Stable Liquid Water Droplet on a Water Monolayer Formed at Room Temperature on Ionic Model Substrates

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Using molecular dynamics simulation, we show direct evidence of the unexpected phenomenon of ‘‘water that does not wet a water monolayer’’ at room temperature. This phenomenon is attributed to the structure of the water beneath the water droplet, which exhibits an ordered water monolayer. Remarkably, there remains a considerable number of dangling OH bonds in this room temperature water monolayer, in contrast with the absence of dangling OH bonds at cryogenic temperature.

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The wetting properties of surfaces [1,2] are fundamental to physics [3], chemistry [4] and biology [5]. Generally, water always wets other water. Recently, hydrophobiclike ice monolayers on metal surfaces have been observed at extremely low temperatures [6]. This result has been attributed to the fact that no dangling OH bonds [7] exist in the ice monolayer, which itself features a two-dimensional (2D) hydrogen bond (H-bond) network. Clearly, room temperature ‘‘hydrophobiclike water’’ is of much greater importance and application since liquid water is essential for various processes, including many biological activities [2]. However, as for the superconductor and Bose–Einstein condensation, results achieved under cryogenic temperatures are usually not transferable to room temperature except in cases when a new mechanism can be introduced. At room temperature, thermal fluctuations usually break the H-bond networks, leading to dangling OH bonds that in turn provide opportunities for H-bond formation. Thus, as compared to the cryogenic temperature case, the water monolayer at room temperature is more hydrophilic. This phenomenon probably accounts for the lack of reports of hydrophobiclike water layers at room temperature, even though an ordered water monolayer has been observed on many solid surfaces at room temperature [8,9].

In this Letter, using molecular dynamics simulation, we show the feasibility of stable liquid water droplets on a water monolayer at room temperature. This serves as direct evidence of ‘‘water that does not wet a water monolayer’’ at room temperature, in the context of a solid modeled structure. This phenomenon is attributed to the ordered structure of the water monolayer, which greatly enhances the numbers of H bonds inside the monolayer. This in turn reduces the likelihood of H-bond formation between the water molecules inside this monolayer and other molecules. The key to this room temperature behavior is the appropriate physical partial atom charge quantity and distribution, which provides strong and appropriate Coulomb interactions that counteract the effects of thermal fluctuations. Interestingly, in contrast to the necessary condition of ‘‘no dangling OH bonds’’ at cryogenic temperatures [6,7], there exists a considerable number of dangling OH bonds in the room temperature water monolayer. Our findings may have implications for water treatment, nonfouling surfaces, catalysis engines, and biological sensors.

Our theoretical surface had dimensions of $6.395 \times 6.816\ \mathrm{nm}^2$ with a planar hexagonal structure of neighboring bond lengths (denoted l) of 0.142 nm, as shown in Fig. 1(a). Positive and negative charges of the same magnitude q were assigned to the atoms located diagonally in neighboring hexagons. Overall, the modeled solid surface was neutral. This surface charge or dipole distribution resembles certain surfaces, i.e., InSb(110), suggesting both unrecognized possibilities associated with existing materials and potential for new materials that exhibit this property (see Ref. [10]).

Initially, 838 water molecules, with a water film thickness of about 1.1 nm next to the surface, completely covered the surface and the simulation box size was

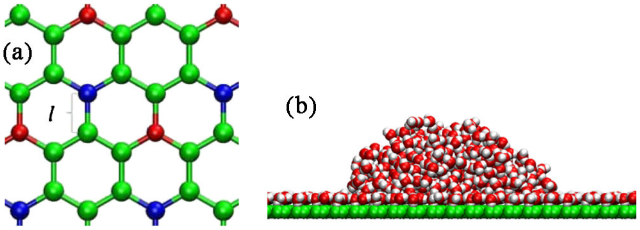

FIG. 1 (color online). (a) Geometry of the solid surface model. Red and blue spheres represent the atoms of the solid with positive and negative charges, respectively, while the green spheres represent neutral solid atoms. (b) Side view snapshot of a water droplet on a water monolayer on a modeled surface.

