

Formation of Water Layers on Graphene Surfaces

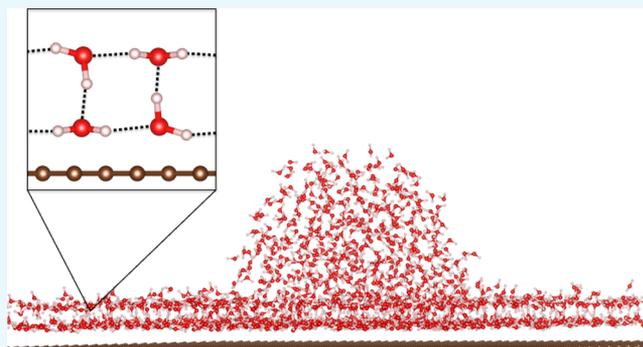
Akira Akaishi^{*,†,‡} Tomohiro Yonemaru^{*,†,‡} and Jun Nakamura^{*,†,‡}

[†]Department of Engineering Science, The University of Electro-Communications (UEC-Tokyo), 1-5-1 Chofugaoka, Chofu, Tokyo 182-8585, Japan

[‡]CREST, Japan Science and Technology Agency, 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan

S Supporting Information

ABSTRACT: Although graphitic materials were thought to be hydrophobic, recent experimental results based on contact angle measurements show that the hydrophobicity of graphitic surfaces stems from airborne contamination of hydrocarbons. This leads us to question whether a pristine graphitic surface is indeed hydrophobic. To investigate the water wettability of graphitic surfaces, we use molecular dynamics simulations of water molecules on the surface of a single graphene layer at room temperature. The results indicate that a water droplet spreads over the entire surface and that a double-layer structure of water molecules forms on the surface, which means that wetting of graphitic surfaces is possible, but only by two layers of water molecules. No further water layers can cohere to the double-layer structure, but the formation of three-dimensional clusters of liquid water is confirmed. The surface of the double-layer structure acts as a hydrophobic surface. Such peculiar behavior of water molecules can be reasonably explained by the formation of hydrogen bonds: The hydrogen bonds of the interfacial water molecules form between the first two layers and also within each layer. This hydrogen-bond network is confined within the double layer, which means that no “dangling hydrogen bonds” appear on the surface of the double-layer structure. This formation of hydrogen bonds stabilizes the double-layer structure and makes its surface hydrophobic. Thus, the numerical simulations indicate that a graphene surface is perfectly wettable on the atomic scale and becomes hydrophobic once it is covered by this double layer of water molecules.



Developing a microscopic understanding of the wettability of pristine graphene is greatly advanced by numerical simulations. Water droplets on graphene surfaces have been studied for over a decade by molecular dynamics (MD) simulations.^{17,18} The water contact angle can be calculated using the Young equation in terms of surface tension.^{19–21} The water contact angle strongly depends on the interaction between graphene and a water molecule. In fact, the interaction strength qualitatively affects the wettability of graphene in simulations.^{22,23} Vast theoretical works have focused on precisely determining the interaction parameters between graphene and a water molecule.^{16,24–26} The recent study by Wu and Aluru provided the interaction parameters for the Lennard-Jones potential on the basis of first-principles calculations.¹⁶ Using these parameters, they found that the water contact angle on a pristine graphene surface is approximately 36.4°, which is less than the previously reported values and increases with the increasing density of contaminating hydrocarbons on the graphene surface.¹⁶ Although these numerical studies have revealed the wettability of pristine graphene, there still exists huge discrepancy in the droplet size between experiments and

INTRODUCTION

After the discovery of exfoliated graphene,¹ significant attention has been focused on next-generation graphene-based materials because of graphene's exceptional electronic and thermal properties.^{2,3} These materials are expected to lead to several applications, such as semiconducting devices,^{1,4} and thermoelectric devices.^{2,3,5} To develop practical applications, understanding the adhesion between these materials and water in ambient air is vital. Over the past decades, graphene was thought to be hydrophobic;⁶ however, recent experimental results have called into question the wettability of graphene. The experimentally observed hydrophobicity of graphitic surfaces are partly due to airborne contamination on the surface.^{7–15} Spectroscopic measurements, for example, indicate that the hydrophobicity is due to adherent hydrocarbons.¹² Numerical simulations also indicate that the presence of hydrocarbons enhances the surface hydrophobicity of graphene.¹⁶ Thus, the simple question arises as to whether graphene surfaces are inherently hydrophilic or hydrophobic.

