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Hydrophobic-induced Surface Reorganization: Molecular Dynamics Simulations of Water Nanodroplet on Perfluorocarbon Self-Assembled Monolayers

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Abstract

We carried out molecular dynamics simulations of water droplets on self-assembled monolayers of perfluorocarbon molecules. The interactions between the water droplet and the hydrophobic fluorocarbon surface were studied by systematically changing the molecular surface coverage and the mobility of the tethered head groups of the surface chain molecules. The microscopic contact angles were determined for different fluorocarbon surface densities. The contact angle at a nanometer length scale does not show a large change with the surface density. The structure of the droplets was studied by looking at the water density profiles and water penetration near the hydrophobic surface. At surface densities near close packed coverage of fluorocarbons, the water density shows an oscillating pattern near the boundary with a robust layered structure. As the surface density decreased and more water molecules penetrated into the fluorocarbon surface, the ordering of the water molecules at the boundary became less pronounced and the layered density structure became diffuse. The water droplet is found to induce the interfacial surface molecules to rearrange and form unique topological structures that minimize the unfavorable water-surface contacts. The local density of the fluorocarbon molecules right below the water droplet is measured to be higher than the density outside the droplet. The density difference increases as the overall surface density decreases. Two different surface morphologies emerge from the water-induced surface reorganization over the range of surface coverage explored in the study. For surface densities near closed packed monolayer coverage, the height of the fluorocarbons is maximum at the center of the droplet and minimum at the water-vapor-surface triple junction, generating a convex surface morphology under the droplet. For lower surface densities, on the other hand, the height of the fluorocarbon surface becomes maximal at and right outside the water-vapor-surface contact line and decreases quickly towards the center of the droplet, forming a concave shape of the surface. The interplay between the fluorocarbon packing and the water molecules is found to have profound consequences in many aspects of surface-water interactions, including water depletion and penetration, hydrogen bonding, and surface morphologies.

1. Introduction

Hydrophobic interactions play an important role in diverse phenomena in physics, chemistry, and biology. A thorough understanding of hydrophobic interactions at a molecular level is crucial in both fundamental research and technological applications. Examples include surface coating, emulsions, oil recovery, wetting behavior in microfluidics and nanofluidics applications, lipid membranes and micelle formations, and protein adsorption and folding. Still,

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the exact nature of hydrophobic interactions at a molecular level remains elusive and controversial.¹⁻¹²

Control of surface hydrophobicity is one of the main issues in surface science and interfacial engineering. An important task in this topic is to prepare highly hydrophobic surfaces in a controlled manner. Manipulation of the surface hydrophobicity requires a thorough understanding of the microscopic interactions that determine macroscopic wetting characteristics. In general, a hydrophobic surface with contact angles up to around 130° can be prepared by optimizing the chemical properties of nonpolar materials, while preparing a so-called superhydrophobic surface with higher contact angles often requires molecular scale control of the surface.¹³ Genzer and Efimenko¹⁴ demonstrated that the tunability of surface hydrophobicity can be achieved by controlling the surface configuration of hydrophobic perfluoroalkane molecules in mechanically assembled monolayers (MAM). The experimental water contact angle was shown to change mostly in proportion to the magnitude of the experimental surface stretch before decreasing slightly at the largest stretches. The mechanical stretching process controls the density and spacing of the surface molecules. The preparation of the MAM at larger stretches leads to a denser layer. The slight decrease in contact angle at the maximum stretches was speculated to be due to the increased surface roughness by corrugated molecules at densities above the monolayer coverage. However the lack of information on the molecular details from the experiment leaves a thorough understanding of the experimental observations difficult and challenging, and the detailed molecular mechanism of the process still remains unclear. It is in this kind of situations where molecular dynamics simulations can play a powerful role to offer further insight, by providing a detailed quantitative picture of the surface attached molecules and the water with atomistic resolution.

Molecular dynamics simulations have been extensively used to study surface wetting phenomena.^{12,15-24} Microscopic equivalence of contact angle has been casually applied to nanometer-scale droplets on a wide variety of surfaces, such as polymers¹⁵, cellulose¹⁶, silica^{12,17}, graphite and carbon nanotube¹⁸ among others, in order to establish a connection between microscopic calculation and macroscopic wetting properties of the surfaces. Sometimes contact angle was used as a reference to tune the intermolecular interaction parameters.^{17,18} In most cases^{12,15-19,21-24}, the surfaces were held fixed during the simulations in order to save computation time or for the lack of proper interaction parameters.

