# Static and dynamic hydrophobicity on a nano-sized groove/ridge surface

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## ARTICLE INFO

## ABSTRACT

Static and dynamic hydrophobicity is of importance to many industries. Since structures at the nano-scale influence wetting at the macro-scale, molecular dynamics simulations were conducted to investigate the hydrophobicity of a groove/ridge textured surface. The equilibrium states of water droplets on surfaces with different ridge heights and groove widths were obtained. The contact angles of these static droplets were evaluated and then three different forces were used to evaluate the dynamic hydrophobicity of each surface. Forces were applied to each droplet in the direction parallel to the ridges and also perpendicular to the ridges. The surfaces' hydrophobicity was evaluated quantitatively using the differences in the advancing and receding contact angles. It was found that although the contact angles of the static droplets were larger in the direction perpendicular to the ridges, the droplets were dynamically more hydrophobic in the direction parallel to the ridges. It was also shown that as the ridge surface fraction increased the ridge height had less of an effect on the hydrophobicity.

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## 1. Introduction

It was observed by Wenzel [1] that some droplets completely filled the roughness of surfaces and he was able to calculate the apparent contact angle given the surface roughness for droplets in the so called Wenzel state. Later Cassie and Baxter [2] recognized that some droplets sat on top of the roughness of surfaces and derived another equation to calculate the apparent contact angle for droplets in the so called Cassie state. Since then controlling the hydrophobicity of surfaces has been a goal in many industries. It is known that the appropriate surface characteristics can enhance or inhibit hydrophobicity. Identifying and manipulating these characteristics has been the focus of many studies at the macro, micro and nano-scales [3–9]. These controlling characteristics can be applied to surfaces in several different ways including adjusting the surface energy and/or applying appropriate surface roughness. While the application of coatings to surfaces has been widely used, coatings wear off and may not be appropriate for all environments. There are many factors that affect the wetting of a surface.

At the micro-scale experiments have been carried out to investigate hydrophobicity. Song et al. [10] evaluated the sliding acceleration of water droplets on various line-patterned surfaces.

They showed that the siding acceleration of a droplet can be controlled by changing the pattern structure and its chemical properties. It was also noted that sliding angle and hysteresis was dependent on the line-pattern thickness. An earlier study by Yoshimitsu et al. [11] conducted experiments at the micro-scale recording the sliding angle of water droplets on grooved and pillared surfaces as a function of droplet weight. They found that the grooved surface had the lowest sliding angle if the droplet was moving parallel to the groove. The next lowest sliding angle belonged to the pillared surface, and the largest angle belonged to the grooved surface with the droplet moving perpendicular to the grooves.

These afore mentioned studies shed light on hydrophobicity at the micro-scale, however nanostructures are also known to affect hydrophobicity. Several studies [12–15] have proven that multiple length scales of surface roughness including the nano-scale can contribute to decreasing contact angle hysteresis and improving hydrophobicity at larger scales. Therefore it is important to understand hydrophobicity at the nanoscale to improve hydrophobicity at the mirco-scale and macro-scale. Due to the difficulty of conducting experiments at the nano-scale, Molecular Dynamics (MD) simulations have been employed to simulate surfaces and droplets at the nano-scale. Jeong et al. [16] investigated two pillar structures both with a pillar surface fraction of 25%. Later Ambrosia et al. [17] considered pillars with different pillar surface fractions and showed that pillar surface fractions greatly affect the

hydrophobicity of a surface. Yong and Zhang [18] published an interesting study of a liquid mercury droplet on grooved copper structures with various roughness factors using MD simulations and found that static contact angles agreed quite well with the Wenzel and Cassie theories. They further noted that when the roughness factor is large, contact angles deviated from Cassie's predictions. Their cases only included static droplet contact angles, and static hydrophobicity does not always correspond with dynamic hydrophobicity. Hirvi and Pakkanen [19] used MD simulations and showed the resulting sliding distances for water droplets on grooved and pillared polyethylene and poly vinyl chloride. They found that the pillared polyethylene surface gave the longest distance traveled given an initial velocity. However they did not investigate the effect of the surface fraction or height of the texture.

As studied before with pillared surfaces, the surface fraction of the textured surface is especially of interest because it is a factor in the Cassie-Batxer [2] equation predicting contact angles of droplets on textured surfaces which do not completely wet the surface. In their equation

$$\cos\theta = f(\cos\theta_0 + 1) - 1 \qquad (1)$$

the apparent contact angle, $\theta$, of a droplet is approximated by the surface fraction of the texture, $f$, and the contact angle of droplet on a completely flat surface, $\theta_0$. Therefore if the droplet sits on top of the texture and does not completely wet the surface, the Cassie–Baxter equation shows surface fractions of t he texture will play a significant role in the magnitude of the contact angle of the droplet. Since texture surface fraction has such an influence on droplet contact angles and surface hydrophobicity it was found necessary to study this area deeper.

In this study MD simulations were used to investigate the static and dynamic behavior of nano-sized water droplets on grooved graphite surfaces with various Ridge Surface Fractions (RSFs). Although pillar surface fractions have recently been investigated, groove/ridge surface fractions have very unique characteristics and was the focus of this research. This study will bring a new understanding of static and dynamic hydrophobicity on grooved surfaces with varied surface fractions and depths at the nano-scale. It is shown that static contact angles do not correlate with dynamic hydrophobicity. Unique to previous studies, the dynamic hydrophobicity of a grooved surface when a nano-scaled droplet is moving parallel to the ridges is compared to that of a droplet moving perpendicular to the ridges as three different forces are applied to the droplet on a surface with four different RSFs and five different ridge heights.