The hydrophobicity or hydrophilicity of a surface is often associated with the wettability of the surface. The water wettability is experimentally evaluated by measuring the contact angle.⁶ The contact angle and thus the wettability depend significantly on the strength of the interactions between water and the surface. What is the wettability of pristine graphene?

Received: March 28, 2017
Accepted: May 10, 2017
Published: May 18, 2017

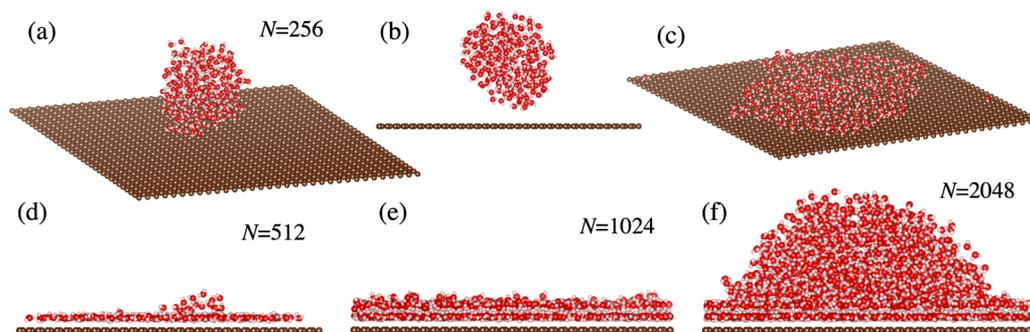


Figure 1. Snapshots of MD simulations of a water droplet falling onto a (32×32) graphene supercell surface. (a, b) Water droplet is positioned above the graphene surface and (c) is adsorbed and spreads out over the surface. (d–f) As the number of water molecules increases, a layered structure appears.

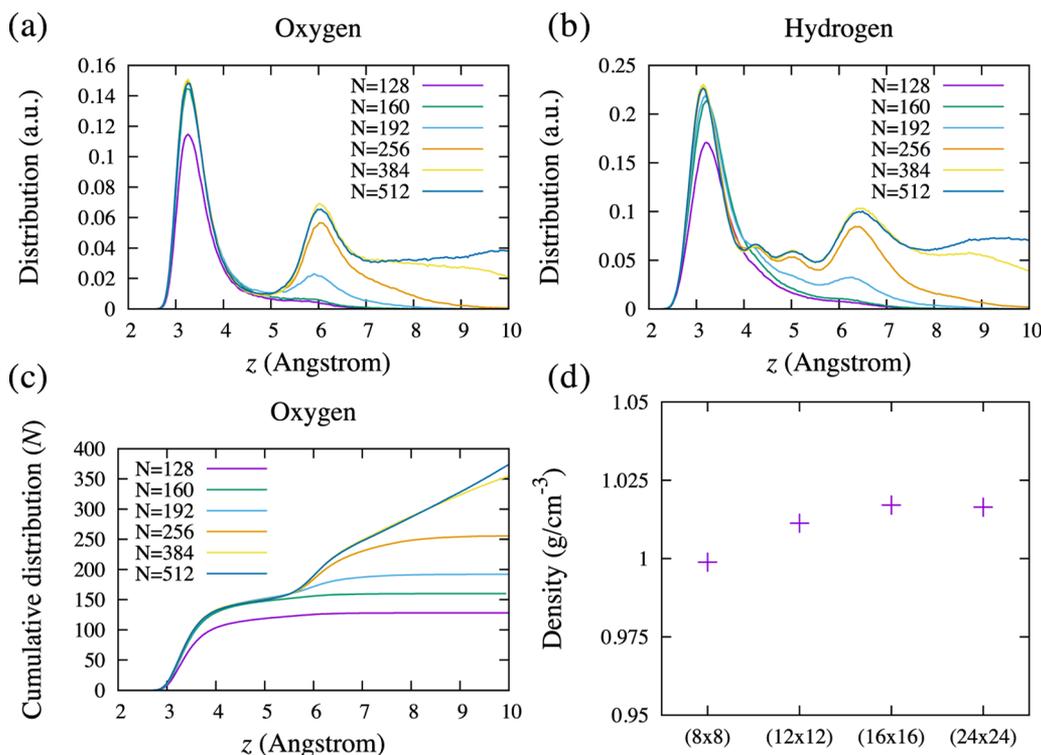


Figure 2. Density distribution functions of the (a) oxygen and (b) hydrogen atoms as a function of distance from the graphene surface. (c) Cumulative distributions of oxygen atoms. (d) Density of the first water layer for several sizes of graphene supercells.

simulations. This dilemma prevents us from understanding the graphene wettability from a macroscopic point of view.

