the residence time of water molecules in the interface reveals the replacement of these molecules with other water molecules from the upper layers. The reason behind the difference in the residence time diagrams for the studied surfaces is that stronger interaction occurs among water molecules of the interface and adjacent layers while a weaker interaction occurs between the substrate and interfacial molecules that reside closer to the substrate.

IV. CONCLUSION

In this work the structural and dynamical behaviors of water on gold and graphene surfaces were studied to reveal the effect of chemical and geometrical properties of the surfaces. Based on the calculated density profiles for water on both surfaces, interface and adjacent regions were defined and further analyses on these regions were presented. The acquired results from the contour map and adsorption energy of water on both surfaces point to a more uniform interaction on graphene and stronger adsorption of water on gold. These results are in agreement with the obtained data from the movement of water on graphene and the stillness of the nanodroplet on gold. Therefore the movement of water on the surface can be controlled based on the relation between the surface properties and the motion of the water.

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M.D. and S.M.F. contributed equally to this paper.

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