## 2. Simulation details

Molecular dynamics simulations were used to model static and dynamic water droplets on grooved graphite surfaces at the nanoscale. A parallel MD package called NAMD [20] was used to simulate the physical movement of atoms by summing up the forces on each atom and solving Newton's equation of motion for each time step of 2.0 fs. Simulations of 5124 TIP3P water molecules were run on graphite surfaces with spatially fixed graphite atoms. The TIP3P water model has three charges, +0.417 $e$ for the H atoms and −0.834 $e$ for the O atom with an angle of 104.52° between the atoms and uses Lennard-Jones parameters of $\sigma$ = 3.15061 Å and $\varepsilon$ = 0.152 kcal/mol. A standard cutoff radius of 12 Å with a switching distance of 10 Å was used in the simulations. The NVT ensemble was used keeping the number of molecules, volume and temperature constant as simulations were conducted. As the droplets were run to equilibrium on the graphite surface laid out in the x–z plane for the static cases, the computational domain was

140 Å × 180 Å × 140 Å in the $x$, $y$, and $z$ directions, respectively. As the applied force was added for the dynamic cases the surface and computational domain was extended to 280–300 Å depending on the period of the ridge and groove size in the direction of the droplets movement ($x$-direction for the movement parallel to the ridges and $z$-direction for the movement in the perpendicular direction). Periodic boundary conditions were imposed to simulate an infinite plane.

The grooved graphite surfaces had ridges in the $x$-direction and were 7.36 Å in width. The grooves between the ridges varied to give four RSFs. Four groove widths of 22.10 Å, 12.28 Å, 7.36 Å, and 4.91 Å in the $z$-direction gave four RSFs of 25% ($R_1$), 37.5% ($R_2$), 50% ($R_3$), and 60% ($R_4$), respectively. There were six ridge heights ranging from 0.00 Å ($H_0$) to 16.75 Å ($H_5$) at an increment of 3.35 Å due to graphite's layered structure. Simulations were run for an initial water box of 5124 water molecules at a constant temperature of 298.15 K until equilibrium was reached. Then simulations continued for an additional 4.0 ns and contact angles were measured every 5 ps and averaged. The contact angles were defined at the edge of the droplet surface where the density of the water molecules was 50% of that of the center of the droplet. Uncertainty of the contact angles were calculated using the standard deviation of the contact angles over the final 4.0 ns of the simulation and are shown as error bars in the figures. Due to the anisotropic shape of the static water droplet, contact angles were measured perpendicular and parallel to the ridges.

To validate the simulations of water on a graphite surface, the contact angles of Fowkes and Harkins [21] of 85.3–85.9° on a flat surface were used as the reference for this study. It was found that Lennard-Jones parameters of $\sigma$ = 1.9924 Å and $\varepsilon$ = 0.0355 kcal/mol gave the time average contact angle of 85.9° on a flat surface. As interactions between different substances occurred the characteristic energy used was $\varepsilon_{ij} = (\varepsilon_i \cdot \varepsilon_j)^{1/2}$.

Initially MD simulations of the water droplet ran until equilibrium was reached on each surface. Then after evaluating the contact angles parallel and perpendicular to the grooves, a force was applied parallel and perpendicular to the droplet and the advancing and receding contact angles of the droplet were calculated and recorded.

## 3. Results

### 3.1. Static water droplets

Since the groove/ridge structure is one dimensional, in most cases the contact angles in the $x$–$y$ plane were different than the contact angles in the $z$–$y$ plane. This difference was most apparent in the cases with surface fractions of $R_1$ and $R_2$. In these cases the water molecules had enough room to fill the grooves even when the grooves were deep. Table 1 shows the contact angles in the $x$–$y$ plane (parallel to the ridge, ‖) and $z$–$y$ plane (perpendicular to the ridge, ⊥) for each ridge surface fraction at each ridge height.

**Table 1**
Contact angles parallel to the ridge (‖) and perpendicular to the ridge (⊥) for each surface fraction and ridge height.

| Ridge surface fraction | $H_1$ (°) | $H_2$ (°) | $H_3$ (°) | $H_4$ (°) | $H_5$ (°) |
|---|---|---|---|---|---|
| 25.0% ‖ | 93.7 | 94.3 | 92.3 | 85.7 | 87.8 |
| 25.0% ⊥ | 110.8 | 110.8 | 134.9 | 133.8 | 135.4 |
| 37.5% ‖ | 99.0 | 106.9 | 107.6 | 114.8 | 120.0 |
| 37.5% ⊥ | 112.7 | 131.0 | 130.9 | 129.6 | 131.4 |
| 50.0% ‖ | 103.8 | 111.7 | 113.7 | 113.1 | 113.6 |
| 50.0% ⊥ | 102.1 | 115.7 | 118.5 | 116.3 | 107.3 |
| 60.0% ‖ | 103.5 | 108.7 | 108.7 | 109.6 | 108.7 |
| 60.0% ⊥ | 105.7 | 108.0 | 110.2 | 110.1 | 111.5 |