In this study we investigated the interactions of water droplet at a nanometer length scale with perfluorocarbon monolayer surfaces by using classical molecular dynamics simulations. The surface density was varied systematically in order to gain insights into the correlations between the surface topology and hydrophobic interactions at a molecular level. The effects of the mobility of the tethered surface molecules on the surface structure and on the behavior of water droplets were also examined. Previous studies on hydrophobic interactions often focused on the behavior of water, while paying less attention to the interfacing surface. Furthermore, as pointed out above, the surfaces are often held frozen and/or have no detailed atomic or molecular resolutions, which results in a significant loss of atomistic details of the system behavior and a failure to capture the changes in surface topology induced by the water droplet. This study aims to provide more thorough understanding of the surface hydrophobicity at a molecular level. To this end we have built the surface anchored molecules with full atomistic resolution and have taken a close look at the surface molecules as well as at the water molecules. We show that, in addition to the changes in water structure near the surface, the underlying surface layer also experiences a significant topological change, which is driven by the delicate balance of hydrophilic and hydrophobic interactions between water and surface molecules. Our results suggest that the water molecules locally induce a reorganization of the surface molecules, which leads to unique local surface morphologies. The findings from this work may also be relevant to a variety of biological processes, such as protein stability and protein folding,

where solvent molecules near hydrophobic and hydrophilic segments of a protein molecule can induce the local structural and conformational changes of the protein molecule that can be a key step to important biological processes.

2. Simulation Method

A monolayer of 400 (20×20) C₁₀F₂₂ perfluoro-*n*-decane molecules was generated on top of an inert substrate atomic monolayer in a rectangular box with surface area corresponding to a given area per molecule between 24 and 44 Å² and a box height of 30 nm. Each fluorocarbon molecule was endtethered to the substrate via an “anchor” fluorine atom at the CF₃ head group. The *z*-coordinates of the anchor atoms are held constant throughout the simulations so that the fluorocarbon molecules remain tethered to the substrate, while the (*x*, *y*) coordinates were set to be either fixed or variable, depending on the lateral mobility of the anchor atoms being either turned on or off. For the cases with static anchors, the grafting atoms were placed in a hexagonal lattice in order to replicate typical close-packed self-assembly. The substrate atoms below the surface molecule remained static at all times during the simulations.

The all-atomic OPLS force field²⁵ was used to describe the interactions of the surface fluorocarbon molecules, and the explicit water molecules were modeled using the TIP4P model. A monolayer of dummy atoms with a neutral charge was used as substrate. The main role of the substrate is to prevent the surface fluorocarbon molecules from flipping down to the inverted stance and the water molecules from penetrating the solid surface, both of which reflect the typical laboratory experimental conditions. The depth of Lennard-Jones potential well, ϵ , of the substrate atoms is roughly two orders of magnitude smaller than the other ϵ parameters in the system, hence the effects of the substrate-fluorocarbon and substrate-water van der Waals interactions on the overall dynamics of the system are deemed negligibly small.

The molecular dynamics simulations have been run with the GROMACS software package. (version 3.3.2)²⁶ The initial configuration of the surface fluorocarbon molecules was first relaxed to an energetically stable structure by minimizing the potential energy using the standard steepest descent algorithm. Following the energy minimization, the temperature of the system is brought up to the room temperature of 300 K by equilibrating the system for 500 ps using the Berendsen thermostat. Once the surface reached equilibrium, as determined by a relatively constant level of the potential energy over a reasonably long period of time, a water droplet with approximately 3300 water molecules in a rectangular shape (5nm × 5nm × 6nm) was placed on top of the equilibrated surface. A typical molecular dynamics simulation was run for 5 ns for data acquisition. The time step of integration for the discretized Newton's equation was 1.0 fs. The first 1 ns of the simulation was excluded in the data processing and analysis in order to allow for the water molecules to reach an equilibrium. The system temperature was maintained at 300 K using the Nosé-Hoover thermostat, and the system volume was kept constant throughout the simulations, hence the simulations are in the NVT ensemble. Figure 1 shows typical snapshots of the system (a) at the beginning at *t* = 0 ns, and (b) at the end at *t* = 5 ns of the simulation.

The long-range electrostatic interactions were treated by the Particle Mesh Ewald (PME) algorithm, and the cut-off length of 1.2 nm was applied for the short-range electrostatic and van der Waals interactions represented by the Lennard-Jones 12-6 potential. Periodic boundary conditions were applied in all three directions in the simulations. The conventional geometric combination rules for OPLS force field, $\epsilon_{ij} = \sqrt{\epsilon_i \cdot \epsilon_j}$ and $\sigma_{ij} = \sqrt{\sigma_i \cdot \sigma_j}$, were used for the Lennard-Jones parameters for the cross interactions.

The simulated range of per-molecule surface area from 24 to 44 Å² spans the density around the experimental value of perfluoroalkane surface density for the hexagonal close packing at

27 Å².²⁷ The typical simulation ran at the computation speed of ~1 ns/day in a parallel run on eight CPUs (two Intel® Xeon® X5355 2.66 GHz Quad Core processors) installed on a Linux cluster.