$6.395 \times 6.816 \times 20.0\ \text{nm}^3$. The simulation time was 4 ns for each value of q, and the last 2 ns data were collected for analysis. The periodic boundary conditions were applied in all directions. MD simulations were performed using a time step of 1.0 fs with Gromacs 3.3.1 [11] in an *NVT* ensemble at a temperature of 300 K. The atoms of the solid with Lennard-Jones parameters $\varepsilon_{ss} = 0.105\ \text{kcal/mol}$, $\sigma_{ss} = 3.343$ Å, and the SPC/E water model [12] were used. The particle-mesh Ewald method [13] with a real space cutoff of 1 nm was used to treat long-range electrostatic interactions and 10 Å cutoff was applied to the van der Waals interactions. Specifically, our model specified a hydrogen bond between water if the O-O distance was less than 3.5 Å and simultaneously the angle H—O...O was less than 30°.

Generally, due to the charges on the atoms of the solid, the surface exhibited a tendency towards hydrophilicity [14], and when q was large enough, water completely wetted the surface. Surprisingly, when $0.6e \leq q \leq 1.0e$, the water molecules began to assemble during the simulation and, with sufficient simulation time, a water droplet would appear on the surface. The other solid surface area remained covered by water molecules [Fig. 1(b)]. Interestingly, as q increased over the interval of $0.6e - 1.0e$, the contact angle of the droplet also increased (Fig. 2). From the exponential curve fitted for the contact angle vs q, one can deduce the existence of a critical value of $q_c \approx 0.5e$, below which the droplet disappears. This behavior has been demonstrated using numerical simulations.

Our simulation suggests that water molecules on the solid surface outside the droplet also exhibit abnormal behavior. Generally, for a hydrophobic solid surface, there are only a few sparsely distributed water molecules on the solid surface outside the droplet. Our calculations indicate that the rest of the solid surfaces outside the droplet are covered by water molecules with an average thickness of $\sim$4.0 Å [see Fig. 1(b)], consistent with the existence of an experimentally observable monolayer [9]. Thus, the water droplet is in fact above a water monolayer. Moreover, our analysis of the structure of the first water layer under the droplet shows that it has an ordered structure similar to that of the monolayer outside the droplet (see below). Hereafter, we call this first layer under the droplet water the water monolayer. We emphasize that our observation of *water that does not wet a water monolayer* occurs at room temperature and that clear droplets are observed for the first time.

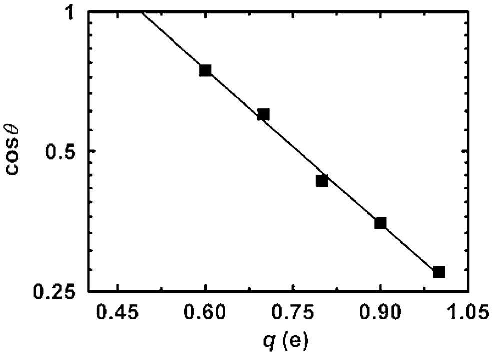

FIG. 2. Cosine values of the contact angle θ vs the charge value q. From the exponential function $\cos\theta \approx 3.5\exp(-q/0.38)$ fitted to the data (black line).

At cryogenic temperatures, the water monolayer can be weakly hydrophobiclike due to the lack of dangling OH bonds [6,7]. We have computed the average number of H bonds formed by a water molecule in the monolayer under the droplet with its neighboring water molecules in the same layer (namely, within-monolayer H bonds), as well as the average number of H bonds formed between a water molecule in the monolayer under the droplet and the water molecules above this monolayer (namely, between-droplet-monolayer H bonds). As shown in Fig. 3, the former increases, whereas the latter decreases, as q increase (for $q = 0.5e$, we still called the first water layer the "under droplet monolayer" for simplicity, even though there is no clear droplet at this q value). Their sum slowly decreases as q increases for $q < 0.8e$ and then remains at $\sim$2.9 for $q \geq 0.8e$. Note that when q is sufficiently large, in the monolayer, half of the water molecules bind to the surface mainly through electrostatic interaction between their O atoms and the positive charges on the surface. For water molecules in the other half, any hydrogen atom that has a strong electrostatic interaction with a negative charge on the surface necessarily points toward the surface (see Ref. [10] for details). For each water molecule that can form H bonds with other water molecules, there is approximately one site that is occupied on account of the electrostatic interaction with the surface charges. Thus, the value

