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The effect of pillar surface fraction and pillar height on contact angles using molecular dynamics

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ABSTRACT

Predicting hydrophobicity is very important in manufacturing products with self-cleaning properties. This study focuses on the effect of graphite surfaces with pillars of different surface fractions and heights on the contact angles of a nano-sized water droplet. This study used molecular dynamics simulations to investigate the hydrophobic properties of water droplets on the nano-scale. The contact angles were calculated and averaged over time for each case. Results showed the droplets in either the Wenzel state or the Cassie state. In general, as the pillar height increases the static contact angle increases to a certain point when the pillar height no longer has a significant effect on the contact angle. Over all, the smaller the pillar surface fraction the larger the change in the contact angle as the pillar height increased. As pillar surface fractions decreased from 36%, simulated contact angles undershot Cassie predictions at increasing amounts due to part of the water droplet sagging below the pillar tops. Graphite displayed anisotropic characteristics due to its layered structure which caused the contact angles to increase as surface roughness increased even though its Young contact angle was less than 90 degrees.

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1. Introduction

Water has been studied for thousands of years because of not only its importance to human life but also its unique properties. More recently the interaction of water on solid surfaces has been studied and attention has been drawn to hydrophobicity, the ability of a surface to repel water. Effective hydrophobicity can be affected by many factors, especially surface roughness. The Wenzel [1] state and the Cassie and Baxter [2] state are two models that characterize droplets on rough surfaces. Wenzel identified a state where the droplet fills the space in the roughness on surfaces. In this case Wenzel modified Young's equation to approximate the contact angle, θ, on a rough surface as

$$\cos \theta = r \cos \theta_0 \qquad (1)$$

where θ_0 is the contact angle on a perfectly flat surface known as the Young contact angle and r is the surface roughness factor. The surface roughness factor is the ratio of the actual area of the rough surface to the geometric projected area. This factor is 1 for a smooth surface and as the surface becomes rough it increases according to the roughness. In this study, roughness is in the form of a periodic array of quadrangular pillars (see Fig. 1) and as the pillar height

increases the roughness factor increases. Droplets that completely fill the roughness are said to be in the Wenzel state.

However, the liquid does not always fill in the roughness on the surface. In some cases the droplet sits on top of the surface roughness which corresponds to a more hydrophobic surface. In this case, where the Wenzel approximation fails, Cassie and Baxter were able to derive another equation to approximate the contact angle as

$$\cos \theta = f (\cos \theta_0 + 1) - 1 \qquad (2)$$

where θ is again the contact angle on the rough surface, θ_0 is the contact angle on a perfectly flat surface, and f is the ratio of the actual solid/liquid interface to the geometric projected area. This factor is 1 for a flat surface and for the present pillared surface it is equivalent to the Pillar Surface Fraction (PSF – to be defined below). Droplets that follow this description are said to be in the Cassie state.

Yet the Wenzel state and the Cassie state do not fully classify all droplet configurations on rough surfaces as presented by Marmur [3]. Furthermore, recent studies have shown that the classical Wenzel and Cassie models fail to predict contact angles on various surfaces [4–7]. Both the Wenzel and Cassie equations imply the contact angle is dependent on the surface area that the droplet covers. As early as 1945, Pease [4] proposed that the contact angle is a one-dimensional property and not dependent on surface area. Gao and McCarthy [5] observed contact angles that were
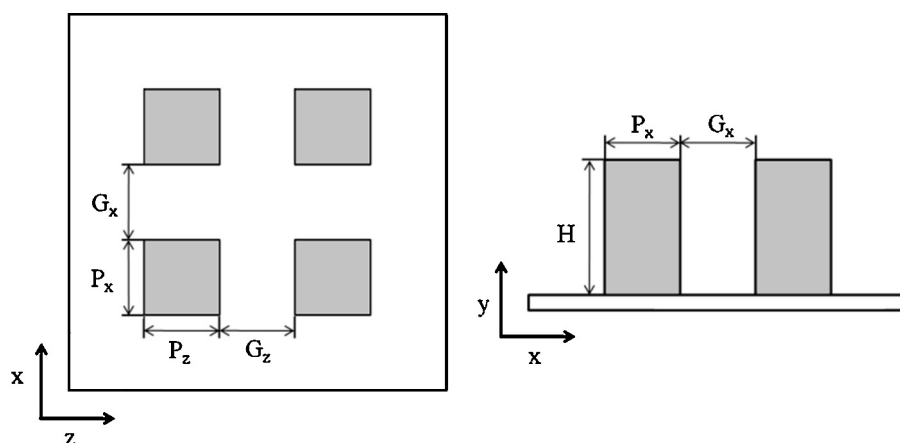
Fig. 1. Schematic of the pillar positions and dimensions.