3. Results and Discussion

First we describe the overall qualitative observations of the droplet behavior before discussing the results of quantitative analyses. The shape of the water droplet transforms from the initial rectangular shape to roughly a capped spherical shape within the first 100 picoseconds in each simulation and remains so for the rest of the simulation. It is observed that the detailed shape of the droplet at equilibrium is almost perfectly a spherical cap on the higher fluorocarbon density surfaces, while it is slightly deformed to vertically elongated shapes on lower density surfaces. We also observe that the position of the water droplet remains almost unchanged during the simulation for high-density surfaces, while the droplet becomes more mobile laterally as the surface density of fluorocarbon decreases, presumably due to the higher mobility of the surface molecules and the bigger spatiotemporal fluctuations of the surface height at lower surface densities. For the surfaces at lower densities with the anchors freely mobile in lateral directions, the surface fluorocarbon molecules are observed to rearrange and bring themselves closer to each other to create hexagonal close-packed structures, resulting in a local increase in the surface density and generating patches of holes suggesting the presence of a fluorocarbon phase transition. In this case, the water nanodroplet stays on top of fluorocarbon molecules and avoids the holes throughout the simulations. The water droplet placed on top of the fluorocarbon surface, as opposed to being on top of an empty hole as an isolated spherical droplet, gains stability through the weak yet ubiquitous and persistent van der Waals attractions between water molecules and the surface fluorocarbon molecules, which is typically on the order of the thermal energy $k_B T$.

When a liquid droplet with its vapor phase is placed on a solid substrate, the three phases - liquid, solid, and vapor - reach a mechanical equilibrium when the three surface tensions at the liquid-solid, solid-vapor, and liquid-vapor interfaces balance at the three-phase contact line, as described by Young's equation²⁸:

$$\gamma_{SV}\gamma_{SL} + \gamma_{LV}\cos\theta_{eq}, \quad (1)$$

where γ_{SV} , γ_{SL} , and γ_{LV} are the solid-vapor, solid-liquid, and liquid-vapor surface tension, respectively, and θ_{eq} is a macroscopic contact angle at equilibrium. The macroscopic contact angle characterizes the wetting properties of a given liquid-solid combination, and is frequently used in both numerical and experimental studies as a quantity that measures surface hydrophobicity.^{4,12,14-24} In the case of perfect wetting, a liquid spreads to form a uniform layer to cover the whole surface, and the contact angle is zero. In the other extreme case of perfect dewetting, a liquid forms a perfect sphere on the surface and the contact angle is 180 degrees. In most cases, a liquid partially wets the surface and the contact angle is a direct reflection of the degree of wetting. When the liquid is water, the contact angle increases as the surface becomes more hydrophobic. In case of nanodroplets with diameters of 10 nm or less, it has been suggested that the effect of line tension be included as a correction term in eq. (1) in order to properly describe the relationship between contact angle and surface tensions.^{17,18,22}

In this study, we determined the contact angle between the water nanodroplet and the fluorocarbon monolayer by using a simple geometric method that has been developed in previous studies.^{18,22} The method is essentially a numerical adaptation of the conventional technique to measure contact angle experimentally at a macroscopic scale to a system at a nanometer length scale. In this scheme the liquid-vapor interface is determined, which is then

fit to a function of choice, and finally the fitting function is extended to the surface to determine the contact angle. The detailed procedure is described next.

The first step to determine the contact angle in this approach is to obtain the time-averaged spatial density profile $\rho(r, z)$ of water droplet by cylindrically binning the water molecules around a reference axis perpendicular to the surface through the droplet's center of mass, where r is the horizontal distance from the reference axis, and z the coordinate along the surface normal direction with the position of the substrate layer defined as $z = 0$. The bins in the cylindrical coordinates used in the density calculations have a height of $\Delta z = 0.1$ nm and a base area of $\Delta A = 1$ nm², hence the radial bin boundaries being located at $r_i = \sqrt{i \cdot \Delta A / \pi}$ where $i = 1, 2, \dots$ is an index for the radial bins. After the density profile $\rho(r, z)$ is obtained, the liquid-vapor interface can be determined by fitting the radial density profile $\rho(r)$ of each horizontal layer at a fixed z to the following hyperbolic tangent function²⁸:

$$\rho(r) = \frac{1}{2}(\rho^l + \rho^v) - \frac{1}{2}(\rho^l - \rho^v) \tanh \left[\frac{2(r - r_e)}{d} \right], \quad (2)$$

where ρ^l and ρ^v are the density of bulk liquid and vapor, respectively, with ρ^v assumed to be zero, r_e is the location of the equimolar Gibbs dividing surface, and d is the thickness of the interface. A typical fit is shown in figure 2(a). The equimolar Gibbs dividing surface from the fit was taken as the liquid-vapor interface. The interface was then fit to a function of choice, which finally was extended to the surface for contact angle measurement. It is common to fit the interface to a circle^{15,17,18,21-23}, while a polynomial¹² has also been used when the shape of droplet deviates from sphere. In our case, the liquid-vapor interface of the water droplet on fluorocarbon surface fits well to a circle when the surface area per molecule is on the lower side (i.e. higher density) between 24 and 30 Å², while the shape deviates significantly from a circle when the area per fluorocarbon becomes higher. Therefore we chose a fourth-order polynomial as a fitting function to accommodate the entire range of the surface density explored in this study. A typical polynomial fit to the interface is shown in figure 2(b). Finally, the contact angle was determined by extrapolating the fit to the surface (solid horizontal black line in figure 2(b)) and measuring the tangential slope at the surface.