To understand the wettability of graphene, the atomic-scale behavior of interfacial water molecules on the surface must be studied. Water molecules have been confirmed to form layered structures on a graphene surface,^{27–37} and such structures are also confirmed to be formed on the surface of carbon nanotubes.³⁸ The formation of an icelike water monolayer is also studied on metal surfaces and is reported to affect the hydrophobicity/hydrophilicity of the surfaces.^{39–42} In addition, two-dimensionally confined water layers are reported to form a regular structure in the interfacial layer between graphene and mica⁴³ and between graphene layers.⁴⁴ The existence of the interfacial water layer on the metal oxide surface is also reported using the first-principles calculations.⁴⁵ A similar double-layer structure in confined geometry of hydrophobic surfaces is also reported.^{46–48} Although the formation of the interfacial water layers is reported on top of several hydro-

phobic surfaces, the relationship between the layer formation and the wettability has not been discussed so far.

Here, we show that our simulations suggest that a double layer of water molecules forms on the graphene surface and plays a critical role in the wettability of graphene. To investigate the behavior of water in surface-constrained systems, we focus on the formation of hydrogen bonds. By examining hydrogen-bond formation, we clarify the formation mechanism of the double-layer structure. Moreover, we examine how the microscopic layered structure of water molecules affects macroscopic hydrophobic/hydrophilic properties. The results of examining the wettability of graphene surfaces from a microscopic standpoint suggest a new paradigm in the wettability of graphene.

RESULTS AND DISCUSSION

Formation of Layered Structures. A water cluster was dropped onto a graphene surface. Figure 1 shows the snapshots