significantly different from the Cassie prediction. With provocatively titled papers such as "How Wenzel and Cassie Were Wrong" and "Cassie and Wenzel: Were They Really So Wrong?" published in recent years it is clear that there are many other factors to consider in solid–liquid interactions [5,8]. Yet many other studies [6–8] call into question or give evidence for both the Wenzel and Cassie equations. Many factors need to be considered when attempting to control wetting on a rough surface [3–9]. Generally studies [7,9] agree that there are at least two limitations for the Wenzel and Cassie equations. The structures that form the texture should be much smaller than the liquid droplet and the structures need to be uniformly distributed to accurately predict the contact angles. Brandon et al. [10] studied droplets on a chemically heterogeneous surface and observed that the larger the droplet is compared to the scale of heterogeneity and/or roughness on the surface, the closer contact angle approaches the Cassie predicted contact angle. In addition to these factors, the position of the three phase contact line has an effect on the contact angle [7,10]. This study will refer to the Wenzel and Cassie equations but also show where they do not align with the computational results obtained here.

With improved computer speeds, molecular dynamics (MD) simulations of droplet interactions on rough surfaces are modeled at the nano-scale. Many studies [11–14] show water droplets to behave similar on the nano- and macro-scales since they observe good agreement between macro-scale experimental data and nano-scale MD simulations.

In the present study, MD simulations were used to investigate the hydrophobicity of a graphite surface with quadrangle pillars of different surface fractions and heights. The goal of this research is to understand how the pillar's surface fraction and pillar height of a layered anisotropic graphite surface affect the static contact angle of a water droplet at the nano-scale. To reach this goal, molecular dynamics simulations were prepared for a water droplet of 5124 molecules and run to equilibrium on surfaces with five different pillar heights and four different PSFs of a graphite surface. Then the contact angles were measured, averaged over time, and analyzed.

2. Computation method

The parallel molecular dynamics simulation package called NAMD was used to model the movement of a water droplet on a solid fixed graphite surface with quadrangle pillars [15]. Molecular dynamics simulations model the physical movement of atoms by calculating the sum of the different forces on those atoms and solving the Newton's equations of motion. To calculate those forces, the position of each atom is needed along with the interacting bonded and non-bonded potentials. The bonded potentials include atomic

bonds and angles between atoms. Non-bonded potentials include the Lennard–Jones and electrostatic potentials. The Lennard Jones potential, U_{LJ} accounts for the van der Waals forces attracting and repelling atoms depending on the distance r_{ij} between the two atoms.

$$U_{LJ} = \varepsilon_{ij}\left[\left(\frac{R_{min}}{r_{ij}}\right)^{12} - \left(\frac{R_{min}}{r_{ij}}\right)^{6}\right] \qquad (3)$$

where ε_{ij} and R_{min} are the characteristic surface energy and van der Waals radius, respectively.

The long-range electrostatic interactions were calculated using the Ewald method [16]. As the distance between atoms increase the Lennard–Jones potential quickly approaches 0 and is truncated at a cutoff radius of 12 Å with a smoothing function turned on at a switching distance of 10 Å. The potentials were numerically integrated using the velocity Verlet algorithm with a time step of 2.0 fs.

A NVT ensemble was used, which holds the number of atoms, volume and temperature constant as the calculations were being made. The temperature was set to 298.15 K and controlled using the velocity scaling method as calculations were conducted on 5124 TIP3P water molecules. The TIP3P water model has three charges, −0.834e for the O atom and +0.417e for the H atoms with an angle of 104.52° between the atoms. The O—H bonds are 0.9572 Å in length. Evaporation was insignificant in the simulations.

The (0 0 0 1) graphite surface was chosen for its hexagonal tabular structure and it was fixed spatially to reduce computational time. Its dimensions were $L_x \times L_z = 255\,\text{Å} \times 149\,\text{Å}$ with periodic boundaries in each direction. Three layers of graphite were used under the pillars to ensure enough thickness to simulate an infinitely thick graphite surface. For a fixed pillar size, four different gaps in the x and z directions between the pillars was used to give surface fractions of 15%, 20%, 25%, and 36%. The pillar's lateral dimensions were $P_x \times P_z = 8.51\,\text{Å} \times 7.37\,\text{Å}$. Fig. 1 shows the pillar dimensions. The gaps between the pillars $G_x \times G_z$ and corresponding pillar surface fraction are found in Table 1. The y-direction of the domain was 255 Å to ensure that it was large enough so that

Table 1
Lateral pillar and gap dimensions and corresponding pillar surface fractions.

P_x (Å)	P_z (Å)	G_x (Å)	G_z (Å)	Pillar surface fraction
8.51	7.37	12.76	12.28	15%
8.51	7.37	9.93	9.82	20%
8.51	7.37	8.51	7.37	25%
8.51	7.37	5.67	4.91	36%