International Journal of Heat and Mass Transfer 79 (2014) 647–654

Contents lists available at ScienceDirect

International Journal of Heat and Mass Transfer

journal homepage: www.elsevier.com/locate/ijhmt

Static and dynamic behavior of water droplet on solid surfaces with pillar-type nanostructures from molecular dynamics simulation

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ARTICLE INFO

Article history:
Received 25 April 2014
Received in revised form 14 August 2014
Accepted 22 August 2014
Available online 16 September 2014

Keywords:
Water droplet
Cassie
Wenzel
Vibration
Molecular dynamics simulation

ABSTRACT

Predicting the droplet state accurately is significant in manufacturing rough surfaces with superhydrophobic properties. We use molecular dynamics simulation to investigate the static behavior of the water droplet on solid surfaces featuring pillared structures. Results show that the droplet in either the Wenzel state or the Cassie state depends on the height of the pillars and the pillar surface fraction. We then apply a vibration to the smooth or rough surface and evaluate the dynamic behavior of the water droplet. In general, the smooth surface becomes more hydrophobic due to the presence of vibration and the water droplet on the pillared surface is able to transform from the Wenzel state to the Cassie state even though the former is originally favored. In addition, the vibration must meet certain conditions to achieve this transition and the droplet will separate from solid surface while continuing to enhance the vibration.

1. Introduction

The hydrophobicity and superhydrophobicity are very common phenomena in nature, such as lotus leaves [1] and water strider legs [2]. Droplets exhibit a high contact angle (>150°) and small contact angle hysteresis (<10°) on the surface of lotus or strider legs, therefore, droplets are easy to fall off from the lotus surface or the strider could walk on the water. Understanding the wetting phenomena is useful in many areas, e.g., self-cleaning [3], water recovery [4,5] and heat transfer enhancement of the dropwise condensation [6–8]. The wettability or dewettability is affected by many factors including the properties of the interactions between liquid and solid, surface roughness, and even additional electric field [9] or vibration of the substrate [10]. Existing research has indicated that the lotus leaf is covered by numerous microstructures, which contribute to the leaf superhydrophobicity [11]. In general, microtextured or nanotextured hydrophobic surfaces can transform into superhydrophobic state like lotus leaves. When a water droplet is placed on a structured hydrophobic surface, it will exhibit two different states. If the water droplet can suspend on the microstructures, it exhibits the Cassie state [12], otherwise the droplet is penetrated by the microstructures and shows the Wenzel state [13]. Studies have shown that many factors should be taken into account when trying to control the droplet state on the microtextured or nanotextured surface. Jeong et al. [14] investigated the static and dynamic behavior of water droplets on solid surfaces featuring pillar-type nanostructures using molecular dynamics simulation, and the droplets exhibited different states depending on the height and the lateral and gap dimensions of the pillars. Koishi et al. [15] performed molecular dynamics simulation to measure the contact angle hysteresis for a water droplet placed on a nanopillared surface and found that the droplet could be in the Cassie state or the Wenzel state depending on the size and initial state of the droplet. Yen [16] explored the wettability of a nanoscale water droplet on the Si(1 1 1), Si(1 0 0) and Si(1 1 0) surfaces with various surface morphologies using molecular dynamics simulation and disclosed interesting physics about the influences of wall lattice and surface microstructure. Lundgren et al. [17] indicated that the relative sizes of the domains and the droplets played an important role on heterogeneous patterned surfaces and showed clearly the importance of the detailed topography and composition of the solid surface.

As mentioned in previous studies, the droplet exhibits two different states on the rough surface and the transition from the Wenzel state to the Cassie state were also studied. Koishi et al. [18] computed the free-energy barrier separating the Wenzel and Cassie state based on both raining experiments and a statistical-mechanics method on the molecular level. Bahadur et al. [9] found that applying a voltage is a powerful tool to alter the relative stabilities of the Cassie and Wenzel states and enable dynamic control of droplet morphology on rough surface. Krupenkin et al. [19] demonstrated experimentally and theoretically that the droplet behavior can be reversibly switched between the Cassie state and the Wenzel state by the application of electrical voltage and current. In

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http://dx.doi.org/10.1016/j.ijheatmasstransfer.2014.08.047
0017-9310/

addition, water droplet can transform from the Wenzel state to the Cassie state by heating the substrate or directly heating the droplet using a pulsed laser [20]. Compared to other methods, vibration proved to be an effective and convenient method to achieve this transition based on previous studies. Lamb [21] obtained a general expression for different vibration modes of a free liquid drop surrounded by an outer fluid. Celestini and Kofman [22] continued exploring the Lamb's theory and developed a new expression about the case of a liquid drop in partial contact with a substrate. Reyssat et al. [23] investigated self-propulsion of drops on gradients of texture with the assistance of vibration and proposed that an asymmetric dewetting takes place for each cycle of the vibration, which caused an incremental drift of the droplet towards the region of high texture density. Experiments [24] showed that the vibration could be used to overcome the energy barrier for transition from the Wenzel state to the Cassie state, moreover, the threshold for the transition follows a scaling law comparing the kinetic energy imparted to the drop with the work of adhesion. Lei et al. [25] observed that the vibration amplitude which induces a droplet to bounce off from the superhydrophobic surface at the resonant frequency is remarkably smaller than the detaching amplitudes of neighboring frequencies. Kou et al. [26] investigated the influence of vibration on the interaction between the droplet and smooth surface by using molecular dynamics simulation and indicated that the wetting degree could be modulated by the substrate vibration period and substrate vibration amplitude.