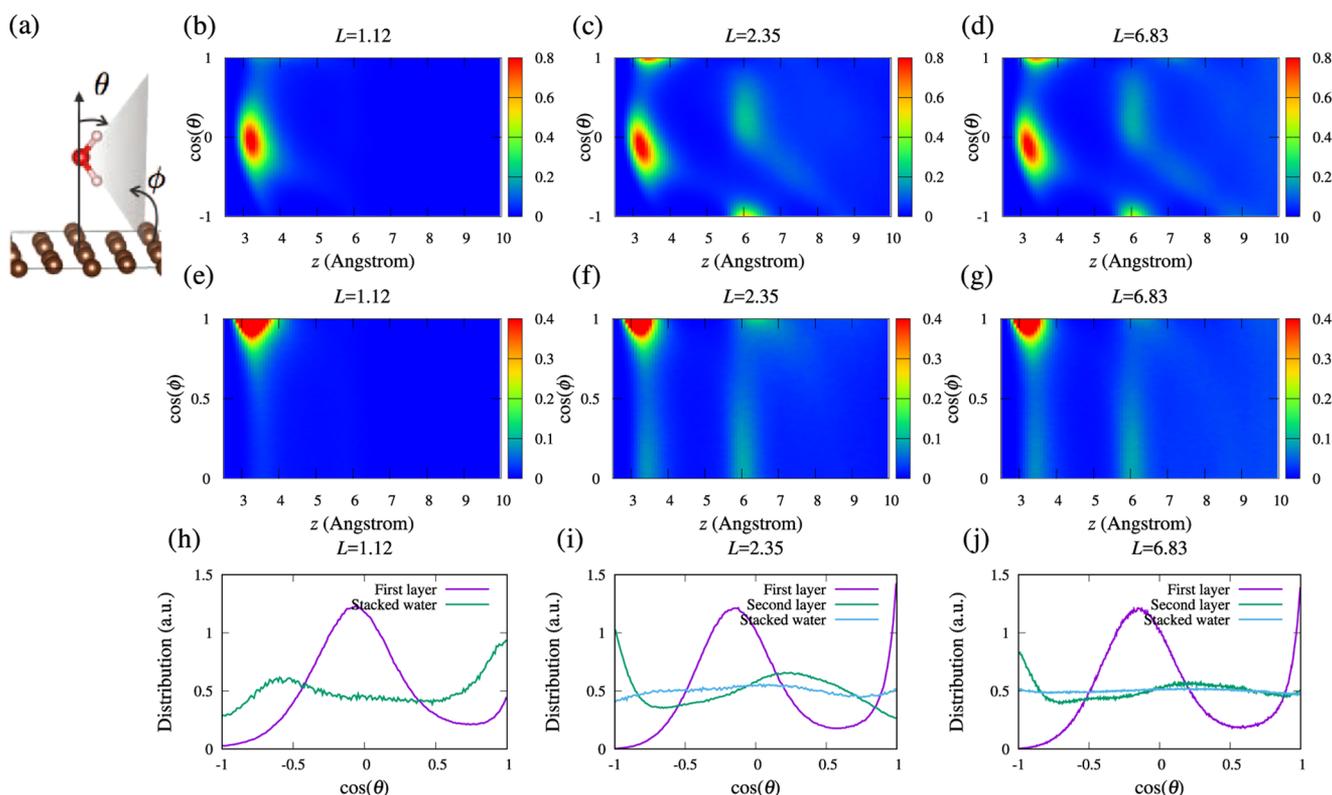


Figure 3. (a) Schematic view showing the angle of the O–H bond and the angle of the H–O–H plane. (b–d) Probability distributions of $\cos \theta$ for $L = 1.12, 2.35$, and 6.83 with respect to the distance from the graphene surface and (e–g) those of $\cos \phi$. (h–j) Distribution of $\cos \theta$ for water molecules for each layer position: Distributions are calculated for $0 \text{ \AA} \leq z < 5 \text{ \AA}$ for the first layer, $5 \text{ \AA} \leq z < 8 \text{ \AA}$ for the second layer, and $8 \text{ \AA} \leq z$ for the water cluster stacked on the double-layer structure.

of the simulation with the boundary conditions of the (32×32) graphene supercell. In Figure 1, N denotes the number of water molecules. As the simulation time progresses, a small water cluster spreads and forms a two-dimensional island structure [see Figure 1c]. For larger water droplets, the graphene surface becomes fully covered by water molecules. At the level of simulations, these numerical observations indicate that the graphene surface can be wetted, which means that the surface is hydrophilic on the atomic scale. Upon increasing the number of molecules, it was confirmed that water molecules formed a double-layer structure on the surface [Figure 1e]. Above the double layer, the water molecules form no specific arrangements other than three-dimensional lump structures [Figure 1f].

To examine how water molecules behave on a graphene surface, we have investigated the spatial probability distribution of water molecules on the surface. Figure 2 shows the distribution functions of the density of oxygen and hydrogen atoms of water as a function of distance z from the graphene surface. For the oxygen atoms, the density distribution shows two peaks at $z = 3.4$ and 6.1 \AA , as shown in Figure 2a. The appearance of these two peaks for the oxygen distribution indicates that the water molecules form a layered structure on the graphene surface. For the distribution of the hydrogen atoms [Figure 2b], four peaks appear for $N \geq 384$. Two peaks appear, that is, one at $z = 3.2 \text{ \AA}$ and one at $z = 6.5 \text{ \AA}$, near the peak positions of the oxygen distribution. In addition, two rather small peaks appear at $z = 4.3$ and 5.1 \AA , which are located between the first two layers. These characteristic peak distributions of the oxygen and hydrogen atoms are maintained even as the number of water molecules increases, meaning that

the double-layer structure of water remains unchanged at the graphene/water interface. No clear peaks are found for $z > 9 \text{ \AA}$. The appearance of the peaked distribution of hydrogen atoms suggests that the direction of the O–H bonds in the first two layers is highly oriented.

We investigate the water molecules involved in the first layer by the cumulative distribution function with respect to distance z , as shown in Figure 2c. From the value of the cumulative distributions at the point between the first and second layers, the number, N_{layer} , of water molecules in the first layer is estimated to be about 150 for the periodic boundary conditions of the (16×16) graphene supercell. The density of the first layer is evaluated to be 1.015 g/cm^3 , which remains quantitatively unchanged irrespective of the size of the unit cell in the simulations [see Figure 2d]. In what follows, instead of the number of molecules, N , we define the number of layers to be $L = N/N_{\text{layer}}$.

