Comparison between microscopic structures of surficial water on hexagonal boron nitride and graphene

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Microscopic structures of surficial water on atomically flat surfaces were theoretically investigated using a classical molecular dynamics simulation. Polar hexagonal boron nitride (h-BN) and non-polar graphene surfaces were employed, which have the same hexagonal atomic configuration but different interaction with water molecules. The stability of various water clusters present in surficial water was determined to be independent of the polarity of the h-BN and graphene surfaces. In addition, water present in the region more than 0.7 nm from the surface had a similar microscopic structure to free water.

The microscopic structure of surficial water is a key factor to determine various physical properties of material surfaces, such as wettability and friction. Water molecules in liquid bulk water interact strongly with each other via hydrogen bonding and they form a complex hydrogen bonding network that determines the various unique characteristics of water. In contrast, water molecules in surficial water interact with the material surface in addition to intermolecular interaction; therefore, they exhibit different hydrogen bonding network structures from that of the bulk water.

We have previously reported the microscopic structure of surficial water on graphene. Graphene is a fundamental surface to investigate surficial water because it is a non-polarized and atomically flat material. However, the structure of surficial water on other materials has not yet been clarified. Here, classical molecular dynamics (MD) simulations were used to investigate the structure of surficial water on hexagonal boron nitride (h-BN) sheet, which is an atomically flat material with a hexagonal network similar to graphene, but is polarized. One goal of the present study is to determine whether the hydrogen bonding network of water molecules on h-BN sheet is different from that on graphene and dependent on the polarity.

h-BN can also form nanotube-like structures (h-BN nanotubes) that consist of rolled up h-BN sheet. The interaction between h-BN sheet/ nanotubes and liquid water has been researched using classical MD and ab initio simulations. These studies have clarified the layered structure and adsorption site of surficial water on h-BN sheet/ nanotubes; however, the hydrogen bonding network of surficial water has not yet been elucidated.

Density functional theory simulations were first conducted to estimate the atomic charges of boron and nitrogen atoms in h-BN sheet. A bilayer h-BN sheet with the AB (Bernal) stacking structure was prepared with 116 boron and 116 nitrogen atoms [Fig. 1(a)]. The electrostatic potential was calculated using Dmol3 in the Materials Studio 8.0 package with Zhao and Truhlar’s Minnesota 2006 local functional, and a numerical triple zeta plus polarization basis set (M06L/TPN).

Classical MD simulations were then conducted for 60, 100, 160, and 427 H₂O molecules on the bilayer h-BN sheet and on bilayered graphene with the AB (Bernal) stacking structure. The rectangular simulation boxes were 2.13 × 2.21 × 7.00 nm with periodic boundary conditions along the three axes [Fig. 1(b)]. The classical equation of atomic motion was numerically solved using the velocity Verlet algorithm with a time step of 1.0 fs. The classical MD simulations were conducted using MS Forcite Plus in Materials Studio 8.0, with COMPASS II (Condensed Phase Optimized Molecular Potentials for Atomic Simulation Studies). The MD temperature were set to 250 K with a Nosé thermostat, where the water diffusion coefficient in these MD simulations with COMPASS II corresponds to the experimental value obtained at 300 K. Long-range Coulomb interactions were calculated using the Ewald method. The atomic charges were set to −1.23 eC for boron (h-BN), 1.23 eC for nitrogen (h-BN), −0.41 eC for hydrogen (H₂O), and 0.82 eC for oxygen (H₂O). The substrates were fixed during all simulations. The carbon atoms in graphene were set to have no charge. The main calculation for each simulation model was conducted for 20 ns after 0.5 ns equilibration.

Figure 2 shows the density distributions of water along the axis perpendicular to the substrates (z axis). The origin of the...
The z axis is taken to be the surfaces of h-BN and graphene. For the box with 60 H$_2$O molecules, a single-layered water structure is formed on both h-BN and graphene substrates [Fig. 2(a)]. With increasing water molecules in the simulation box, the density distribution of water varies to a double-layered structure [Fig. 2(b)] and a triple-layered structure [Fig. 2(c)]. The single-layered, double-layered, and triple-layered models are denoted 1L, 2L, and 3L models, respectively. The box with 427 H$_2$O molecules has a region in which the density of water is ca. 1.0 g cm$^{-3}$ above the third layer of water [Fig. 2(d)]. This model is named the bulk model. Here, we define the water molecules located from the surfaces ($z = 0$) to 0.5 nm as the first layer, those from 0.5 to 0.7 nm from the surface as the second layer, and those from 0.7 to 1.2 nm as the third layer.

