**Natural and Biomimetic Artificial Surfaces for Superhydrophobicity, Self-Cleaning,
Low Adhesion, and Drag Reduction**

Dissertation

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By

Yong Chae Jung, M.S.

Graduate Program in Mechanical Engineering

The Ohio State University

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Dissertation Committee:

Professor Bharat Bhushan, Adviser

Professor J. William Rich

Professor Noriko Katsube

Professor Rebecca Dupaix

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ABSTRACT

Nature has developed materials, objects, and processes that function from the macroscale to the nanoscale. The emerging field of biomimetics allows one to mimic biology or nature to develop nanomaterials, nanodevices, and processes which provide desirable properties. Hierarchical structures with dimensions of features ranging from the macroscale to the nanoscale are extremely common in nature to provide properties of interest. There are a large number of objects including bacteria, plants, land and aquatic animals, and seashells with properties of commercial interest. Certain plant leaves, such as Lotus leaves, are known to be superhydrophobic and self-cleaning due to the hierarchical roughness of their leaf surfaces. The self-cleaning phenomenon is widely known as the “Lotus effect.” These surfaces with high contact angle and low contact angle hysteresis with a self-cleaning effect also exhibit low adhesion and drag reduction for fluid flow. In this thesis, the theoretical mechanisms of the wetting of rough surfaces are presented followed by the characterization of natural leaf surfaces. The next logical step is to realize superhydrophobic surfaces based on understanding of the leaves. Next, a comprehensive review is presented on artificial superhydrophobic surfaces fabricated using various fabrication techniques and the influence of micro-, nano- and hierarchical structures on superhydrophobicity, self-cleaning, low adhesion, and drag reduction. An aquatic animal, such as a shark, is another model from nature for the reduction of drag in

fluid flow. The artificial surfaces from the shark skin have been created, and the influence of structure on drag reduction efficiency is discussed. Furthermore, oleophobic surfaces can be used as a biomimetic coating that prevents contamination of the underwater parts of ships by biological and organic contaminants, including oil. The thesis discusses the wetting behavior of oil droplets on various superoleophobic surfaces.

DEDICATION

Dedicated to my parents, my wife, and my lovely daughters

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VITA

April 1974 Born – Kwangju, South Korea

2001 B.S. Mechanical Engineering
Sungkyunkwan University, South Korea

2004 M.S. Mechanical Engineering
University of Southern California, CA

2005 – present Graduate Research Associate
The Ohio State University

PUBLICATIONS

Research Publications

1. Bhushan, B. and Jung, Y. C., “Micro and Nanoscale Characterization of Hydrophobic and Hydrophilic Leaf Surface,” *Nanotechnology* **17** (2006) 2758-2772
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TABLE OF CONTENTS

Abstract	ii
Dedication	iv
Acknowledgements	v
Vita	vii
List of Tables	xv
List of Figures	xvii
 Chapter 1: Introduction	 1
1.1. Definitions and applications	4
1.2. Natural superhydrophobic, self-cleaning, low adhesion, and drag reduction surfaces	7
1.3. Natural superoleophobic, self-cleaning, and drag reduction surfaces	9
1.4. Roughness-induced superhydrophobicity, self-cleaning, low adhesion, and drag reduction	9
1.5. Roughness-induced superoleophobicity	15
1.6. Scope of the thesis	15
 Chapter 2: Modeling of Contact Angle for a Liquid in Contact with a Rough Surface	 17
2.1. Contact angle definition	17

2.2. Heterogeneous interfaces and the Wenzel and Cassie-Baxter equations.....	18
2.2.1. Limitations of the Wenzel and Cassie equations	25
2.2.2. Range of applicability of the Wenzel and Cassie equations	29
2.3. Contact angle hysteresis.....	33
2.4. Stability of a composite interface and role of hierarchical structure	37
2.5. The Cassie-Baxter and Wenzel wetting regime transition.....	41
Chapter 3: Lotus Effect Surfaces in Nature	49
3.1. Plant leaves	49
3.2. Characterization of superhydrophobic and hydrophilic leaf surfaces.....	51
3.2.1. Experimental techniques	51
3.2.2. SEM micrographs	52
3.2.3. Contact angle measurements	54
3.2.4. Surface characterization using an optical profiler	56
3.2.5. Surface characterization, adhesion and friction using an AFM.....	60
3.2.5.1. Comparison of two AFM measurement techniques.....	60
3.2.5.2. Surface characterization.....	60
3.2.5.3. Adhesive force and friction.....	64
3.2.6. Role of hierarchical roughness.....	66
Chapter 4: How to Make a Surface for Superhydrophobicity, Self-Cleaning, Low Adhesion, and Drag Reduction	69
4.1. Roughening to create one-level structure	73
4.2. Coating to create one-level hydrophobic structures.....	76
4.3. Methods to create two-level (hierarchical) structures.....	78