Orientation Analyses. To examine the bond orientation in the double layer, we have analyzed the direction of O–H bonds and the orientation of the H–O–H plane of the water molecules. Figure 3 shows the distributions of the angle θ , representing the direction of O–H bonds with respect to the normal to the graphene surface, and the distributions of the angle ϕ between the H–O–H plane and the graphene plane. Both distributions are plotted as a function of z (distance from the graphene surface). For $L \approx 1$, where only a single layer forms, a peak appears at $\cos \theta = 0$ for the O–H bond distribution and at $\cos \phi = 1$ for the H–O–H plane distribution [see Figure 3b,e, respectively]. This indicates that the O–H bonds are parallel to the graphene surface.^a Such specific orientations of water molecules in the first layer are also

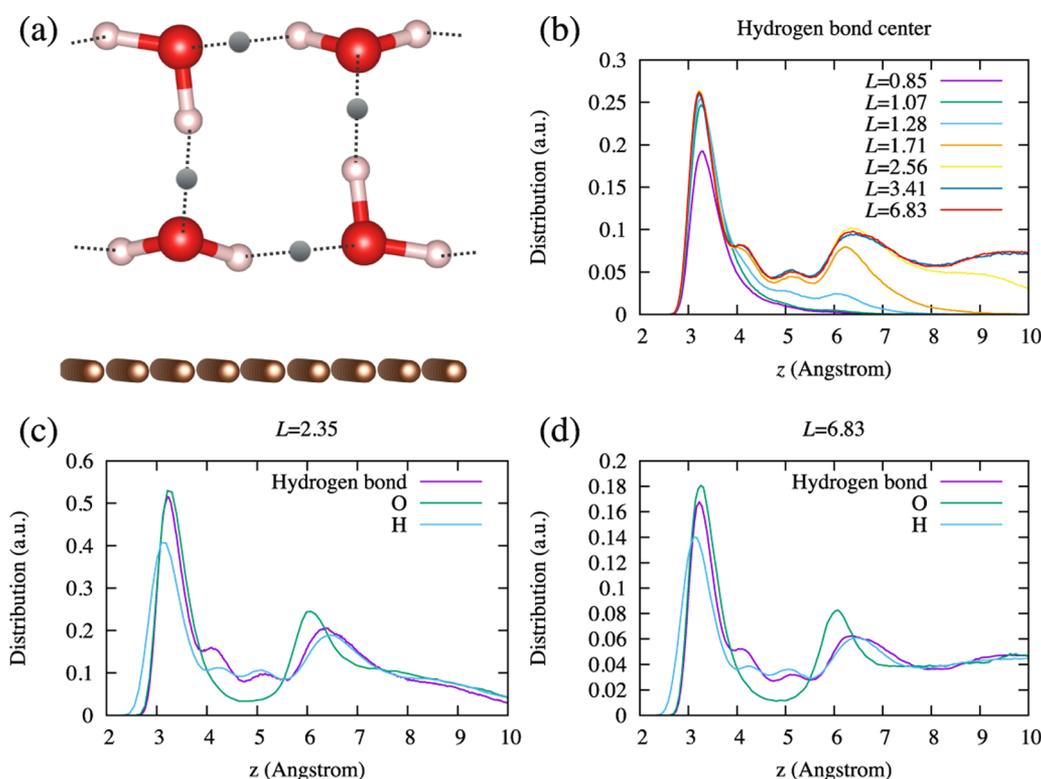


Figure 4. (a) Schematic view of the layered structure on the graphene surface. The red, white, and brown balls indicate oxygen, hydrogen, and carbon atoms, respectively. The black dotted lines indicate hydrogen bonds and the gray balls indicate the center of the given hydrogen bond. (b) Probability distribution of the hydrogen bond centers as a function of z . (c, d) Distribution of the hydrogen bond centers, oxygen atoms, and hydrogen atoms for $L = 2.2$ and 6.4 .