The contact angles determined by the polynomial fit described above are shown in figure 3(a) for the surfaces with mobile and static anchors at different surface densities. The contact angles range between 125° and 135° for the simulated surface densities of fluorocarbons, with no apparent trend or pattern against the change in surface density or the anchor mobility. The overall range of the contact angles in figure 3(a) is in good agreement with the values from experiments and other simulation studies on similar systems.^{14,21} On the other hand, the marginal and irregular changes in contact angle with respect to the relatively large variations in surface fluorocarbon density, as shown in figure 3(a), raise an interesting question on the validity of contact angle as an indicator of surface wetting characteristics at a nanometer length scale.

As a comparison, we carried out additional simulations to obtain the surface tensions, and used them to determine the contact angle from Young's equation. The simulations for the solid-gas surface tensions were done on two parallel monolayers, with 25 (5×5) fluorocarbon molecules with static anchors in each monolayer, placed at the top and the bottom of a rectangular box, facing to each other. The surface area of the box was the given area of the monolayer, and the box height was 12.6 nm. The simulations were performed at constant temperature (300K) and constant volume, and periodic boundary conditions have been applied. Each simulation was run for 20 ns. In the simulations for the solid-liquid surface tensions, the gap between the two parallel monolayers was filled with water molecules. The surface tensions of the solid-liquid

and the solid-gas interfaces were calculated using the pressure tensors.²⁹ The results are shown in figure 3(b). The surface tensions display a systematic trend with the surface density of fluorocarbons. However the contact angles determined by Young's equation do not match with the contact angles in figure 3(a) and show no apparent trend with surface fluorocarbon density. The fact that the contact angles calculated from Young's equation do not match with those determined directly from droplet density profile in figure 3(a) could suggest that Young's equation is not valid in the simulated system due to finite size of the droplet, i.e. its nanometer length scale. However, the large fluctuations in the surface tensions at this length scale put a fundamental limitation on the accuracy of the contact angle calculations using Young's equation, prohibiting any quantitative analysis. As it can be seen from Figure 3(b) the contact angle is determined from the difference between very large numbers and therefore, the value obtained is smaller than the error bars in the calculations.

It is important to emphasize that the differences between the contact angles observed experimentally and those presented in this work do not necessarily contradict each other. The experiments are macroscopic observation with the well-known limitations in measurements of contact angle.³⁰ The simulations provide a microscopic reflection of how much the water likes the surface, however due to the microscopic size of the droplet the Young's equation is not valid and higher order corrections are necessary. However, the determination of all the parameters necessary for the complete determination of the relationship between the microscopic contact angle, the size of the droplet and the thermodynamic surface tension are beyond the accuracy of current simulation techniques with sizes as those presented here.

In the cases where the anchors of the fluorocarbon molecules are freely mobile in lateral directions, the overall "nominal" area per molecule can be misleading and it is hardly relevant in properly capturing the true character of the surface. A more relevant quantity in terms of the water-surface interactions is an "effective" or "local" area per molecule, which we define as the area per surface molecule specifically in the region below the water droplet. The contact angles for the systems with mobile anchors against the effective area per molecule are shown as the green squares in figure 3(a), and the relation between nominal and effective area per molecule in figure 3(c). For the nominal areas per-molecule between 24 and 28 Å², which is roughly around or below the experimental value of 27 Å² for the closed-packed perfluoroalkane monolayer²⁷, the nominal and the corresponding effective area per molecule remain relatively similar to each other within 2 Å²/molecule. For the lower-density surfaces with nominal area per fluorocarbon at or above 30 Å², on the other hand, the effective area per molecule saturates at around 29 Å²/molecule, which is close to the area per molecule for a close-packed fluorocarbon monolayer measured from experiments. This strongly suggests the presence of a phase transition of the simulated perfluorocarbon monolayer between a very dilute gas phase and a close packed phase at 29 Å²/molecule. The exact nature of this transition is beyond the scope of the present work.

The structure of the water density profiles at the interface with hydrophobic surfaces has been a topic of great interest and controversy over the past few decades.¹⁻¹² The existence of a vapor-like depletion layer of water molecules near an extended hydrophobic surface has been widely discussed through a number of analytical, numerical, and experimental studies. Due to the subtle nature of the hydrophobic interactions, the experimental results on the depletion layer have been elusive and controversial.^{7,10} Here we examine the density depletion of water near extended hydrophobic surfaces by taking advantage of the detailed atomistic information available from the molecular dynamics simulations. Figure 4 shows the oxygen density profiles along the direction normal to the surface (z-direction) through the center of mass of the droplet for the systems with the area per molecule for the fluorocarbons ranging from 28 Å²/molecule to 44 Å²/molecule, both with mobile and static anchors. Each vertical dashed line is the average z-coordinate of the top fluorine atoms in the surface fluorocarbon molecules, representing the

approximate position of the corresponding surface. The water density is normalized to the bulk value at 1.0 g/cm^3 . The water depletion layer, which we define as the region between the surface and the position where the water density falls below half the bulk density (horizontal dotted line), is shown in double arrows. Water depletion is observed for all five systems according to this definition. The width of the depletion layer ranges 1-2 Å, which is smaller than the size of a single water molecule. If we consider the finite size of fluorine atoms, the surface positions in figure 5 should be shifted to the right-hand side by the atomic radius of fluorine, $\sim 1.6 \text{ Å}$, which will reduce or completely erase the depletion layer, resulting in the absence of water depletion for all but the case for $36 \text{ Å}^2/\text{molecule}$ with static anchors. This strongly suggests that the water depletion is either very weak or absent in the simulated water droplet-fluorocarbon systems. This is more or less consistent with the results of the recent studies showing that the thickness of depletion zone can range from a subangstrom or less for soft hydrophobic/aqueous liquid interface⁷ to a few angstroms near a smooth flat solid surface.¹¹ It is not clear that a subangstrom layer is a measure of depletion, however we follow the nomenclature usually used in this context in the literature.