Chapter 5: Fabrication and Characterization of Micro-, Nano- and Hierarchical

Structured Surfaces	81
5.1. Experimental techniques	81
5.1.1. Contact angle, surface roughness, and adhesion.....	81
5.1.2. Droplet evaporation studies	82
5.1.3. Bouncing droplet studies.....	82
5.1.4. Vibrating droplet studies.....	83
5.1.5. Microdroplet condensation and evaporation studies using ESEM	83
5.1.6. Generation of submicron droplets.....	84
5.1.7. Waterfall/jet tests	88
5.1.8. Wear and friction tests	89
5.2. Micro- and nanopatterned polymers	90
5.2.1. Contact angle measurements.....	92
5.2.2. Effect of submicron droplet	94
5.2.3. Scale dependence on adhesive force	94
5.3. Micropatterned Si surfaces	96
5.3.1. Cassie-Baxter and Wenzel transition criteria	99
5.3.2. Contact angle measurements.....	102
5.3.3. Observation of transition during the droplet evaporation	107
5.3.4. Scaling of the Cassie-Baxter and Wenzel transition for different series	112
5.3.5. Contact angle hysteresis and wetting/dewetting asymmetry	113
5.3.6. Observation of transition during the bouncing droplet	118
5.3.7. Observation and measurement of contact angle using ESEM	125

5.4. Ideal surfaces with hierarchical structure	130
5.5. Hierarchical structured surfaces with wax platelets and tubules	131
5.5.1. Nanostructures with various platelet crystal densities	138
5.5.2. The influence of hierarchical structure with wax platelets on the superhydrophobicity	144
5.5.3. The influence of hierarchical structure with wax tubules on the superhydrophobicity	149
5.5.3.1. Morphological characterization, wettability and adhesion forces of <i>T.</i> <i>majus</i> tubules	149
5.5.3.2. Morphological characterization, wettability and adhesion forces of Lotus tubules	154
5.5.4. Self-cleaning efficiency of hierarchical structured surfaces	158
5.5.5. Observation of transition during the bouncing droplet	160
5.5.6. Observation of transition during the vibrating droplet	166
5.5.6.1. Model for the adhesion and inertia forces of the vibrating droplet.....	166
5.5.6.2. Vibration study results	168
5.6. Mechanically durable CNT-composite hierarchical structured surfaces	173
5.6.1. The influence of CNT-composite hierarchical structure on the superhydrophobicity	176
5.6.2. Durability of various surfaces in waterfall/jet tests	178
5.6.3. Durability of various surfaces in AFM and ball-on-flat tribometer tests.....	180
Chapter 6: Fabrication and Characterization of Biomimetic Structures for Fluid Drag Reduction	187

6.1. Experimental techniques	187
6.2. Model for calculation of pressure drop and slip length	188
6.3. Fabrication and characterization of biomimetic structures	190
6.3.1. Pressure drop in the channel using water flow and calculated slip length.....	193
6.3.2. Pressure drop in the channel using air flow	198
Chapter 7: Modeling, Fabrication and Characterization of Oleophobic/philic Surfaces	
.....	201
7.1. Modeling of contact angle for various interfaces	201
7.2. Experimental techniques	202
7.3. Fabrication and characterization of oleophobic surfaces	204
7.3.1. Wetting behavior on flat and micropatterned surfaces	208
7.3.2. Wetting behavior on flat and micropatterned surfaces with C ₂₀ F ₄₂	212
7.3.3. Wetting behavior on nano- and hierarchical structures and shark skin replica	
.....	215
Chapter 8: Closure	218
Bibliography	221

LIST OF TABLES

Table 1. Wetting of a superhydrophobic surface as a multiscale process (Nosonovsky and Bhushan, 2007c, 2008c)	28
Table 2. Summary of experimental results for uniform and non-uniform rough and chemically heterogeneous surfaces. For non-uniform surfaces, the results shown for droplets larger than the islands of non-uniformity. Detailed quantitative values of the contact angle in various sets of experiments can be found in the referred sources (Nosonovsky, 2007c)	32
Table 3. Microbump and nanobump map statistics for hydrophobic and hydrophilic leaves, measured both fresh and dried leaves using an optical profiler and AFM (Bhushan and Jung, 2006)	59
Table 4. Roughness factor and contact angle ($\Delta\theta = \theta - \theta_o$) calculated using R_f on the smooth surface for hydrophobic and hydrophilic leaves measured using an AFM, both microscale and nanoscale (Bhushan and Jung, 2006)	68
Table 5. Typical materials and corresponding techniques to produce micro/nanoroughness.....	71
Table 6. Pros and cons of various fabrication techniques.....	73
Table 7. Roughness factor for micro- and nanopatterned polymers (Jung and Bhushan, 2006).....	93
Table 8. Chemical structure of the major components of <i>n</i> -hexatriacontane, <i>T. majus</i> and Lotus waxes. The major component is shown first (Bhushan et al., 2008a, 2009c; Koch et al., 2009b)	134
Table 9. Roughness statistics for nanostructure surface measured using an AFM (Scan size 10 μm x 10 μm). Nanostructures were fabricated with <i>n</i> -hexatriacontane, <i>T. majus</i> and Lotus waxes (Bhushan et al., 2008a, 2009c; Koch et al., 2009b)	140

