Effect of Roughness on Wettability of a Surface by Nano-droplets: Correlation With the Slip Length in Nanofluidics

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ABSTRACT

Surface characteristics govern friction, flow, wettability and many other properties in solid-liquid interfaces [1-7]. Wettability of surfaces in contact with a liquid medium is usually determined by measuring the contact angle of a single droplet put on the surface. Liquid repelling surfaces show larger contact angles. This has been used to create novel surfaces which are either liquid loving or liquid repelling (hydrophilic and hydrophobic in case of liquid being water; oleophobic, oleophilic in the case of liquid being oil). Wettability is believed to be affected by many properties, including temperature, surface-liquid interaction and physical topology of the surface, such as roughness. In this work the results of molecular dynamics simulations will be presented to show how nano-patterning of the surface affect the oleophobic properties of a surface. We have simulated nano-droplets of hexadecane coming into contact with model surfaces with various one dimensional (grooves) and two dimensional (spikes) features. The effects of the roughness and spread of this roughness patterns on the surface on the nano-droplet contact angle are studied. Our study shows one may control the oleophobic properties of the surface by adjusting these nano-patterns on the surface. Subsequently the same surfaces have been used to simulate and study flow of hexadecane in the nano-channels and correlations between the slip-length [2], droplet contact angle, and roughness are drawn.

Keywords: molecular dynamics simulations, surface wettability, nano-drops, adhesion, surface effects, oil repelling substrate, oleophobic, oleophilic

1 INTRODUCTION

Surface wettability has crucial effects on spreading of fluid on the surface and flow. The emergence of nanotechnology and miniaturization in the form of nano/micro electromechanical (NEMS/MEMS) devices require a deeper understanding of liquid-solid interactions in such small scales. Application of nano-fluidics in such devices requires working with extremely small parts whose adhesion/mass ratio is significantly larger than those in macro-scale applications. Fine Details of the surface characteristics at that scale affect its interaction with the liquid and how it wets the surface. So it is of great interest to the industry to understand wettability at the nanoscale and to devise strategies that effectively control spreading of the droplet onto the surface. Surface wettability can be affected by many factors including the interaction energy of the liquid and solid interfaces, and physical characteristics of the surface such as roughness. In macroscale and experimental approach, the wettability of the surface is usually measured by contact angle of a droplet put on the surface. Here we have adopted a similar approach by using molecular dynamics simulations.

The subsequent effect of roughness on the flow and the degree of boundary slip is also important to investigate. While in the MD simulations it is shown that the wettability can be controlled by the change of interaction strength between the liquid and substrate, controlling the wettability via variation of the surface topography has not been studied enough. Such surface patterning technologies are available now through methods such as lithography, vapour and chemical deposition and laser ablation.

Therefore, it is important to understand how distribution of roughness in the form of 1 and 2 dimensional features on the surface can be used to control the spreading dynamics of nano-drops onto the surface. Here we have used hexadecane nano-drops and have investigated the spreading of the drops on the surface and their eventual equilibrium contact angle. Here we will compare the effect of variations of roughness features including the average roughness height and width. The effects of using 1D roughness patterns (grooves) versus 2D patterns (spikes) on the surface are also studied and compared.

In this paper we report some of the findings from molecular dynamics simulations that should help with the choice of material, substrate, and design strategies at the nanoscale for NEMS/MEMS systems that may control the wetting of substrates.

2 SIMULATION METHODS

Molecular dynamics simulation methods are used to simulate the systems of alkane nano-droplets put on (100) planes of exposed flat substrates. Various crystalline

surfaces of different roughness characteristics are used. Here we have varied the roughness frequency (width) while keeping the roughness height constant and have calculated the contact angle. Then we have kept the roughness width constant and varied the roughness height to determine the effect of the roughness height on the contact angle.

The nano-drop simulation begins with using a configuration obtained from a bulk system. The size of this initially cubic drop measures ~7 nm. This drop is put close enough to the surface so that the attractive van der Waals forces attract it to the surface. Before this happens the nano-droplet attains a spherical shape due to the vacuum inside the simulation box.

The average contact angle is determined by using the snapshots and fitting a circle on the nano-droplet after equilibration and measuring the contact angle for each snapshot (see Figure 4). Image processing software was use for this purpose. Depending on the surface pattern there was some evidence of the inhomogeneous contact angle (droplet cross section changed from circular to oval) when measured from XZ or YZ view. So the contact angle was measured from both directions and the results are reported for all cases. The contact angle (θ_{av}) reported here is the average of these two contact angles.