Existing studies have investigated the influence of roughness structure on droplet state in nanoscale or macroscale. However, to the authors' best knowledge, the transition from the Wenzel state to the Cassie state of a nanoscale droplet or the escape phenomenon caused by vibration on a rough surface has not yet been studied. In this work, the static behaviors and the dynamic state transition caused by vibration of a water droplet on solid surfaces with pillar-type nanostructures are studied using molecular dynamics simulation. The main purpose of this work is to understand how the coupled existence of pillars and vibration affects the water droplet state on the rough surface.

2. Simulation details

All simulations are performed based on the LAMMPS package [27]. To investigate the droplet behavior on the solid surface, a graphite surface of 25 nm long and 25 nm wide and an initial water box of dimensions $5 \times 5 \times 5$ nm^3 (3921 water molecules) are built. The CHARMM (Chemistry at Harvard Macromolecular Mechanics) force field is employed. Its functional form is

$$U_{total} = U_{bond} + U_{angle} + U_{vdW} + U_{coulomb} \quad (1)$$

$$U_{bond} = \sum_{bond,i} k_i^{bond}(r_i - r_{oi})^2 \quad (2)$$

$$U_{angle} = \sum_{angle,i} k_i^{angle}(\theta_i - \theta_{oi})^2 \quad (3)$$

The first two terms on the right-hand side of Eq. (1) denote the stretching and bending bonded interactions, respectively. In Eq. (2), k_i^{bond} is the bond force constant of bond i and $r_i - r_{oi}$ is the distance that the atom has moved from equilibrium position. In Eq. (3), k_i^{angle} is the angle force constant of angle i and $\theta_i - \theta_{oi}$ is the angle change from equilibrium. The bond distance and angle of the water molecule are fixed using the SHAKE algorithm. Nonbonded interactions include the van der Waals potential U_{vdW} and electrostatic potential $U_{coulomb}$. The van der Waals interactions are represented using a Lennard-Jones potential as Eq. (4), where ε and σ are the characteristic surface energy and van der Waals radius, respectively.

$$U_{vdW}(r_{ij}) = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] \quad (4)$$

$$U_{coulomb}(r_{ij}) = \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}} \quad (5)$$

where $r_{ij} = \|r_i - r_j\|$ in both Eqs. (4) and (5) gives the distance between a pair of atoms or charges, q_i and q_j are the partial atomic charges of atom i and j, respectively, and ε_0 is the vacuum permittivity. The van der Waals interactions between different species i and j are calculated by using Lorentz–Bertholet mixing rule

$$\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}, \quad \sigma_{ij} = (\sigma_i + \sigma_j)/2 \quad (6)$$

The present study employs the TIP3P water model [28] that has a single Lennard-Jones center representing an oxygen atom together with 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 solid surface representing graphite with the characteristic surface energy of 0.0355 kcal/mol and a van der Waals radius of 3.4 Å is treated as a rigid body and there is no relative motion between solid atoms. The long-range electrostatic interactions are calculated using the PPPM (particle–particle particle-mesh) method and the Lennard-Jones potential is truncated at a cutoff radius of 14 Å. The NVT ensemble which keeps the number of atoms, volume and temperature constant is used with a Nosé-Hoover thermostat at 298 K. The thermostat applied on the water molecules avoids the temperature rise caused by artificial vibration. A periodic boundary condition is applied for the three dimensions of $250.52 \times 250.98 \times 250$ Å in the x, y, and z directions, respectively, and the solid surface locates on the x–y plane. Newton's equation of motion is integrated numerically using the velocity Verlet algorithm for 1–2.5 ns with a time step of 2 fs.

To investigate the droplet static behavior and dynamic transition caused by vibration, the smooth surface and 15 types of rough surfaces are established. The water molecules are arranged on the rough solid surface as a rectangular block initially as shown in Fig. 1. Quadrangular pillars are arranged with lateral size 10×10 Å and three different gaps in the x and y directions 6×6 Å, 10×10 Å and 15×15 Å, respectively, and the height of the pillars is changed from 3.35 to 16.75 Å for every gap size. All simulations are performed in two stages. The purpose in the first

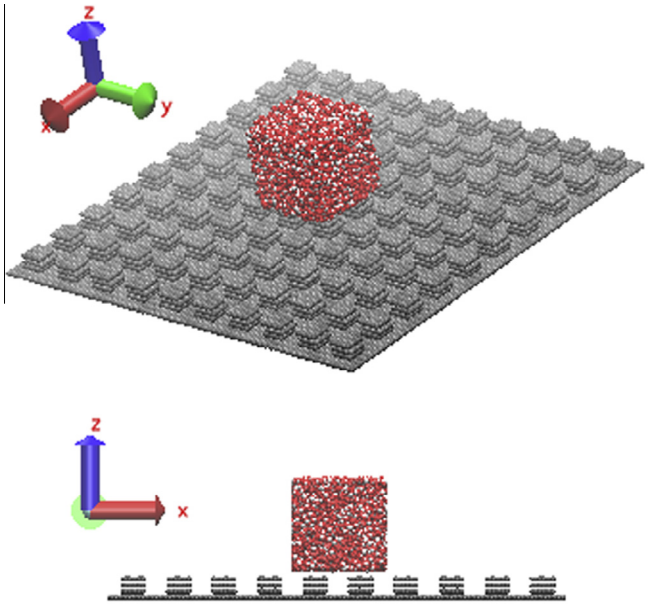

Fig. 1. Initial water box on a rough surface.