Table 10. Summary of static contact angles and contact angle hysteresis measured and calculated for droplets in Wenzel regime and Cassie-Baxter regime on the various surfaces with <i>n</i> -hexatriacontane using the calculated values of R_f and f_{LA} (Bhushan et al., 2008b, 2009d).....	147
Table 11. Summary of the measured resonance frequency at the fixed amplitude value of 0.4 mm, the calculated inertia force of a vibrated droplet, and adhesive force between the droplet and surface on the various surfaces fabricated with <i>n</i> -hexatriacontane and Lotus wax. Positive value of ΔF means that the droplet bounced off before the transition occurs. The variation represents ± 1 standard deviation (Jung and Bhushan, 2009a)	171
Table 12. Typical physical properties of various specimens and calculated contact diameters and contact stresses at three loads used in AFM and ball-on-flat tribometer measurements. It is assumed that contacts are single-asperity contact (Jung and Bhushan, 2010b)	186
Table 13. Summary of the static contact angles and contact angle hysteresis measured on the various surfaces. Nanostructures and hierarchical structures were fabricated with $0.8 \mu\text{g}/\text{mm}^2$ of Lotus wax after storage at 50°C with ethanol vapor. The variation represents ± 1 standard deviation (Jung and Bhushan, 2010a)	193
Table 14. Summary of philic/phobic nature in various interfaces (Jung and Bhushan, 2009b).....	204

LIST OF FIGURES

Fig. 1	Montage of some examples from nature: (a) Lotus effect (Bhushan et al., 2009b), (b) glands of carnivorous plant secrete adhesive to trap insects (Koch et al., 2009a), (c) pond skater walking on water (Gao and Jiang, 2004), (d) gecko foot exhibiting reversible adhesion (Gao et al., 2005), (e) scale structure of shark reducing drag (Reif, 1985), (f) wings of a bird in landing approach, (g) spiderweb made of silk material (Bar-Cohen, 2006), and (h) antireflective moth's eye (Genzer and Efimenko, 2006).	2
Fig. 2	A schematic diagram of condensed water vapor from the environment forming meniscus bridges at asperity contacts which lead to an intrinsic attractive force.	6
Fig. 3	SEM micrographs (shown at three magnifications) of Lotus (<i>Nelumbo nucifera</i>) leaf surface which consists of microstructure formed by papillose epidermal cells covered with 3-D epicuticular wax tubules on surface, which create nanostructure, and image of water droplet sitting on the Lotus leaf (Bhushan et al., 2009b).	7
Fig. 4	Schematic and wetting of the four different surfaces. The largest contact area between the droplet and the surface is given in flat and microstructured surfaces, but is reduced in nanostructured surfaces and is minimized in hierarchical structured surfaces.	8
Fig. 5	Schematic of velocity profiles of fluid flow without and with boundary slip. The definition of slip length b characterizes the degree of boundary slip at solid-liquid interface. The arrows represent directions for fluid flow.	14
Fig. 6	Schematic of liquid droplet in contact with a smooth solid surface (contact angle, θ_o).	18
Fig. 7	Schematics of configurations described by the (a) Wenzel equation for the homogeneous interface (Eq. 6), (b) Cassie-Baxter equation for the composite interface with air pockets (Eq. 9), and (c) the Cassie equation for the homogeneous interface (Eq. 10) (Nosonovsky and Bhushan, 2008d).	20
Fig. 8	(a) Contact angle for rough surface (θ) as a function of the roughness factor (R_f) for various contact angles of the smooth surface (θ_o), and (b) schematic of square-based hemispherically-topped pyramidal asperities with complete packing (Nosonovsky and Bhushan, 2005).	21
Fig. 9	(a) Schematic of formation of a composite solid-liquid-air interface for rough surface, (b) contact angle for rough surface (θ) as a function of the roughness factor (R_f) for various f_{LA} values on the hydrophilic surface and the hydrophobic	