At a smaller area per fluorocarbon molecule (i.e., higher fluorocarbon surface density), such as $28 \text{ Å}^2/\text{molecule}$, the density of water oscillates around the bulk value for the first two or three hydration shells from the surface, reflecting a high degree of spatial ordering of water molecules in this region. The water density higher than the bulk value also implies that the very first water layer may form a relatively tight boundary at the interface, suggesting lower local fluctuations and a robustness of the interfacial water density structure. At larger distances from the surface, the water density levels off to the uniform bulk density, a typical indication of a random isotropic distribution of the molecules. The first peak of the oscillating water density for the surface with an area per fluorocarbon molecule at 28 Å^2 is located at $\sim 3 \text{ Å}$ from the surface, approximately the contact distance between water oxygen atom and surface fluorine atom. The ordering of the water molecules near the hydrophobic surface becomes less apparent as the surface density of fluorocarbons decreases. As shown in figure 4, the height of the first peak in the oscillating region of water density decreases for the surface with the area of 36 Å^2 per fluorocarbon molecule, and the density oscillation almost completely disappears at $44 \text{ Å}^2/\text{molecule}$. At the same time, the density of the water molecules near the surface decreases more gradually from its bulk value to zero for the lower surface densities, implying a softer interface and less ordering in the region. The bigger fluctuation and roughness of the fluorocarbon surface at lower densities can be considered to play a crucial role in creating such a soft interface and less ordering of water molecules.

The penetration of water molecules into the grafted fluorocarbon layer is shown in figure 5, where the density profiles of the water oxygen (solid blue line) and the surface carbon (solid red line) atoms along the direction normal to the surface are plotted using the left-side axis for three different areas per fluorocarbon molecule at 28, 36, and 44 Å^2 , with static anchors. The densities were calculated using only the molecules in a cylinder of radius 1.0 nm around the droplet axis. Clearly the water penetration into the fluorocarbon surface is minimal for the smallest area per molecule (i.e., the highest surface density) at $28 \text{ Å}^2/\text{molecule}$, and gradually increases as the per-molecule area increases (i.e., the surface density decreases) to $36 \text{ Å}^2/\text{molecule}$ to $44 \text{ Å}^2/\text{molecule}$. The lateral mobility of the anchors appears to have little or no effect on the degree of penetration for the areas per fluorocarbon molecule at 28 and $36 \text{ Å}^2/\text{molecule}$ (not shown). The density profile of the surface chains changes gradually from highly-ordered to a more random structure in figure 5, and its correlation with the degree of water penetration is evident.

Closely related to the water depletion near the hydrophobic surface is the hydrogen bond network of the water molecules around the surface. The disruption of hydrogen bonds due to topological constraints, combined with the absence of attractive interactions, is generally

accepted to be the key mechanism for the formation of a depletion layer in water density near an extended hydrophobic surface. In order to locate hydrogen bonds, we used the following geometric criteria widely used in the literature^{31,32}: among all the possible Donor-Hydrogen-Acceptor (D-H-A) combinations, those with D-A distances equal to or less than 0.35 nm and H-D-A angles equal to or less than 30 degrees are counted as hydrogen bonds. The right-side axis in figure 5 shows the average number of hydrogen bonds per water molecule, N_{HB} (green line), along the direction z normal to the perfluorocarbon surface. The center of the H-A bond in a qualifying D-H-A combination was taken as the location of each hydrogen bond. Overall, the hydrogen bond profiles roughly follow a trend similar to the water density profile, and the number of hydrogen bonds per water molecule far away from the surface is around 3.4, which agrees with the literature value for bulk water.³² A closer look at figure 5(a) reveals that the first peak (solid vertical line) for the number of hydrogen bonds per water molecule is located between the first and the second peak for the water density profile (dashed vertical lines), while the number of hydrogen bonds drops quickly near the surface as the very first layer of water molecules interfacing with the surface cannot form hydrogen bonds in the direction towards the surface. The surge in the number of hydrogen bonds between the first and second layer of water molecules means a locally tight structure of the two water layers by the extra hydrogen bonds in the region. This is consistent with the high degree of spatial ordering of water molecules in the first two layers manifested by the oscillating density profile and the robust interfacial structure of the water molecules, as discussed earlier. When the surface density of fluorocarbon decreases and more water molecules penetrate into the surface, as shown in figure 5(b) and (c), the number of hydrogen bonds per water molecules does not vanish immediately inside the surface layer. Instead, it drops rather slowly, as more water molecules that penetrate the surface start to find other water molecules to form hydrogen bonds with, which creates energetic gain to offset the unfavorable hydrophobic interactions and allows water molecules to remain inside the hydrophobic surface layer.