confirmed even for a greater number of layers. For the O–H angle distributions for $L \approx 2$, a new peak at $\cos \theta = 1$ appears at the position of the first layer ($z \approx 3 \text{ \AA}$), in addition to the peak at $\cos \theta = 0$ [see Figure 3c,i]. This means that the O–H bonds in the first layer are primarily oriented either normal or parallel to the graphene surface. Similar results but with different force fields are also reported in refs 36, 50, 51. At the position of the second layer ($z \approx 6 \text{ \AA}$), the distribution of the O–H bond angle shows peaks at $\cos \theta = 0.2$ and -1 . Thus, in the second layer, the O–H bonds are oriented parallel to the graphene surface or to the direction pointing to the graphene. For the distributions of the H–O–H plane angle [Figure 3f], a peak at $\cos \phi = 1$ and a broad peak near $\cos \phi = 0$ appear for both the first and second layers. These analyses are consistent with the observations that the hydrogen distribution slightly peaks at the interlayer region [see Figure 2b]. This water-layer structure on the graphene surface is drawn schematically in Figure 4a. The peak positions at the first and second layers persist even for a larger number of layers, for example, for $L = 6.83$ [see Figure 3d,g, respectively]. Above the double layer (at about $z > 8 \text{ \AA}$), the distribution shows no distinct peaks, which means that the O–H bonds and the H–O–H plane are randomly oriented.

Hydrogen-Bond Formations. Numerous peculiar properties of water are well known to originate from hydrogen-bond formation. We demonstrate that the layered structure is attributed to the formation of hydrogen bonds between water molecules. A hydrogen bond is defined to form if the distance between an oxygen atom of a water molecule and a hydrogen atom of another molecule is less than 2.5 \AA , which is the standard criterion used in previous studies.^{52,53} The position of

the hydrogen bond is defined as the midpoint between the oxygen and hydrogen atoms that partake in the bond. Figure 4b shows the distribution of the hydrogen bond positions as a function of z . The distinct peaks in this distribution are similar to the density distributions for oxygen and hydrogen atoms, as shown in Figure 4c,d, respectively. Thus, as drawn schematically in Figure 4a, the water molecules are definitely oriented in the layered structure. In fact, hydrogen bonds are formed between the first two layers and also within each layer. Such a bilayer structure has also been confirmed experimentally on metal surfaces at low temperature.^{54,55} This conclusion is consistent with the result that the O–H bonds are oriented either parallel or perpendicular to the graphene surface.

Here, we remark our choice of the water models in our classical MD simulations: We have used rigid water models, including extended simple point charge (SPC/E), TIP4P, and TIP5P models, to demonstrate the bilayer formation. The previous study⁵⁵ has used ab initio MD simulations to explain the formation of the bilayer ice structure on Pt surfaces. Although the molecular vibrations significantly affect the static ice structure at low temperature, in our simulations at room temperature, dynamical inter-molecular interactions of hydrogen bonds dominate the formation of the bilayer structure. Thus, we suppose that the molecular vibrations hardly affect the bilayer formation. In addition, we remark the interaction between water and graphene: In our simulations, we have adopted the Lennard-Jones potentials with the parameters evaluated by first-principles calculations.¹⁶ Recent first-principles calculations using density functional theory have revealed that the geometrical and electronic properties strongly affect the water wettability on metal oxide surfaces.⁴⁵ However,

on the pristine graphene surfaces, the interaction between water and graphene is weak and almost uniform, leading to negligibly small polarization of a water molecule.²⁶ This means that the geometrical effects caused by the surface defects are negligible.

The fact that water molecules form the structured layers described above is of significant importance for the water wettability of graphene. In the double layer, water molecules form hydrogen bonds within each layer and between the layers even at room temperature. In other words, the O–H bonds in the second layer do not extend toward the exterior of the layer. Furthermore, the oxygen-atom lone pairs are hydrogen-bonded with the water molecules within the layer. As a result, no “dangling hydrogen bonds” appear on the second layer surface. Although the hydrogen bonds instantaneously break and reform at 298 K on the order of picoseconds because of thermal fluctuations, the hydrogen bonds are confined within the layers to form a long-term statistically stable structure. Therefore, an exterior water molecule essentially cannot form a hydrogen bond on the surface of the second layer, which means that water molecules just above the layered structure do not reduce their energy by forming hydrogen bonds with the layer. This argument is supported by the potential-energy profile of a water molecule. Figure 5 shows the potential energy of a water

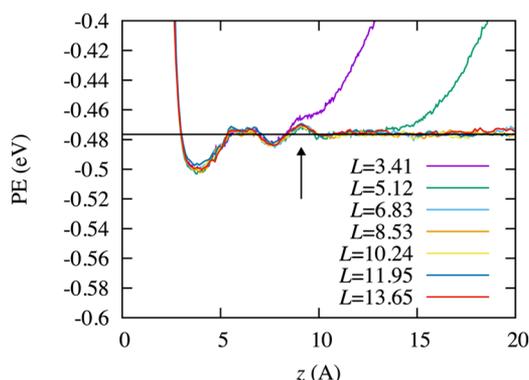


Figure 5. Potential energy per water molecule as a function of z . The potential energy consists of the interactions between water molecules and the Lennard-Jones potential energy between a water molecule and graphene. The black horizontal line indicates the potential energy of a water molecule in a free-standing slab layer (we use a 40 Å thick slab layer), which is obtained by averaging over the water molecules in the center region of the slab. The black arrow at $z = 9.1$ Å indicates the position of the potential barrier between the double layer of water molecules and exterior water molecules.