	surface, and (c) f_{LA} requirement for a hydrophilic surface to be hydrophobic as a function of the roughness factor (R_f) and θ_0 (Jung and Bhushan, 2006).	23
Fig. 10	(a) Liquid droplet in contact with rough surface with liquid is added or removed (advancing and receding contact angles are θ_{adv} and θ_{rec} , respectively) and (b) tilted surface profile (tilt angle, α) with a moving liquid droplet.	27
Fig. 11	Liquid front in contact with a (a) smooth solid surface and (b) rough solid surface, propagation for a distance dt along the curved surface corresponds to the distance dx along the horizontal surface. (c) Surface roughness under the bulk of the droplet does not affect the contact angle (Nosonovsky, 2007c).	30
Fig. 12	Liquid droplet in contact with a solid surface – smooth surface, contact angle θ_0 ; rough surface, contact angle θ ; and a surface with sharp edges. For a droplet moving from left to right on a sharp edge (shown by arrow), the contact angle at a sharp edge may be any value between the contact angle with the horizontal plane and with the inclined plane. This effect results in difference of advancing ($\theta_{adv} = \theta_0 + \alpha$) and receding ($\theta_{rec} = \theta_0 - \alpha$) contact angles (Nosonovsky and Bhushan, 2005).	36
Fig. 13	Two-dimensional pillars with semi-circular bumps/grooves. (a) Schematics of the structure. The bumps may pin the triple line, because an advance of the LA interface results in decrease of the contact angle ($\theta < \theta_0$), making equilibrium stable. Grooves provide with equilibrium positions, which satisfy the Young equation, however, the equilibrium is unstable, because an advance of the LA interface results in increase of the contact angle ($\theta > \theta_0$). (b) Energy profiles for configurations in Fig. 13(a) with bumps and grooves for hydrophilic ($\theta_0 = 30^\circ$) and hydrophobic ($\theta_0 = 150^\circ$) materials. Energy (normalized by $Lr\gamma_{LA}$) is shown as a function of vertical position of the interface z (normalized by the radius of bumps/grooves r). Bumps result in stable equilibriums (energy minima), whereas grooves result in unstable equilibriums (energy maxima) (Nosonovsky, 2007a).	40
Fig. 14	Wetting hysteresis for a superhydrophobic surface. Contact angle as a function of roughness. The stable Wenzel state (i) can transform into the stable Cassie state with increasing roughness (ii). The metastable Cassie state (iii) can abruptly transform (iv) into the stable Wenzel state. The transition i-ii corresponds to equal Wenzel and Cassie states free energies, whereas the transition iv corresponds to a significant energy dissipation and thus it is irreversible (Nosonovsky and Bhushan, 2008d).	44
Fig. 15	Schematics of net free energy profiles. (a) Macroscale description; energy minimums correspond to the Wenzel and Cassie states. (b) Microscale description with multiple energy minimums due to surface texture. Largest and smallest values of the energy minimum correspond to the advancing and receding contact angles. (c) Origin of the two branches (Wenzel and Cassie) is found when a dependence of energy upon h (air layer thickness or vertical position of the liquid-air interface) is considered for the microscale description (solid line) and nanoscale imperfectness (dashed line) (Nosonovsky and Bhushan, 2008d). When the nanoscale imperfectness is introduced, it is observed that the Wenzel state corresponds to an energy minimum and the	

	energy barrier for the Wenzel-Cassie transition is much smaller than for the opposite transition.	47
Fig. 16	Scanning electron micrographs of the relatively rough, water-repellent leaf surfaces of <i>Nelumbo nucifera</i> (Lotus) and <i>Colocasia esculenta</i> and the relatively smooth, wettable leaf surfaces of <i>Fagus sylvatica</i> and <i>Magnolia grandiflora</i> (Bhushan and Jung, 2006).	53
Fig. 17	Contact angle measurements and calculations for the leaf surfaces, (a) before and after removing surface layer as well as calculated values, and (b) fresh and dried leaves. The contact angle on a smooth surface for the four leaves was obtained using the roughness factor calculated (Bhushan and Jung, 2006).	55
Fig. 18	Surface height maps and 2-D profiles of hydrophobic leaves using an optical profiler. For Lotus leaf, a microbump is defined as a single, independent microstructure protruding from the surface. For Colocasia leaf, a microbump is defined as the single, independent protrusion from the leaf surface, whereas a ridge is defined as the structure that surrounds each bump and is completely interconnected on the leaf. A curve has been fitted to each profile to show exactly how the bump shape behaves. The radius of curvature is calculated from the parabolic curve fit of the bump (Bhushan and Jung, 2006).	57
Fig. 19	Surface height maps and 2-D profiles of hydrophilic leaves using an optical profiler. For Fagus and Magnolia leaves, a microbump is defined as a single, independent microstructure protruding from the surface. A curve has been fitted to each profile to show exactly how the bump shape behaves. The radius of curvature is calculated from the parabolic curve fit of the bump (Bhushan and Jung, 2006).	58
Fig. 20	Surface height maps showing the top scan and bottom scan in a 50 μm scan size and the bump peak scan selected in a 2 μm scan size for a Lotus leaf using an AFM in contact mode and tapping mode. Two methods were used to determine a suitable method to obtain high resolution of nanotopography for a Lotus leaf (Bhushan and Jung, 2006).	61
Fig. 21	Surface height maps and 2-D profiles showing the top scan and bottom scan of a dried Lotus leaf in 50 μm scan (because the P-V distance of a dried Lotus leaf is greater than the Z-range of an AFM), and the top scan of both fresh and dried Lotus in a 2 μm scan (Bhushan and Jung, 2006). Splicing technique was used to determine the bump profiles. In order to compensate for the large P-V distance, the total height of the bumps is embedded within the top scan and bottom scan.	62
Fig. 22	Surface height maps and 2-D profiles of Fagus and Magnolia using an AFM in both 50 μm and 2 μm scans (Bhushan and Jung, 2006).	63
Fig. 23	Adhesive force for fresh and dried leaves, and the coefficient of friction for dried leaves for 50 μm and 2 μm scan sizes for hydrophobic and hydrophilic leaves. All measurements were made using an AFM with 15 μm radius borosilicate tip. Reproducibility for both adhesive force and coefficient of friction is $\pm 5\%$ for all measurements (Bhushan and Jung, 2006).	65
Fig. 24	Typical methods to fabricate micro/nanoroughened surfaces.	70