The penetration of the water molecules into the fluorocarbon surfaces at lower densities can be visually confirmed from simulation snapshots. Figure 6 shows the final snapshots at $t = 5$ ns for the areas per surface molecule at (a) 28 and (b) 44 Å²/molecule with static anchors. Clearly, the water molecules on top of the surface with a small area per molecule (i.e., high-density surface) at 28 Å²/molecule mostly remain outside the surface with almost no penetration into the surface, while a significant number of water molecules penetrate into the fluorocarbon surface and remain in the gaps among the fluorocarbon molecules for the surface with an area per molecule at 44 Å²/molecule. This supports the argument that the water penetration into the fluorocarbon surface occurs to a relatively high degree when the surface density of fluorocarbons is low enough to create gaps and pockets sufficiently large to accommodate and stabilize water molecules by means of water-water hydrogen bonds. Snapshots from our simulations (not shown here) demonstrate that there are indeed more water-water hydrogen bonds inside the surface at a lower density than at a higher one. However, a higher degree of water penetration into the surface of hydrophobic molecules may not necessarily mean a higher degree of wetting. Figure 7 shows a histogram of the distances between surface fluorines and the water oxygens for 28 and 44 Å²/molecule with static anchors. The case for 44 Å²/molecule has consistently less F-O pairs for each distance range than for 28 Å²/molecule, meaning that overall the water molecules stay farther away from the surface in the former than in the latter. The results are consistent with the change in the droplet average shape between the two surface densities, as shown in figure 8. The droplet on the 28 Å²/molecule surface is almost perfectly capped-spherical, while the shape of the droplet on the 44 Å²/molecule surface is significantly elongated in vertical direction. Due to the deformation of the droplet shape, the radius of the droplet at the surface contact is much smaller at $r = 1.4$ nm for the 44 Å²/molecule case than the radius of droplet at $r = 2.3$ nm for the 28 Å²/molecule case. This leads to a decrease in the contact area between the water droplet and the surface by a factor of 2.7, assuming an ideal flat interface without surface roughness and water penetration.

In practice, the bigger surface roughness and the higher water penetration for lower-density surfaces increase the effective contact area, partially offsetting the effect of contact area shrinking due to the shape deformation. The F-O distance histogram in figure 7 suggests that the effect of the contact area reduction due to the deformation in the droplet shape is larger than the effect of the contact area increase due to the surface roughness and water penetration.

The origin of the deformation in the droplet average shape for lower surface is not clear. A possible explanation is that the deformation is driven by the larger temporal fluctuations in the motion of the surface fluorocarbon molecules at the lower surface density. Since the water droplet is located right on top of the surface, the vertical component of the surface fluctuations can directly interfere with the domain of water droplet and efficiently transfer extra momentum to the water molecules in contact. On the other hand, the lateral components of the fluctuations do not interfere with the water domain and should have only marginal effect on the lateral motion of the water molecules. The result is a net momentum gain of the water molecules in vertical direction, which can lead to a vertically-stretched droplet.

We have seen so far that the structure of water near the hydrophobic fluorocarbon surface is critically affected by the detailed local surface structure. Now we consider the local changes in surface structure and morphology induced by water molecules. Such changes can be examined by resolving out the local surface density of fluorocarbons below the water droplet in comparison with the surface density outside that region. Figure 9(a) shows the density profiles of surface carbon atoms along the surface normal direction below and outside the water droplet for the surface with area per fluorocarbon molecule at $28 \text{ \AA}^2/\text{molecule}$ and fixed anchors. At this high surface fluorocarbon density with immobile anchors, the local density profiles are almost identical between two local regions in the surface. When the area per fluorocarbon molecule increases (i.e., the surface density of fluorocarbon decreases) to $36 \text{ \AA}^2/\text{molecule}$ with the anchors remaining fixed, as shown in figure 9(b), the local surface fluorocarbon density right below the water droplet becomes bigger than the one outside. This suggests that the hydrophobic surface molecules below the water droplet collapse to each other in order to minimize the water penetration. From a thermodynamic point of view, such a process in principle generates an energetic gain by reducing the number of unfavorable contacts between fluorocarbon and water molecules, which apparently outweighs the entropic cost associated with the collapse. The difference in local fluorocarbon density between below and outside the water droplet is even bigger for the surface with an area per molecule at $44 \text{ \AA}^2/\text{molecule}$ as shown in figure 9(c). The large energetic gain associated with the self-aggregation of the surface fluorocarbon molecules is confirmed by the short-range non-bonding interaction energy among surface fluorocarbon molecules, which drops more than 400 kJ/mol during the simulation for the case of $44 \text{ \AA}^2/\text{molecule}$. That energy is large enough to compensate for the marginal increase in the water-water ($\sim 140 \text{ kJ/mol}$ increase) and water-fluorocarbon ($\sim 50 \text{ kJ/mol}$ increase) short-range non-bonding interaction energies in the simulation. These results suggest that the surface fluorocarbon molecules, originally frustrated with the water penetration, gain a large thermodynamic stability by collapsing to each other at the cost of a small penalty for the water molecules.