This layered structure of water molecules on h-BN is in good agreement with the previous simulation studies.$^7,^{10}$ The triple-layered structure has been reported in both ab initio and classical MD simulations, and the peak position of each layer were around 0.3 nm from the h-BN surface in the previous studies as well as in this paper.

In any of the models, the peak positions of water density on a h-BN sheet are very similar to that on graphene, which indicates that the equilibrium distances between water and the substrate for the h-BN and graphene surfaces are equal. On the other hand, the height of the density peak for h-BN sheet is slightly higher than that for graphene, e.g. the densities of the first water layer is 3.6 g cm$^{-3}$ (h-BN) and 3.2 g cm$^{-3}$ (graphene), and those of the second water layer are 1.5 g cm$^{-3}$ (h-BN) and 1.4 g cm$^{-3}$ (graphene) in the bulk model. The interaction of water molecules with the h-BN surface is slightly stronger than that with the graphene surface. The differences in the distributions are mainly due to a difference of van der Waals interaction because the electric field is almost zero at the first water layer due to cancellation of the electric field by the neighboring B with negative charge and N with positive charge.

Figure 3 shows the orientation distribution of OH bonds in water molecules. The cosine ($\cos \theta$) values represent the angle between the normal vector from the surface and the OH vector from the oxygen atom to the hydrogen atom in the water molecules. When $\cos \theta$ is equal to zero, the OH bonds are oriented parallel to the surface. The right side of Fig. 3 shows the orientations of a H$_2$O molecule for $\cos \theta = \pm 1$.

In the 1L models with h-BN and graphene substrates, most OH bonds at the first layer are oriented parallel ($\cos \theta = 0$) to the surface [Fig. 3(a)]. The OH bonds of water molecules on h-BN are oriented more parallel than those on graphene because...
the water density at the first layer on h-BN is slightly higher than that on graphene. In the 2L, 3L and bulk models with h-BN and graphene substrates [Figs. 3(b)–3(d)], the OH bonds oriented backward to the surface (H-up) increase at the first layer, and the OH bonds oriented toward the surface (H-down) increase at the second layer, compared to the 1L model. The water molecules with H-up OH bonds at the first layer interact with water molecules at the second layer, and the water molecules with H-down OH bonds at the second layer interact with water molecules at the first layer via hydrogen bonds. Water molecules on both h-BN and graphene substrates make an intra-layer hydrogen bonding network in the 1L model, and an extra-layer hydrogen bonding network is additionally formed in the other models. There are little differences in the OH bond orientations between the h-BN and graphene substrates.

A few water molecules make a two-dimensional cluster structure via hydrogen bonding e.g. trimers, tetramers, pentamers, and hexamers.24–26] Fig. 4(a) shows the areal density of two-dimensional water clusters at the first layer on the h-BN and graphene substrates. The conditions of the hydrogen bonds are that the O–O distance between two water molecules should be less than 3.60 Å, the O–H distance should be less than 2.45 Å, and the H–O⋯⋯O angle should be less than 30°.27] In the 1L model, the number of tetramers is larger than the number of other clusters. The water molecules in the 1L model interact via intra-layer hydrogen bonds. The tetramer is the most effective cluster to completely cover the surface because all OH bonds can involve hydrogen bonds. When water molecules are closely packed in the layered structure, several OH bonds of pentamers and hexamers must orient H-up or H-down.

In the 2L, 3L and bulk models, the number of tetramers and pentamers are approximately equal. The next highest number is hexamers. If there are additional layers above the first water layer, then the water molecules can interact with the additional layers via hydrogen bonds. Thus, the tetramers and hexamers are stable for the 2L, 3L and bulk models. This hypothesis is supported by the orientations of the OH bonds (Fig. 3). The number of OH bonds with H-up is high at the first layer, and that with H-down is high at the second layer for the 2L, 3L and bulk models.