Fig. 25	(a) Schematic of modified nanoscale dispensing (NADIS) probe for generation of submicron size droplets. The loaded liquid is limited to the loading area (30 μm diameter circle), (b) scanning electron micrograph of tip in side view and bottom view with different aperture sizes (500 nm and 200 nm) at its apex (Jung and Bhushan, 2008c).	85
Fig. 26	Droplet of liquid in contact with a surface, contact angle θ . The thickness of droplet is h . The contact diameter between droplet and surface is d . The radius of curvature of droplet is r (Jung and Bhushan, 2008c).	86
Fig. 27	Force calibration plot for a droplet with 1.1 μm contact diameter on Si surface. The horizontal distance between point C and point D, h , is a measure of droplet thickness on the surface.	88
Fig. 28	Schematics of waterfall/jet setup shown in front and side views (Jung and Bhushan, 2010b).	89
Fig. 29	Scanning electron micrographs of the two nanopatterned polymer surfaces (shown using two magnifications to see both the asperity shape and the asperity pattern on the surface) and the micropatterned polymer surface (Lotus pattern, which has only microstructures on the surface) (Burton and Bhushan, 2005; Jung and Bhushan, 2006).	91
Fig. 30	Contact angles for various micro- and nanopatterned surfaces on PMMA and PS polymers and calculated values using Wenzel equation (Jung and Bhushan, 2006).	93
Fig. 31	Contact angle measurements for different droplet sizes on various surfaces (Jung and Bhushan, 2008c).	95
Fig. 32	Scale dependent adhesive force for various micro- and nanopatterned surfaces measured using AFM tips of various radii (Jung and Bhushan, 2006).	95
Fig. 33	Surface height maps and 2-D profiles of the micropatterned surfaces using an optical profiler (Bhushan and Jung, 2007).	98
Fig. 34	Calculated static contact angle as a function of geometric parameters for a given value of θ_0 using the Wenzel and Cassie-Baxter equations for two series of the micropatterned surfaces with different pitch values (Bhushan and Jung, 2007).	99
Fig. 35	A liquid droplet suspended on a superhydrophobic surface consisting of a regular array of circular pillars. (a) Plan view. The maximum droop of droplet occurs in the center of square formed by four pillars. (b) Side view in section A-A. The maximum droop of droplet (δ) can be found in the middle of two pillars which are diagonally across (Jung and Bhushan, 2007).	101
Fig. 36	(a) Static contact angle (a dotted line represents the transition criteria range obtained using Eq. (26) and (b) contact angle hysteresis and tilt angle as a function of geometric parameters for two series of the micropatterned surfaces with different pitch values for a droplet with 1 mm in radius (5 μL volume). Data at zero pitch correspond to a flat sample (Bhushan and Jung, 2007; Jung and Bhushan, 2007).	103
Fig. 37	Optical micrographs of droplets on the inclined micropatterned surfaces with different pitch values. The images were taken when the droplet started to move down. Data at zero pitch correspond to a flat sample (Bhushan and Jung, 2007).	

		106
Fig. 38	Evaporation of a droplet on two different micropatterned surfaces. The initial radius of the droplet is about 700 μm , and the time interval between first two photos was 180 s and between the latter was 60 s. As the radius of droplet reaches 360 μm on the surface with 5- μm diameter, 10- μm height, and 37.5- μm pitch pillars, and 420 μm on the surface with 14- μm diameter, 30- μm height, and 105- μm pitch pillars, the transition from the Cassie-Baxter regime to Wenzel regime occurs, as indicated by the arrow. Before the transition, air pocket is clearly visible at the bottom area of the droplet, but after the transition, air pocket is not found at the bottom area of the droplet (Jung and Bhushan, 2008a).	
		108
Fig. 39	Receding contact angle as a function of geometric parameters before (circle) and after (triangle) transition compared with predicted static contact angle values obtained using the Wenzel and Cassie-Baxter equations (solid lines) with a given value of θ_0 for two series of the micropatterned surfaces with different pitch values (Jung and Bhushan, 2008a).	109
Fig. 40	Radius of droplet as a function of geometric parameters for the experimental results (circle) compared with the transition criteria from the Cassie-Baxter regime to Wenzel regime (solid lines) for two series of the micropatterned surfaces with different pitch values (Jung and Bhushan, 2008a).	110
Fig. 41	Dust trace remained after droplet evaporation for the micropatterned surface. In the top image, the transition occurred at 360 μm radius of droplet, and in the bottom image, the transition occurred at about 20 μm radius of droplet during the process of droplet evaporation. The footprint size is about 450 and 25 μm for the top and bottom images, respectively (Jung and Bhushan, 2008a).	111
Fig. 42	(a) Droplet radius, R , for the Cassie-Baxter and Wenzel transition as a function of $P/D = 1/S_f$. It is observed that the transition takes place at a constant value of $RD/P \sim 50 \mu\text{m}$ (dashed line). This shows that the transition is a linear phenomenon (Nosonovsky and Bhushan, 2007c). (b) Contact angle hysteresis as a function of S_f for the 1 st (squares) and 2 nd (diamonds) series of the experiments compared with the theoretically predicted values of $\cos\theta_{\text{adv}} - \cos\theta_{\text{rec}} = (D/P)^2(\pi/4)(\cos\theta_{\text{adv}0} - \cos\theta_{\text{rec}0}) + c(D/P)^2$, where c is a proportionality constant. It is observed that when only the adhesion hysteresis/interface energy term is considered ($c = 0$), the theoretical values are underestimated by about a half, whereas $c = 0.5$ provides a good fit. Therefore, the contribution of the adhesion hysteresis is of the same order of magnitude as the contribution kinetic effects.	114
Fig. 43	Theoretical (solid and dashed) and experimental (squares for the 1 st series, diamonds for the 2 nd series) (a) contact angle as a function of the spacing factor, (b) advancing contact angle, and (c) receding contact angle and values of the contact angle observed after the transition during evaporation (blue) (Nosonovsky and Bhushan, 2007c).	117
Fig. 44	Snapshots of a droplet with 1 mm radius hitting on two different micropatterned surfaces. The impact velocity was obtained just prior to the droplet hitting the	