molecule as a function of z . The potential-energy profile in the z direction has local minima at $z = 3.4$ and 7.6 Å, and the energies at these minima are lower than those of the bulk water. This means that the interfacial water molecules on the graphene surface are stabilized, even at the room temperature, by the formation of the layered structures. Note that a potential-energy barrier appears at $z \approx 9$ Å (see the black arrow in Figure 5), just above the surface of the second layer, indicating the separation in the hydrogen-bond network between the second layer and the stacked water cluster. These observations imply that a graphene surface covered with such a double layer of water molecules has a hydrophobic character, whereas the graphene surface itself is wettable on the atomic scale. For a lower temperature, the formation of the bilayer structures is reinforced because the hydrogen bonds are

more stabilized. On the other hand, in our simulations, the double-layer structure persists up to about 340 K.

CONCLUSIONS

We have examined the wettability of graphene surfaces by MD simulations. The results indicate that a graphene surface is completely wettable on an atomic scale and that water molecules form a double-layered structure on the graphene surface. The hydrogen bonds are confined within and between these two layers and thus no “dangling hydrogen bonds” extend toward the exterior of the double layers. Therefore, the double-layer structure acts as a hydrophobic surface. In other words, graphitic surfaces may be wet but only by the formation of two layers of water molecules, which form a hydrophobic coating that prevents further wetting. This picture sheds light on the relationship between microscopic wettability and hydrophobicity/hydrophilicity on the macroscopic scale. Thus, the microscopic wettability of a surface does not necessarily imply the wettability on a macroscopic scale. This conceptual approach of water wettability can be applied not only to graphene surfaces but also to other hydrophobic surfaces. These fundamental results for interfacial water on a surface suggest that the traditional concepts used to explain hydrophobic or hydrophilic properties may need to be revisited.

COMPUTATIONAL METHODS

We examined MD simulations of water molecules dropped onto a graphene surface. The water model was represented by the SPC/E model.⁵⁶ We checked that the other water models, TIP4P and TIP5P, showed no qualitative changes in our results. A single layer of graphene with a lattice constant of 2.46 Å was assumed, and all graphene carbon atoms were fixed in the simulations. Any interactions between carbon atoms and water molecules were described by the Lennard-Jones potential with the parameters proposed by Wu and Aluru.¹⁶ We checked that for four sets of parameters appeared in ref 16 no qualitative changes of the statistical distribution were observed. The simulations used a time step of 0.1 fs in an NVT ensemble at a temperature of 298 K. The cutoff length is 10 Å, and the treatment of the Coulombic long-range interaction is by the Ewald method. A velocity rescaling thermostat was globally applied to the system. For the main results, we used periodic boundary conditions with a (16 × 16) graphene supercell (the size effect of the boundary box is discussed in the Supporting Information). Statistical quantities were obtained by averaging over 0.1 ns after the system had reached thermal equilibrium. All simulations in the present study were conducted using commercial software SCIGRESS ME 2.0 (Fujitsu Ltd.).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b00365.

Evaluation of the size effects of the simulation box and of the initial conditions of water (PDF)

AUTHOR INFORMATION

Corresponding Authors

*E-mail: akaishi@natori.ee.uec.ac.jp. Tel: +81 (0)42 4435156.

Fax: +81 (0)42 4435156 (A.A.).

*E-mail: yonemaru@natori.ee.uec.ac.jp (T.Y.).

*E-mail: junj@ee.uec.ac.jp (J.N.).

ORCID 

Akira Akaishi: 0000-0001-8013-2131

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by CREST, Japan Science and Technology Agency.

ADDITIONAL NOTE

^aThis preferential direction does not occur when a single water molecule is adsorbed on graphene; the O–H bonds prefer to point to the graphene surface as found in first-principles studies.^{26,49} Even in our MD simulations of a single water molecule, the O–H bonds tend to point to the surfaces.

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