All simulations are done by algorithms and a program that was developed by the first author [8]. For all systems the average contact angle, thermal, physical, and other properties are calculated by standard statistical methods used in MD simulations.

2.1 Modelling the Nano-Droplet Molecules

We have used hexadecane ($C_{16}H_{34}$) as the model liquid. A united atom model [9] where CH_2, and CH_3 groups are treated as single interaction sites is use in the simulations. Such a model has been successfully used in our research group to study crystallization,[10],[11] confinement induced phase transitions, [1], lubrication with gold surfaces [12], and self assembled monolayers [6]. The hexadecane systems are initially equilibrated in the bulk form at 300 K and density of 773 kg/m^3 and then are used as a nano-droplet next to the substrates. For bulk systems the periodic boundary conditions are applied in all three directions whereas for confined and droplet simulations they are applied in the lateral (X and Y) directions only.

2.2 Modelling of the Surfaces

The substrates are modelled by using an explicit atomic structure. Crystalline surfaces are made from 3-4 layers of (100) faces of fcc (face centred cubic) lattice structure. The crystalline structure has a lattice constant of 0.408 nm and the nearest neighbor distance of 0.288 nm. Dimensions of the square surfaces, depending on the system, ranged from 14.69 to 14.77 nm in the lateral (*xy*) directions. Snapshots of various surfaces are shown in Figure 1.

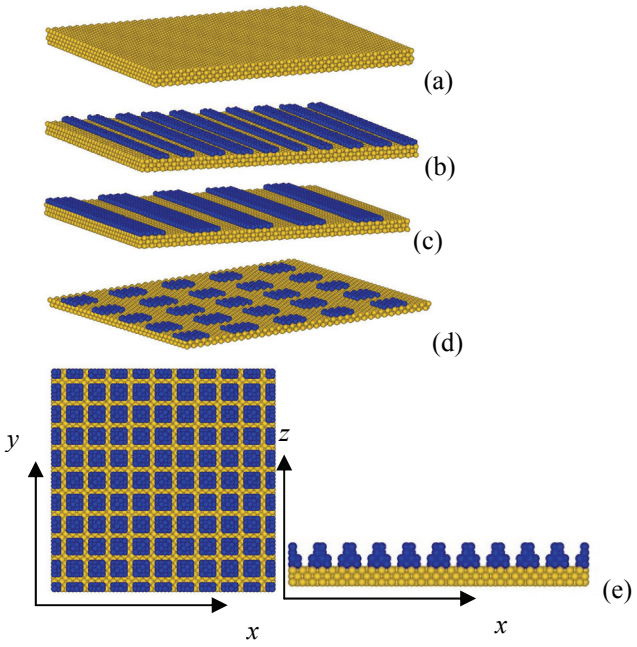

Figure 1 *Roughness patterns made on substrates. The height of the asperities and their distance are changed and the effect is examined on the contact angle. Nano-patterns are shown in blue colour for clarity. Surfaces with various roughnesses feature; a) smooth, (b) and (c) one dimensional roughness with varying roughness width (d) and (e) 2D roughness with varying roughness height. The average roughness height is the same for (a), (b), (c) and (d), for case (e) the roughness height is larger.*

2.3 Potential Model

The potential model included stretching, bond angle, and dihedral potentials given by equations 1, 2 and 3. The van der Waals interactions were modelled via a 6-12 Lennard-Jones potential, given by eq. 4, cut off at r_c=1 nm.

$$\phi(r) = \frac{1}{2}k(r - r_0)^2 \tag{1}$$

$$\phi(\theta) = \frac{1}{2}k_\theta(\cos\theta - \cos\theta_0)^2 \tag{2}$$

$$\phi(\varphi) = \sum_i^5 C_i(\cos\varphi)^i \tag{3}$$

$$\phi_{LJ}(r) = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r}\right)^{12} - \left(\frac{\sigma_{ij}}{r}\right)^{6}\right] - \phi_{shift}, \tag{4}$$

$$\phi_{shift} = 4\varepsilon\left[\left(\frac{\sigma}{r_c}\right)^{12} - \left(\frac{\sigma}{r_c}\right)^{6}\right]$$

The initial random velocity for each atom was assigned to give a Maxwell-Boltzman distribution corresponding to the target temperature of 300K which is kept constant. The droplet simulation and confined systems are simulated under NVT conditions where the number of atoms, volume, and temperature are kept constant. The initial bulk simulation of the hexadecane was also done under NVT condition. The equations of motion were integrated using the velocity Verlet algorithm with a time step of 2.35 fs. A parallel algorithm [8] with link cell and neighbor list methods was used in order to reduce the computational time and effort.