	surface. The pinning of droplet on the surface with 5- μm diameter, 10- μm height and 10- μm pitch pillars, and on the surface with 14- μm diameter, 30- μm height and 26- μm pitch pillars occurred at impact velocity of 0.88 m/s and 0.76 m/s, respectively (Jung and Bhushan, 2008b).	119
Fig. 45	Measured static contact angle as a function of geometric parameters for the droplet with 1 mm radius gently deposited on the surface (circles) and for the droplet with 1 mm radius after hitting the surface at 0.44 m/s (triangles). The data are compared with predicted static contact angle values obtained using Wenzel and Cassie-Baxter equations (solid lines) with a given value of θ_0 (109°) for a smooth surface for two series of the micropatterned Si with different pitch values (Jung and Bhushan, 2008b).	121
Fig. 46	Measured critical impact velocity of droplet with 1 mm radius as a function of geometric parameters (triangles). The data are compared with the criterion of impact velocity for the pinning of droplet (solid lines) for two series of the micropatterned Si with different pitch values (Jung and Bhushan, 2008b).	123
Fig. 47	Bouncing droplets dependency of the kinetic energy of a droplet that provides the regime transition upon the energy barrier calculated from Eq. 30 (squares for series 1 and diamonds for series 2). The fit (solid line) is shown for $A_0=0.12 \text{ mm}^2$ (Nosonovsky and Bhushan, 2008g).	124
Fig. 48	Microdroplet (in dimension of less than 1 mm diameter) growing and merging process under ESEM during increasing condensation by decreasing temperature. Left image: Some small water droplets appear at the beginning, i.e. water droplets 1, 2, 3. Middle image: Water droplets at locations 1 and 3 increase in size and water droplets at location 2 merge together to form one big droplet. Right image: Water droplets at locations 1 and 2 increase in size and water droplets at location 3 merge together to form one big droplet (Jung and Bhushan, 2008a).	127
Fig. 49	Microdroplets on flat and two micropatterned surfaces using ESEM. Second set of images were taken during increasing condensation, and the third set of images were taken during increasing evaporation. Static contact angle was measured when the droplet was stable. Advancing contact angle was measured after increasing condensation by decreasing the temperature of the cooling stage. Receding contact angle was measured after decreasing evaporation by increasing the temperature of the cooling stage (Jung and Bhushan, 2008a).	128
Fig. 50	Contact angle hysteresis as a function of geometric parameters for the microdroplet with about 20 μm radius from ESEM (triangle) compared with the droplet with 1 mm radius (5 μL volume) (circle and solid lines) for two series of the micropatterned surfaces with different pitch values. Data at zero pitch correspond to a flat sample (Jung and Bhushan, 2008a).	129
Fig. 51	Schematic of structure of an ideal hierarchical surface. Microasperities consist of the circular pillars with diameter D , height H , and pitch P . Nanoasperities consist of pyramidal nanoasperities of height h and diameter d with rounded tops.	130

Fig. 52	(a) Schematic of two-step molding process used to fabricate microstructure, in which at first a negative is generated and then a positive, and (b) SEM micrographs of the master of micropatterned Si surface and positive replica fabricated from the master surface measured at 45° tilt angle (shown using two magnifications) (Bhushan et al., 2009d).	132
Fig. 53	Schematic of thermal evaporation system for self-assembly of a wax. Evaporation from the point source to the substrate occurs over hemispherical region (dotted line) (Bhushan et al., 2009d).	136
Fig. 54	Schematic of a glass recrystallization chamber used for tubules formation. The filter paper placed at the bottom of the chamber was wetted with 20 mL of the solvent, and slow evaporation of the solvent was provided by placing a thin filter paper between the glass body and the cap placed above. The total volume of the chamber is about 200 cm ³ (Bhushan et al., 2009b).	136
Fig. 55	SEM micrographs of morphology of the Lotus wax deposited on the flat epoxy replica surface after two treatments of specimens measured at 45° tilt angle, (a) after seven days at 21° C (top), nanostructure on flat epoxy replica was found with no tubules, and (b) after seven days at 50° C with ethanol vapor (bottom), tubular nanostructures with random orientation were found on the surface (Koch et al., 2009b).	137
Fig. 56	SEM micrographs taken at 45° tilt angle (shown using two magnifications) of (a) the flat surface and nanostructures fabricated with various mass of <i>n</i> -hexatriacontane and (b) three-dimensional platelets forming nanostructures on the surface fabricated with 0.2 µg/mm ² mass of <i>n</i> -hexatriacontane. All samples are fabricated with epoxy resin coated with <i>n</i> -hexatriacontane (Bhushan et al., 2008a).	139
Fig. 57	Bar chart showing the measured static contact angle, contact angle hysteresis and tilt angle, calculated contact angles obtained using Wenzel and Cassie-Baxter equations with a given value of θ_0 , and calculated contact angle hysteresis using Cassie-Baxter equation on flat surface and nanostructures fabricated with various mass of <i>n</i> -hexatriacontane. The droplet on flat surface does not move along the surface even at tilt angle of 90°. The bar chart also shows adhesive forces for various structures, measured using a 15 µm radius borosilicate tip (Bhushan et al., 2008a).	143
Fig. 58	Static contact angle and contact angle hysteresis as a function of mass of <i>n</i> -hexatriacontane deposited on nanostructures (Bhushan et al., 2008a).	144
Fig. 59	SEM micrographs of the flat surface, nanostructure, microstructure, and hierarchical structure measured at 45° tilt angle (shown using two magnifications). All samples are fabricated with epoxy resin coated with <i>n</i> -hexatriacontane (Bhushan et al., 2008b).	145
Fig. 60	Bar chart showing the measured static contact angle, contact angle hysteresis and tilt angle, calculated contact angles obtained using Wenzel and Cassie-Baxter equations with a given value of θ_0 , and calculated contact angle hysteresis using Cassie-Baxter equation on various structures. The droplet on flat surface does not move along the surface even at tilt angle of 90°. The bar	