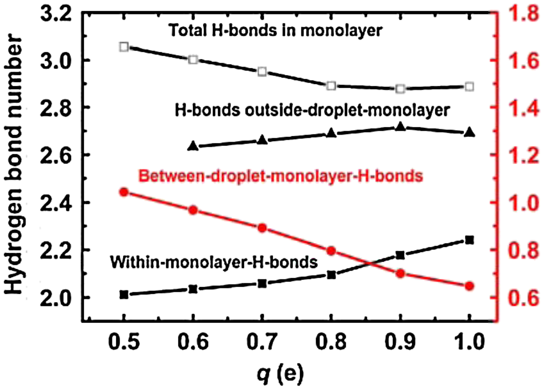

FIG. 3 (color online). Average number of H bonds formed by a water molecule of the monolayer under the droplet with other water molecules in this same monolayer (■), and by a water molecule of the monolayer under the droplet with the water molecules above the monolayer (●, corresponding to right red axis) with respect to q, together with their sum (□). Black triangles (▲) show the average number of H bonds formed by a water molecule of the monolayer outside the droplet.

of ~2.9 approaches the maximum number of H bonds, namely, 3, that any water molecule can form in the monolayer under the droplet. Consequently, there seems to be a competition for H-bond formation between within-monolayer H bonds and between-droplet-monolayer H bonds. An increase of the former reduces the likelihood of formation of the latter. The decrease of the number of the between-droplet-monolayer H bonds results in weaker interactions between the water molecules in the monolayer under the droplet and the water molecules in the actual droplet, as q increases. This makes the upper surface of the monolayer under the droplet more hydrophobic, consistent with the observation in Fig. 2 that the contact angle of the droplet increases as q increases.

The number of H bonds per water molecule in the monolayer outside the droplet is almost constant at 2.6 for $q \geq 0.6e$ (see Fig. 3). This is quite close to the maximal number of H bonds of 3 that any water molecule can form in this monolayer, indicating the absence of room for additional H bonds to be formed for the water molecules in this monolayer. This greatly reduces the water-water attraction between water monolayer and the contacting water above, thus making the water monolayer unfavorable for further growth of water. This is further demonstrated by the observation that the number of H bonds formed for each water molecule in the monolayer under the droplet with the other water molecules above decreases as q decreases, and reaches a value of only ~0.65 for $q = 1.0e$, which is smaller than the value of ~1.0 for $q = 0.5e$ (see Fig. 3). The value 2.6 is considerably smaller than the total value of 2.9 H bonds per water molecule for $q \geq 0.8e$ in the monolayer under the droplet. This discrepancy can be attributed to the ability of the water molecules above the monolayer to provide more opportunities for H-bond formation with the water molecules in the monolayer. This result suggests that there are at least 0.3 free positions at which H bonds can form for each water molecule in the monolayer outside the droplet.

The special arrangement of the charge or dipoles on the solid surface is important for the formation of the 2D ordered water structure as well as the number of internal H bonds. Figure 4(a) displays a snapshot of the structure together with the H bonds in the monolayer outside the droplet for $q = 1e$. This ordered hexagonal structure is further confirmed by the probability distribution of φ [Fig. 4(b)], where φ is the angle formed between the projection onto the x-y plane of a water molecule dipole orientation and a crystallographic direction. Although the heights of the distribution associated with the monolayer under the droplet are lower than the heights for the monolayer outside the droplet, the water molecules in the monolayer under the droplet still retain a good 2D ordered hexagonal structure. At $q = 0.5e$, the peaks of the water monolayer cannot be clearly seen. This is consistent with the observation in Fig. 2 that the critical value of $q_c \approx 0.5e$ is expected, below which the droplet disappears. When $q \geq 0.6e$, there is a clear dipole orientation preference of the water with three peaks at $\varphi = 0°$, 120°, and 240°. To study the effect of varying the substrate unit cell size, we have performed additional simulations by increasing only the neighboring atom bond length l from 0.142 to 0.17 nm. Although q has quite a large value of $1e$, we found that there was no clear peak in the φ distribution [green lines in Fig. 4(b)]. Thus, for this bond length there is no clear water droplet above the monolayer. Similarly, water droplets cannot be seen when l decreases to 0.12 nm.