The interactions of the surface atoms and hexadecane united atoms are also governed by the 6-12 Lennard Jones potential (eq. 4). The interaction parameters of substrate are values are (ε_s/k_B= 47 K) and σ_s=0.2655 nm. So that substrate–CH_2 interaction parameters are $\varepsilon_{sf}=\varepsilon_{CH2}$ and σ_{sf} =0.328 nm. Other potential parameters are given elsewhere in [9], [8], [1].

3 RESULTS

3.1 Effect of Roughness Width On the Contact Angle: 1D and 2D Patterns

The effect of the average roughness spacing (width of the nano-features) on the calculated contact angle is shown in Figure 2. For this case the average roughness height is kept at 0.196 nm. We have shown the results for 1D (e.g Figures 1b and 1c) and 2D (e.g. Figures 1d and 1e) cases. We can see as the width of the roughness features increases the contact angle decreases. Usually θ<90˚ is considered as oleophobic, and θ<90˚ oleophilic. The lowest contact angle (~75˚) is obtained for the smooth surface which has no patterning. This smooth surface is most oleophilic surface in this case. The most oleophobic surfaces in this case, with θ_{av}=99º-107˚ are those with the width at the same order of roughness height (<0.5 nm).

For the case of 2D roughness patterns the average roughness height is kept constant at 0.288 nm. Here the trend is similar to that seen with 1D patterns, that is the wetting becomes stronger as the width of the features decreases. The results show while 1D roughness results at the highest contact angle, the surface quickly becomes oleophilic as the roughness width increases. The 2D features keep the surface oleophobic for a larger range of roughness width up to 0.734 nm. In either case adding small roughness results in improved oleophobic properties of the surface.

3.2 Effect of Roughness height On the Contact Angle

To understand the effect of the roughness height we have calculated the contact angle for various substrates whose roughness width is kept constant at ~0.983 nm.

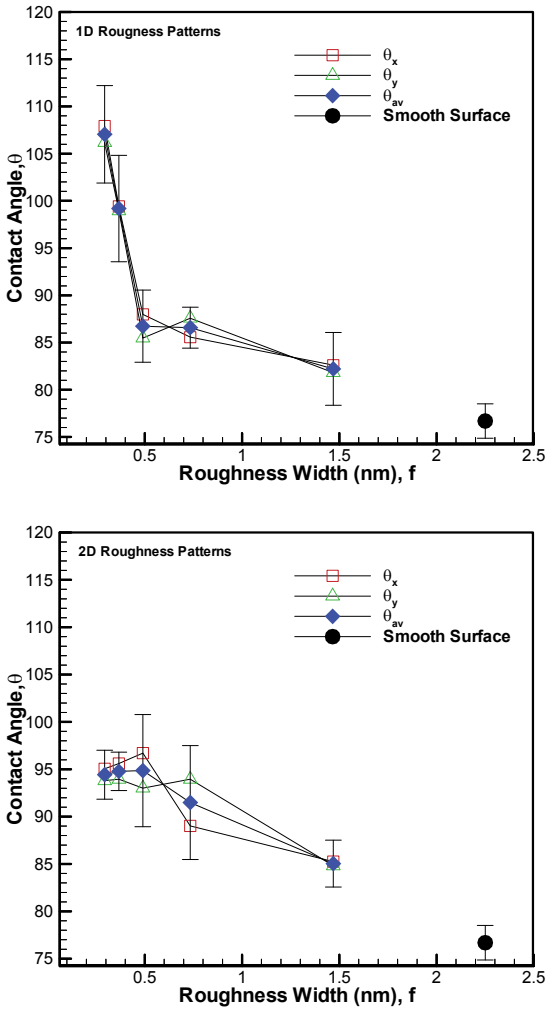

Figure 2 Hexadecane nano-droplet contact angle with surface versus the roughness width of the surface. The results are shown for 1D and 2D roughness patterns. θ_x and θ_y are contact angles measured from XZ and YZ views, show slight anisotropy. The average contact angle is $\theta_{av}=(\theta_y+\theta_x)/2$. The contact angle for smooth surface is shown by a single filled symbol.