	chart also shows adhesive forces for various structures, measured using a 15 μm radius borosilicate tip (Bhushan et al., 2008b).	148
Fig. 61	SEM micrographs taken at 45° tilt angle (shown using two magnifications) of (a) the nanostructure and hierarchical structure fabricated with two different mass (0.6 and 0.8 $\mu\text{g}/\text{mm}^2$) of <i>T. majus</i> wax after storage at 50° C with ethanol vapor and (b) three-dimensional tubules forming nanostructures on the surface fabricated with 0.8 $\mu\text{g}/\text{mm}^2$ mass of <i>T. majus</i> wax after storage at 50°C with ethanol vapor (Bhushan et al., 2009c).	150
Fig. 62	Bar chart showing the measured static contact angle, contact angle hysteresis and tilt angle on various structures fabricated with 0.8 $\mu\text{g}/\text{mm}^2$ mass of <i>T. majus</i> wax after storage at 50°C with ethanol vapor. The bar chart also shows adhesive forces for various structures, measured using a 15 μm radius borosilicate tip (Bhushan et al., 2009c).	152
Fig. 63	Evaporation of a droplet on a microstructured- and hierarchical structured surfaces fabricated with 0.8 $\mu\text{g}/\text{mm}^2$ mass of <i>T. majus</i> wax after storage at 50°C with ethanol vapor. The initial radius of the droplet was about 950 μm , and the time interval between first two photos was 180 s and between the latter was 60 s. As the radius of droplet reached 425 μm (foot print = 836 μm) on the microstructured surface, the transition from Cassie-Baxter regime to Wenzel regime occurred, as indicated by the arrow. On the hierarchical structured surface air pockets, visible at the bottom area of the droplet, exist until the droplet evaporated completely (Bhushan et al., 2009b).	153
Fig. 64	SEM micrographs taken at 45° tilt angle (shown using three magnifications) of (a) nanostructure on flat replica, (b) microstructures in Lotus replica and micropatterned Si replica, and (c) hierarchical structure using Lotus and micropatterned Si replicas. Nano- and hierarchical structures were fabricated with mass 0.8 $\mu\text{g}/\text{mm}^2$ of Lotus wax after storage for seven days at 50° C with ethanol vapor (Koch et al., 2009b).	156
Fig. 65	Bar chart showing the measured static contact angle, contact angle hysteresis and tilt angle on various structures fabricated with 0.8 $\mu\text{g}/\text{mm}^2$ of Lotus wax after storage for seven days at 50°C with ethanol vapor. The bar chart also shows adhesive forces for various structures, measured using a 15 μm radius borosilicate tip. The error bar represents ± 1 standard deviation (Koch et al., 2009b).	157
Fig. 66	Bar charts showing the remaining particles after applying droplets with nearly zero kinetic energy on various structures fabricated using <i>n</i> -hexatriacontane and Lotus wax using 1-10 μm and 10-15 μm SiC particles. The experiments on the surfaces with <i>n</i> -hexatriacontane and Lotus wax were carried out on tilted stages with 10° and 3°, respectively. The error bars represent ± 1 standard deviation (Bhushan et al., 2009a).	159
Fig. 67	Snapshots of a droplet with 1 mm radius hitting various surfaces fabricated with 0.2 and 0.4 $\mu\text{g}/\text{mm}^2$ of <i>n</i> -hexatriacontane after storage at room temperature. The impact velocity was obtained just prior to the droplet hitting the surface. The pinning of droplet on the nanostructure with 0.4 $\mu\text{g}/\text{mm}^2$ mass, and on the microstructure occurred at impact velocities of 1.2 m/s and 0.77 m/s,	

