Wetting properties of structured interfaces composed of surface-attached spherical nanoparticles

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ABSTRACT

The influence of the external pressure and surface energy on the wetting transition at nanotextured interfaces is studied using molecular dynamics and continuum simulations. The surface roughness of the composite interface is introduced via an array of spherical nanoparticles with controlled wettability. We find that in the absence of an external pressure, the liquid interface is flat and its location relative to the solid substrate is determined by the particle size and the local contact angle. With increasing pressure on the liquid film, the interface becomes more curved and the three-phase contact line is displaced along the spherical surface but remains stable due to re-entrant geometry. It is demonstrated that the results of molecular dynamics simulations for the critical pressure of the Cassie-Baxter wetting state agree well with the estimate of the critical pressure obtained by numerical minimization of the interfacial energy.

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1. Introduction

Over the last two decades, there has been a remarkable progress in designing and fabricating the so-called *superhydrophobic* surfaces, which are characterized by small-scale surface roughness that keeps the liquid interface suspended at the tips of the asperities, thus, reducing the liquid-solid contact area [1,2]. Such engineered surfaces typically exhibit large liquid contact angles, small contact angle hysteresis, low adhesion, and reduced hydrodynamic friction, which play important roles in many technological processes, including self-cleaning surfaces, such as glasses and fabrics [3], nonfouling surfaces [4], and drag reduction [5]. Superhydrophobic textures can also enable a more accurate control and manipulation of liquid flows in microfluidic and nanofluidic systems [6–8]. Notably, it was shown that laminar flows over anisotropic textured surfaces can be generally described via the mobility tensor that relates the normal traction at the interface and the effective slip velocity [9]. From a modeling perspective, a detailed comparison between continuum predictions and atomistic simulations demonstrated that there is excellent agreement between the velocity profiles and the effective slip boundary conditions if the length scales of surface patterns are large compared to the liquid molecular size [10,11].

It is well known that, depending on the surface energy and topography, a liquid droplet in contact with a roughened substrate can form either the Wenzel state [12], where the liquid fully penetrates into the surface asperities, or the Cassie-Baxter state [13], where the liquid interface remains suspended at the tips of surface protrusions and small pockets of air become trapped between the surface and the liquid. In the latter case, the *apparent* contact angle is given by the Cassie-Baxter equation:

$$\cos\theta_c = (1-f)\cos\theta - f, \qquad (1)$$

where f is the areal fraction of the liquid-air interface and θ is the *intrinsic* contact angle of a liquid droplet at a smooth surface of the same material. In particular, it follows from Eq. (1) that in the limit when the areal fraction f is close to 1, the apparent contact angle becomes nearly 180°. In practice, however, the distance between surface protrusions should be sufficiently small, which allows the liquid-air interface to remain locally suspended above the surface; otherwise, the liquid would fully wet the substrate. Thus, the main factors that limit the applicability of superhydrophobic surfaces include the breakthrough pressure required to fully wet the substrate, fluid temperature, fragility of the surface texture, and fouling resistance [1].

More generally, the types of surfaces that exhibit highly repellent properties for liquids with both high and low surface tension (for example, water and oil) are called *omniphobic* surfaces [14,15]. Such an unusual property can be achieved by introducing the re-entrant surface curvature, when the three-phase contact

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line is stabilized at the concave regions and the liquid interface remains suspended between surface asperities. The stability of the Cassie-Baxter state could be further improved in the case of hierarchical surface topography, where nanoscale texture is imposed on microscale roughness, and it might involve a combination of many concave and convex segments [16]. Recently, the equilibrium and stability of Cassie-Baxter wetting states on microstructured surfaces were analyzed by minimizing the surface free energy and the potential energy of the external pressure [17,18]. An estimate of the critical value of the external pressure required to overcome the Laplace pressure due the curved interface was obtained for a number of typical 3D microstructures [17,18]. In general, however, the shape of the liquid interface and the critical pressure for the transition from the Cassie-Baxter to Wenzel states on structured surfaces have to be determined numerically.

In recent years, the wetting behavior of liquid droplets on nanotextured surfaces was extensively studied using molecular dynamics (MD) simulations [19–29]. For instance, it was shown that the free-energy barrier associated with the transition from the Wenzel-to-Cassie state is much higher than from the Cassie-to-Wenzel state, provided that the height of pillars at the hydrophobic surface is sufficiently large [19]. It was also found that the apparent contact angle depends sensitively on the pillar cross-sectional shape and height, spacing between pillars, crystal plane orientation at the tops of the pillars, and the interaction energy between pillar atoms and droplet molecules [19,22,24,26–28]. Interestingly, during lateral motion of a liquid droplet over deformable pillar-arrayed substrate, the flexible hydrophilic pillars can accelerate the liquid upon approach and pin the receding contact line [23]. Furthermore, it was recently demonstrated that the wetting transition of a water droplet at a pillar-arrayed surface also depends on the charge density at the base substrate [26]. However, despite considerable computational efforts, the atomic details of the wetting transition at nanostructured surfaces with re-entrant surface curvature remain not fully understood.