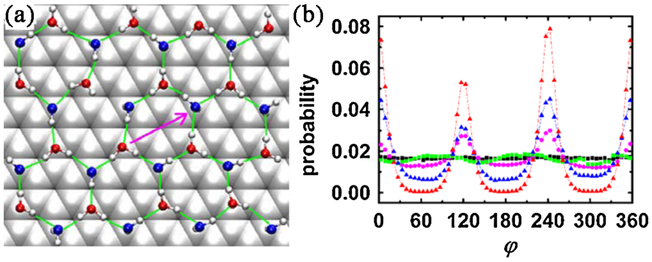

FIG. 4 (color online). Structure of water molecules in the monolayer on the solid surface. (a) A snapshot of the monolayer water molecules outside the droplet showing regular 2D ordered hexagons together with the H bonds that form between neighboring water molecules. Magenta arrow shows the direction we used as the crystallographic direction to compute φ. (b) Probability distribution of the angle φ between the x-y plane projection of one water molecule dipole orientation and a crystallographic direction. Black solid squares (■) and magenta circles (●) correspond to $q = 0.5e$ and $q = 0.6e$, respectively, in the context of a bond length $l = 0.142$ nm. Red triangles (▲) and blue triangles (▲) represent the water monolayer outside the droplet and the monolayer molecules under the droplet, respectively, for $q = 1e$ and $l = 0.142$ nm. Green squares (■) show the case for a larger neighboring bond length $l = 0.17$ nm with $q = 1e$.

We have also performed numerical simulations of the systems at $T = 135$ K, conditions under which the crystalline ice monolayer on a Pt(111) surface displays hydrophobiclike behavior. Since liquid water droplets cannot be formed at this temperature, we only analyzed a water monolayer that contained 414 water molecules. Water monolayer completely wetted the substrate and exhibited an ordered structure when $q \geq \sim 0.3e$ given the water dipole orientation distribution of φ (see Ref. [10], Fig. S5). This partial atom charge value is much lower than the critical value of $q_c \approx 0.5e$ at room temperature. We found that the number of H bonds per water molecule at $q = 0.3e$ was 2.9. Importantly, this number is ~0.3 larger than the number of H bonds per water molecule in the monolayer outside the droplet when $q \geq 0.6e$ at room temperature, but equals the total of 2.9 H bonds per water molecule obtained when $q \geq 0.8e$ at room temperature in the monolayer under the droplet. Our observation implies that there may be no dangling OH bonds in the monolayer at this cryogenic temperature and furthermore shows that the room temperature hydrophobic water monolayer does not require an absence of OH bonds, which is quite different from the monolayer at cryogenic temperatures.

In summary, we directly observe in our simulations the unexpected phenomenon of ‘‘water that does not wet a water monolayer’’ on a solid surface at room temperature. In contrast to observations of ‘‘no dangling OH bonds’’ in the hydrophobiclike water monolayer at cryogenic temperatures, there remains a considerable number of dangling OH bonds in this hydrophobiclike water monolayer at room temperature. The key to this room temperature behavior is the appropriate charge quantity and distribution, which provides strong and appropriate Coulomb interactions that counteract the effects of thermal fluctuations. We note that, although Giovambattista *et al.* have shown that the hydrophobic or hydrophilic property of a surface is strongly dependent of the distribution of surface charges or dipoles [14], our simulation shows that the polar residues on the solid surfaces unexpectedly enhance the contact angle of the droplet above the monolayer on the solid surface, which ‘‘apparently’’ contradicts the traditional view that polar residues always lead to a smaller contact angle of a droplet on a solid surface. It is expected that our finding helps to expand our knowledge of hydrophobicity and hydrophilicity.

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[1] P. A. Thiel and T. E. Madey, Surf. Sci. Rep. **7**, 211 (1987); M. A. Henderson, Surf. Sci. Rep. **46**, 1 (2002); D. Chandler, Nature (London) **437**, 640 (2005); H. S. Ashbaugh and L. R. Pratt, Rev. Mod. Phys. **78**, 159 (2006).