As long as the same model is compared, the clusters on h-BN are denser than those on graphene for all models. This is because the water density at the first layer on h-BN is higher than that on graphene. However, the compositional ratios of water clusters are very similar between h-BN and graphene substrates [Fig. 4(b)] in the same model. In the bulk models, the occupation ratios on h-BN are 5.4% (trimer),
32.2% (tetramer), 31.2% (pentamer), 16.1% (hexamer), 8.6% (heptamer), and 6.5% (octamer), whereas those on graphene are 6.1% (trimer), 33.0% (tetramer), 30.5% (pentamer), 15.9% (hexamer), 8.5% (heptamer), and 6.1% (octamer). The difference is less than 1.0% for any of the clusters. Thus, when the structure of surfaces are atomically flat, the van der Waals interactions between substrates and water molecules do not have a large effect on the compositional ratios of clusters.

Figure 5 shows the tetrahedral orders of surficial water on h-BN and graphene. The tetrahedral order $q$ is given by the following function:

$$q_i = 1 - \frac{3}{8} \sum_{j=1}^{3} \sum_{k=j+1}^{4} \left( \cos \phi_{jk} + \frac{1}{3} \right)^2,$$

where $\phi_{jk}$ is the angle formed between the central oxygen atom $i$, and the two neighboring oxygen atoms, $j$ and $k$. The order $q$ is the summations of six formable angles with four neighboring oxygen atoms. In this definition, the order $q$ ranges from $-3$ to $1$, and $q=1$ represents a perfect tetrahedral structure because $\cos \phi_{jk} = -1/3$ for a perfect tetrahedron. Liquid water with a high-$q$ value indicates an ice-like structure.

Figures 5(a) and 5(b) show the tetrahedral order of the water oxygen at the first water layer on h-BN and graphene substrates, respectively. For comparison, the tetrahedral order of free water was calculated using the same MD system with 256 H$_2$O molecules in a periodic cubic simulation box. The most frequent order is 0.75 in the 1L model, while it is 0.85 in the other models. The number of water molecules with a low $q$ value ($0.4 < q < 0.6$) in the 1L model is greater than that in the other models. In the 1L model, the water molecules arrange as a single layer; therefore, a tetrahedral structure cannot be formed. When additional water molecules adsorb on the first water layer, the water molecules can form tetrahedral structures. The $q$ distributions in the 2L, 3L, and bulk models are similar to that in free water; however, the peak heights in their models are lower than the peak height of free water. In addition, the peak height in the 2L model is lower than that in the 3L and bulk models. Therefore, if there are more than three water layers on the substrate, the water molecules partially form ice-like structures, even at the first layer, provided that the number of tetrahedral structures at the first water layer is smaller than that in free water. In any models, there is little difference in the tetrahedral order between water on h-BN and water on graphene.

Figures 5(c) and 5(d) show the tetrahedral orders at the second water layer on h-BN and graphene substrates. The $q$ distributions at the second layer are very similar to that for free water. In the second layer, the distribution at a low $q$ value ($0.4 < q < 0.6$) decreases, and the peak height at $q=0.85$ increases compared with the first layer. The similarity of the tetrahedral order between water at the second layer and free water results in three-dimensional water structures making a transition from surficial water to free water at 0.7 nm from the ideal flat surface.

The surficial water structures on h-BN and graphene substrates were investigated using classical MD simulations. More water molecules adsorb on h-BN than on graphene, which reflects the differences in wettability. A high density of water molecules at the first water layer on h-BN results in an increase of two-dimensional water clusters. On the other hand, the orientations of OH bonds and compositional ratio...
of water clusters on h-BN are very similar to those on graphene. The tetrahedral order on h-BN is also consistent with that on graphene.

We also executed the same procedures for a single-layered h-BN sheet and single-layered graphene substrate to evaluate the validity of the results obtained from the simulations for double-layered h-BN and graphene. The similarities and differences are in good agreement with the conclusions of this paper. Therefore, it was concluded that the stability of various water clusters present in surficial water is independent of the polarity of h-BN and graphene substrates with atomically flat surfaces. However, the water structure when water molecules specifically interact to an adsorption site on the surface has not yet been clarified. In future work, we will investigate the structure of surficial water on a polar non-flat surface.

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