In this paper, molecular dynamics and continuum simulations are preformed to investigate the effects of external pressure and surface energy on the wetting transition at nanotextured surfaces with re-entrant curvature. We consider a polymeric liquid film partially wetting the surface of a spherical particle, which is fixed rigidly at a solid substrate. It will be shown that the position of the liquid/vapor interface is determined by the particle radius and the local contact angle at the particle surface. With increasing external pressure on the liquid film, the liquid/vapor interface is displaced towards the substrate and becomes more curved until it touches the substrate at the critical pressure. We find an excellent agreement between the results of molecular dynamics simulations and numerical minimization of the surface energy for the critical pressure as a function of the local contact angle.

The rest of the paper is organized as follows. The description of molecular dynamics and continuum simulations is given in the next section. The relationship between the local contact angle and the surface energy for a liquid droplet on a flat substrate, and the pressure dependence of the shape and location of the suspended liquid film as well as the comparative analysis of the critical pressure as a function of the contact angle are presented in Section 3. The results are summarized in the last section.

2. Simulation details

We study wetting properties of structured interfaces that consist of an array of spherical particles on a solid substrate and a suspended liquid film, as shown schematically in Fig. 1. The large-scale molecular dynamics simulations were carried out using
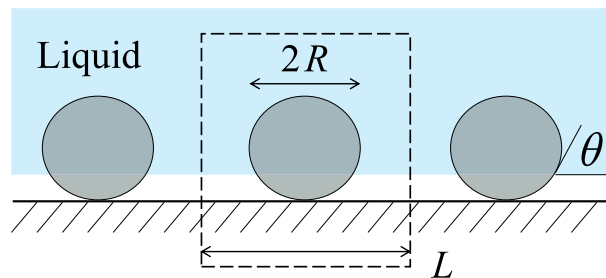
Fig. 1. A schematic illustration of the structured interface that consists of an array of spherical particles attached to the solid substrate and a suspended liquid film. The local contact angle of the liquid interface at the surface of the solid particle is denoted by θ. The dashed box indicates the spatial domain used in molecular dynamics and continuum simulations.

the parallel code LAMMPS developed at Sandia National Laboratories [30]. In our model, any two atoms interact via the truncated Lennard-Jones (LJ) potential

$$V_{LJ}(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right], \tag{2}$$

where the parameters ε and σ represent the energy and length scales of the liquid phase. The interaction between atoms of a liquid and a solid is also described by the LJ potential but with the parameters ε_{wf} and σ_{wf} that are measured in units of ε and σ, respectively. The solid atoms are fixed on either lattice sites or on a surface of a sphere and they do not interact with each other. Furthermore, the size of liquid and solid atoms is chosen to be the same, i.e., $\sigma_{wf} = \sigma$, throughout the study. For computational efficiency, the cutoff radius is set $r_c = 2.5\sigma$ for all types of interactions.

We consider a polymeric fluid, where atoms are connected to form linear chains with $N_p = 10$ atoms each, which makes the surface tension of the liquid/vapor interface greater than for monatomic liquids [38]. In addition to the LJ potential, the interaction between nearest-neighbor atoms in a polymer chain is described via the FENE (finitely extensible nonlinear elastic) potential

$$V_{FENE}(r) = -\frac{k}{2} r_o^2 \ln[1 - r^2/r_o^2], \tag{3}$$

with the parameters $k = 30\varepsilon\sigma^{-2}$ and $r_o = 1.5\sigma$ [32]. The combination of the LJ and FENE potentials with this parametrization yields an effective harmonic potential that allows vibration of nearest-neighbors but prevents polymer chains from unphysical crossing each other [32]. We also comment that relatively short polymer chains considered in the present study form a polymer melt well below the entanglement limit of about 70 beads per chain [32]. The MD simulations were carried out at a constant temperature of $1.0\varepsilon/k_B$, which was maintained via the Nosé-Hoover thermostat applied to the fluid phase [30]. Here, k_B denotes the Boltzmann constant. At this temperature, the dependence of the surface tension at the liquid/vapor interface as a function of the chain length was reported in Ref. [38]. The equations of motion were solved numerically using the velocity Verlet integration algorithm [31,30] with the time step $\Delta t_{MD} = 0.005\tau$, where $\tau = \sigma\sqrt{m/\varepsilon}$ is the characteristic LJ time.

Our computational domain includes a liquid film in contact with a solid sphere, which is in turn rigidly fixed on a solid substrate (see the dashed box in Fig. 1). The solid substrate consists of 2500 atoms arranged on square lattice sites within the xy plane with dimensions $L \times L = 50.0\sigma \times 50.0\sigma$, and, therefore, the areal density is $1.0\sigma^{-2}$. The interaction energy between fluid monomers and atoms of the lower stationary substrate is fixed to 1.0ε. Secondly, the solid particle consists of 4000 atoms uniformly distributed on a surface of a sphere with the radius $R = 17.8\sigma$, and, correspondingly, with