For mobile anchors the local effect of surface collapse seems to be even more enhanced, as shown in figure 10. That is, the surface with an area per molecule of $28 \text{ \AA}^2/\text{molecule}$, figure 10(a), already shows a difference in local surface fluorocarbon density below and outside the water droplet, as opposed to the case with fixed anchors, figure 9(a). This is qualitatively consistent with the effective area per molecule we introduced earlier in the discussion regarding figure 3. The anchor mobility of the surface fluorocarbon molecules appears to facilitate a local collapse of the surface molecules in response to the presence of water molecules at a density near the close packed configuration. The same effect is observed at the lower fluorocarbon surface density shown in Figure 10(b).

The changes in surface morphologies induced by water droplet can be probed further by inspecting the horizontal profiles of the top surface layer. Figure 11 shows the 2D topology of the time-averaged height of the surface fluorocarbons around the center of mass of the droplet for the area per molecule at $44 \text{ \AA}^2/\text{molecule}$ with static anchors. Despite the large disorder and roughness, the surface shows a clear elevation in a ring shape around the distance of 2 nm (bright yellow color in figure 11), which is just outside water-vapor-surface interface (dotted circle). Inside the ring of elevation, the surface height appears slightly lower in comparison with the surface level outside the elevated ring region. This observation is confirmed in figure 12(a), which shows the topology of the fluorocarbon surface in the radial direction. Indeed, the fluorocarbon surface is lower in the region close to the center of the droplet and higher near and right outside the edge of the droplet where the droplet boundary touches the surface. The maximum elevation is about $1 \text{ \AA}$ from the lowest bottom, which is small but persistent. Such a unique surface topology at the interface with water, combined with the higher local fluorocarbon density at the region below the droplet as shown in figures 9 and 10, suggests a possible mechanism of surface organization. The surface fluorocarbon molecules inside the water-vapor-surface interface, facing direct contact with water molecules from above, collapse to each other in order to minimize the area of contact with the water molecules. This brings down the average height of the fluorocarbon surface in the region, as observed in figure 12(a). The higher local surface density of fluorocarbons below the droplet implies that some fluorocarbon molecules outside the three-phase contact line may also lean into the collapsed region, rendering the surface region interfaced with droplet to become more resistant to water penetration. Meanwhile, most of the surface fluorocarbon molecules located just outside the water-surface-vapor contact line spontaneously rearrange and tightly align around the interface, generating the elevation in surface topology along the circular boundary and lowering the surface height outside next to the elevation. The collapse of the surface fluorocarbon molecules in the central region at lower surface fluorocarbon density opens up spaces between collapsed bundles of fluorocarbon molecules below the water droplet, which allows some water molecules to penetrate, as shown in figure 6(b).

The spontaneous reorganization of the surface fluorocarbon molecules is observed for the higher density surfaces of fluorocarbons, as shown in figure 12(b). In this case, however, the surface topology seems to take a different shape; the surface fluorocarbon molecules appear to avoid the region near the three-phase boundary line and lean toward the inner side of the droplet, as evidenced by the dip in the surface level near the boundary line at $r = 2 \text{ nm}$ and the monotonic increase in surface height towards the center of the droplet in figure 12(b), which generates a convex profile of the fluorocarbon monolayer under the water droplet. The magnitude of the change in fluorocarbon surface height due to the reorganization in this case is even smaller and may be a potential challenge for experimental test.

4. Summary and Conclusions

In this article we presented the study of water nanodroplets on self-assembled monolayers of perfluorocarbon molecules using molecular dynamics simulations. Despite the tremendous success in applications of Young's equation and contact angle to a wide variety of macroscopic systems for characterizing the hydrophobic properties of surface, their validity at length scales around and below 10 nm remains elusive. Our results show that the solid-liquid and solid-gas surface tensions vary in a systematic way with the change in surface fluorocarbon density. However the contact angles, measured directly from the water density profiles, displayed only a mixed and marginal agreement with the macroscopic experimental measurements, and did not present any consistent trend against the changes in the surface density of fluorocarbons. We also determined contact angles from the surface tensions by using Young's equation, and they also showed no apparent pattern against the change in surface density of fluorocarbons. The relatively large fluctuations in the surface tensions caused difficulty in determining the

contact angles according to the Young's equation. The results strongly suggest that, while surface tension may remain valid to reflect the changes in surface density of fluorocarbons at a molecular length scale, the contact angle and Young's equation applied to a system at a molecular length scale do not properly represent the surface characteristics unlike the way they do when applied to macroscopic systems. This means that Young's equation and the conventional concept of contact angle do not offer any insight into the systems at a nanometer length scale. Future work may include the line tension corrections to see any difference in contact angle behavior.