[2] P. Ball, Chem. Rev. **108**, 74 (2008).

[3] S. Meng, Z. Y. Zhang, and E. Kaxiras, Phys. Rev. Lett. **97**, 036107 (2006); G. Hummer and S. Garde, Phys. Rev. Lett. **80**, 4193 (1998); S. Haq, J. Harnett, and A. Hodgson, Surf. Sci. **505**, 171 (2002); H. Gawronski, J. Carrasco, A. Michaelides, and K. Morgenstern, Phys. Rev. Lett. **101**, 136102 (2008); S. Meng, L. F. Xu, E. G. Wang, and S. W. Gao, Phys. Rev. Lett. **89**, 176104 (2002); P. J. Feibelman, Science **295**, 99 (2002); K. Andersson, A. Nikitin, L. G. M. Pettersson, A. Nilsson, and H. Ogasawara, Phys. Rev. Lett. **93**, 196101 (2004); S. Yamamoto *et al.*, J. Phys. Chem. C **111**, 7848 (2007).

[4] R. Zangi, M. Hagen, and B. J. Berne, J. Am. Chem. Soc. **129**, 4678 (2007); T. Koishi *et al.*, Phys. Rev. Lett. **93**, 185701 (2004).

[5] G. Cicero, J. C. Grossman, E. Schwegler, F. Gygi, and G. Galli, J. Am. Chem. Soc. **130**, 1871 (2008); N. L. Fawzi, A. Phillips, J. Z. Ruscio, M. Doucleff, D. E. Wemmer, and T. Head-Gordon, J. Am. Chem. Soc. **130**, 6145 (2008); R. H. Zhou, X. H. Huang, C. J. Margulisand, and B. J. Berne, Science **305**, 1605 (2004); A. Serr, D. Horinek, and R. Netz, J. Am. Chem. Soc. **130**, 12 408 (2008); J. Y. Li, X. J. Gong, H. J. Lu, D. Li, H. P. Fang, and R. H. Zhou, Proc. Natl. Acad. Sci. U.S.A. **104**, 3687 (2007); X. J. Gong, J. Y. Li, H. J. Lu, R. Z. Wan, J. C. Li, J. Hu, and H. P. Fang, Nature Nanotech. **2**, 709 (2007); N. Giovambattista, C. F. Lopez, P. J. Rossky, and P. G. Debenedetti, Proc. Natl. Acad. Sci. U.S.A. **105**, 2274 (2008).

[6] G. A. Kimmel, N. G. Petrik, Z. Dohnálek, and B. D. Kay, Phys. Rev. Lett. **95**, 166102 (2005).

[7] H. Ogasawara, B. Brena, D. Nordlund, M. Nyberg, A. Pelmenschikov, L. G. M. Pettersson, and A. Nilsson, Phys. Rev. Lett. **89**, 276102 (2002).

[8] J. Hu, X. D. Xiao, D. F. Ogletree, and M. Salmeron, Science **268**, 267 (1995); M. F. Reedijk, J. Arsic, F. F. Hollander, S. A. deVries, and E. Vlieg, Phys. Rev. Lett. **90**, 066103 (2003); C. Y. Ruan, V. A. Lobastov, F. Vigliotti, S. Y. Chen, and A. H. Zewail, Science **304**, 80 (2004).

[9] P. B. Miranda, L. Xu, Y. R. Shen, and M. Salmeron, Phys. Rev. Lett. **81**, 5876 (1998).

[10] See EPAPS Document No. E-PRLTAO-103-006941 for supplementary information. For more information on EPAPS, see http://www.aip.org/pubservs/epaps.html.

[11] E. Lindahl, B. Hess, and D. van der Spoel, J. Mol. Model. **7**, 306 (2001).

[12] H. J. C. Berendsen, J. R. Grigera, and T. P. Straatsma, J. Phys. Chem. **91**, 6269 (1987).

[13] T. A. Darden, D. M. York, and L. G. Pedersen, J. Chem. Phys. **98**, 10 089 (1993).

[14] N. Giovambattista, P. G. Debenedetti, and P. J. Rossky, J. Phys. Chem. B **111**, 9581 (2007).