All these substrates are produced with 2D roughness patterns. Surfaces with various average roughness height, R_a, in the range of 0.288-1.152 nm were simulated and the contact angle of the nano-droplet was calculated. In Figure 3 we have plotted drop contact angle versus the average roughness height. There is striking evidence that as the average roughness height increases the contact angle of the droplet increases. The surface obviously becomes more oleophobic by increasing the height of the roughness. However the rate of this increase is much smaller for roughness heights higher than 0.576 nm. The contact angle for the droplet reaches values up to 122˚in this case showing great improvement in oil repelling properties of the surface in comparison to when the surface is smooth. The snapshots shown in Figure 4 are for the case of the

smooth surface and the case corresponding to R_a=1.152 nm. These snapshots show very interesting transformation of surface properties, where introducing roughness with required characteristics has converted an oleophilic substrate into an oleophobic one. Comparing the effects of roughness width and height on the wettability of the surface one may conclude that the roughness height plays a stronger role in altering the wettability of the surface.

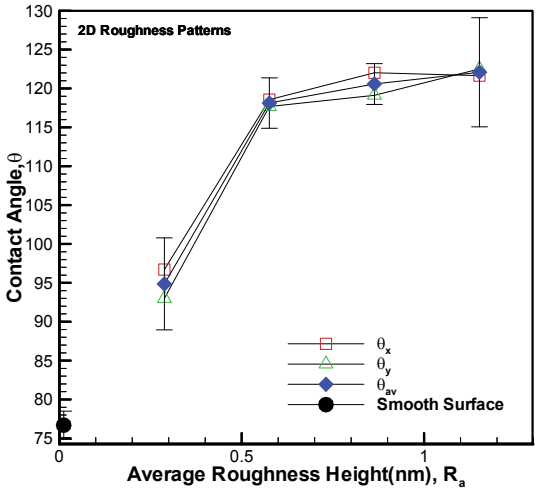

Figure 3 *Hexadecane nano-droplet contact angle with surface against average roughness height of the surface. All results are for 2D roughness patterns. The contact angle for smooth surface is shown by a single filled symbol.*

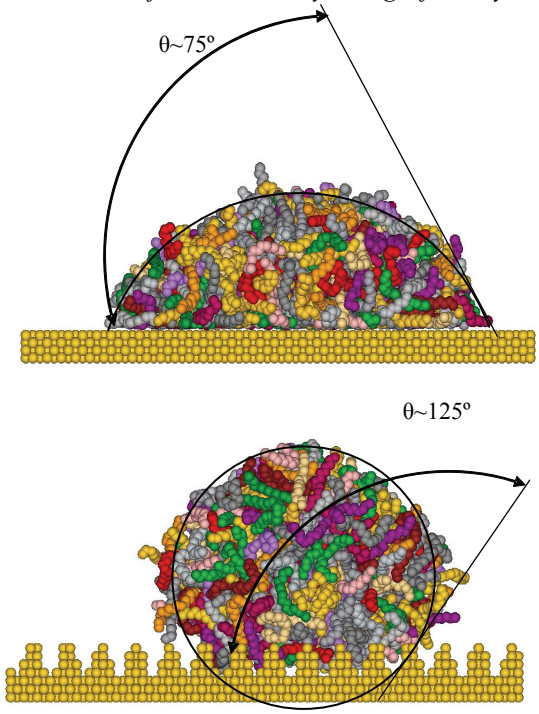

Figure 4 *spreading of hexadecane [$C_{16}H_{34}$] nano-drop is controlled by introducing roughness to the surface, rendering it oleophobic. Note the smaller contact angle (θ) of the nano-drop for the surface with rough features.*

CONCLUSIONS

We used molecular dynamics simulations to study the effect of surface roughness on the wettability of the surface by an oily liquid hydrocarbon. Here we have shown that a surface which is oleophilic can be rendered oleophobic by introducing roughness patterns on the surface. We have shown the roughness height plays more important role in transforming the surface wettability characteristics. Introducing 2D roughness patterns onto the surface also helps to keep the surface oleophobic for larger range roughness width. We have also studied the dynamics and diffusion of the droplet on the surface with various surface topologies. The effects of such patterns on the flow and on the slip boundary conditions are also studied.

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