The ordering of the water molecules near hydrophobic surfaces is most robust and tight for higher surface densities of fluorocarbons, while the lower surface fluorocarbon density with increasing water penetration tends to diffuse the interface and to reduce the spatial ordering of water molecules. The existence of water depletion - a liquid-to-vapor-like transition at interface - near a flat hydrophobic surface, which has been discussed in the literature, was tested for the simulated systems. The depletion zone was measured to be non-existent or at most smaller than the size of one water molecule. The structure of the hydrogen bond network among the water molecules was shown to be highly dependent on the interfacial surface structure, and to play a crucial role in determining the water density structure at the interface. Depending on the surface density of the fluorocarbon molecules, the local fluorocarbon density profile under the water droplet can become significantly higher than outside, due to a collapse of the surface molecules in response to frustration with water penetration. We find that larger penetration of water molecules into the fluorocarbon surface does not necessarily lead to a higher degree of wetting, as measured by water-fluorocarbon contacts, possibly because the deformation in the droplet shape significantly decreases the water-surface contact area which apparently outweighs the competing factors such as the surface roughness and the water penetration.

The delicate balance of many different interactions among water molecules and the surface fluorocarbons in combination with the change in surface fluorocarbon density produced unique interfacial behaviors for both the water molecules and the fluorocarbon surface. Just as the hydrophobic surface induces the structural changes to the water droplet on it, the water droplet induces structural changes to the underlying surface. Depending on the surface density of fluorocarbons, two different surface morphologies have been observed and a possible mechanism of the morphology formation has been proposed. The fluorocarbon density dependent surface reorganization induced by water droplet may be reminiscent of many biological processes such as lipid membrane formation and protein folding. The delicate changes in surface topology at the water-vapor-surface interface should also be relevant for the determination of the line tension and may be worth for further study.

Acknowledgments

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6. References

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Figure 1.

Typical snapshots of the simulated system at (a) $t = 0$ and (a) $t = 5$ ns. The atoms in water molecules are shown in red (oxygen) and white (hydrogen), the surface fluorocarbon molecules in white (fluorine), cyan (carbon), and green (anchor), and the inert substrate atoms in pink. The case for the per-molecule surface area of $28 \text{ \AA}^2/\text{molecule}$ with mobile anchors is shown.

Figure 2.

(a) The fitting of the radial density of water droplet to the hyperbolic tangent function in eq (2) to determine the liquid-vapor interface. The red dots are the density profile of water from the simulation at a fixed z ($z = 3$ nm in this case) and the blue line is the fitting curve. The equimolar surface at $r = r_e$ was taken as the interface. (b) A typical fit of the liquid-vapor interface (dots) to a fourth-order polynomial (dotted line). The horizontal solid line is the location of the surface. The case shown is for an area per fluorocarbon of $28 \text{ \AA}^2/\text{molecule}$ with fixed anchors.

(a)

(b)

(c)

Figure 3.

(a) Contact angles of water droplet on fluorocarbon surface with static and mobile anchors for different areas per molecule. The contact angles were determined by fitting to a fourth-order polynomial. The contact angles for the cases of surface molecules with mobile anchors are plotted against nominal (solid blue circle) and effective (solid green square) areas per molecule. (b) The solid-liquid and solid-gas surface tensions, calculated from pressure tensors, and the corresponding contact angles in the inset, determined by Young's equation, for different areas per molecule. (c) The nominal vs. effective area per molecule below water droplet for the surfaces with mobile anchors.

Figure 4.

The normalized water density profiles as a function of the distance from the surface (z -direction) through the center of mass of the droplet, for the areas per fluorocarbon ranging from 28 to $44\text{\AA}^2$ /molecule.

Figure 5.

The left-side axis represents the density profiles of oxygen atoms in water molecules (solid blue line) and the carbon atoms in surface fluorocarbons (solid red line) along the vertical direction for areas per fluorocarbon of (a) 28, (b) 36, and (c) 44 $\text{\AA}^2/\text{molecule}$. The axis on the right side represents the average number of hydrogen bonds per water molecule (solid green line) along the direction normal to the surface.

Figure 6. The final snapshots of the interface at $t = 5$ ns for areas per fluorocarbon of (a) 28 and (b) 44 $\text{\AA}^2/\text{molecule}$, with static anchors. The surface molecules are shown in the lower half in grey (fluorine), blue (carbon), and green (anchor), while water molecules in red (oxygen) and white (hydrogen).

Figure 7. Histograms of the distances between the surface fluorine atoms and the water oxygen atoms for area per fluorocarbon of 28 and 44 Å²/molecule, with static anchors.

Figure 8.

The shape of the water droplet on the surface for areas per fluorocarbon of 28 (blue) and 44 Å²/molecule (red), with static anchors. The horizontal lines represent the topology of the fluorocarbon surface.

Figure 9.

The density profiles of surface carbon atoms as a function of the distance normal to the surface for molecules below (black) and outside (red) water droplet. The fluorocarbon areas per molecule are (a) 28, (b) 36, and (c) 44 Å²/molecule, and all correspond to fixed anchors.

Figure 10. Same as Figure 9 but for mobile anchors at (a) 28 and (b) 36 Å²/molecule.

Figure 11.

The average two-dimensional topology of the surface height around the center of mass of the droplet for area per fluorocarbon of $44 \text{ \AA}^2/\text{molecule}$ with static anchors. The dotted circle represents the location of the liquid-surface-vapor interface.

Figure 12.

The surface topology in the radial direction from the center of mass of the water droplet for fluorocarbon areas per molecule of (a) 44 and (b) 28 Å²/molecule, with static anchors.