	respectively (Jung and Bhushan, 2009a).	161
Fig. 68	Bar chart showing the measured critical impact velocity of a droplet with 1 mm radius at which transition occurs on various structures. The arrow indicates that the critical impact velocity can possibly be more than 1.5 m/s or the transition is not occurred (Jung and Bhushan, 2009a).	164
Fig. 69	Bar chart showing the measured static contact angle of a droplet on various surfaces. The contact angles of the left bar for each sample were measured using a droplet with 1 mm radius gently deposited on the surface. The contact angles of the middle and right bars for each sample were measured using the droplet after hitting the surface at 0.44 m/s, and critical or highest impact velocity (Jung and Bhushan, 2009a).	165
Fig. 70	Droplet of liquid in contact with a solid surface – contact angle θ ; radius of droplet R ; distance between the center of droplet and the solid H (Jung and Bhushan, 2009a).	167
Fig. 71	Optical micrographs of droplets on the microstructured surface with n -hexatriacontane before and after vibration at amplitude of 0.4 mm for 1 st mode ($n = 2$) and 2 nd mode ($n = 3$) of vibration. The frequencies for 1 st mode and 2 nd mode were measured to be 86 Hz and 208 Hz, respectively (Jung and Bhushan, 2009a).	169
Fig. 72	Optical micrographs of droplets on various surfaces with n -hexatriacontane before and after vibrating at frequency of 30 Hz. The transition of a droplet on the nanostructure with $0.12 \mu\text{g}/\text{mm}^2$ mass of n -hexatriacontane and on the microstructure occurred at amplitudes of 2.4 mm and 2.0 mm, respectively (Jung and Bhushan, 2009a).	170
Fig. 73	Bar chart showing the calculated adhesive force responsible for the separation between the droplet and surface and inertia force of a droplet vibrated on various structures. The inertia forces were obtained as the transition or droplet bounce off occurred. If the inertia force of the droplet vibrated on the surface can overcome the adhesion force between the droplet and surface (ΔF is positive), the droplet can be vertically separated from the surface (bouncing off) before the composite solid-liquid-air interface is destroyed (Jung and Bhushan, 2009a).	172
Fig. 74	Schematic of spray method to deposit a mixture of CNT, epoxy, and acetone on surfaces (Jung and Bhushan, 2010b).	174
Fig. 75	SEM micrographs taken at 45° tilt angle, show three magnifications of nano- and hierarchical structures fabricated with CNT after three hours at 120°C (Jung and Bhushan, 2010b).	175
Fig. 76	Bar chart showing the measured static contact angle and contact angle hysteresis on (a) nano- and hierarchical structures fabricated with CNT after three hours at 120°C, and (b) various structures fabricated with $0.8 \mu\text{g}/\text{mm}^2$ of Lotus wax after storage for seven days at 50°C with ethanol vapor. The error bar represents ± 1 standard deviation (Jung and Bhushan, 2010b).	177
Fig. 77	Static contact angle and contact angle hysteresis as a function of exposure time at water pressure of 10 kPa and water pressure of exposure for 20 min for the droplet with a 1 mm radius ($5 \mu\text{L}$ volume) gently deposited on the surfaces with	

	(a) CNT and (b) Lotus wax. The data are reproducible within $\pm 5\%$ (Jung and Bhushan, 2010b).	179
Fig. 78	Surface height maps before and after wear tests with a 15 μm radius borosilicate ball at 100 nN and 10 μN for nanostructures with (a) CNT and (b) Lotus wax using an AFM (Jung and Bhushan, 2010b).	181
Fig. 79	Coefficient of friction as a function of number of cycles using a ball-on-flat tribometer for the surfaces with (a) CNT and (b) Lotus wax at room temperature ($22 \pm 1^\circ\text{C}$) and ambient air ($45 \pm 5\%$ RH). The data are reproducible within $\pm 5\%$ based on three measurements (Jung and Bhushan, 2010b).	184
Fig. 80	Optical micrographs before and after wear test at 10 mN (100 cycles) using a ball-on-flat tribometer for the surfaces with (a) CNT and (b) Lotus wax (Jung and Bhushan, 2010b).	185
Fig. 81	Schematic of the experimental flow channel connected with a differential manometer. The thickness, width, and length of the channel are H , W , and L , respectively (Jung and Bhushan, 2010a)	188
Fig. 82	(a) SEM micrographs taken at top view, 45° tilt angle side view and 45° tilt angle top view, show shark skin (<i>Squalus acanthias</i>) replica. The shark skin replica show only three ribs on each scale. It is clearly visible that the V-shaped riblets' height varies between 200-500 μm and their space varies between 100-300 μm , and (b) optical microscope images (shown using two magnifications) show the rib patterned surface fabricated as a model of artificial shark skin surfaces (Jung and Bhushan, 2010a).	192
Fig. 83	Pressure drop as a function of flow rate in the channel with various surfaces using water flow. The figure in the bottom is magnified in flow rate between 0 and 500 $\mu\text{L/s}$. Data are compared with predicted pressure drop values for a hydrophilic surface obtained using the Eq. 46 for laminar and turbulent flows (solid lines) (Jung and Bhushan, 2010a).	195
Fig. 84	Bar chart showing the slip length in the channel with various surfaces using water flow in laminar flow ($0 < \text{Re} < 300$). The slip length was calculated using the Eq. 53 and the pressure drop measured on various surfaces. The error bar represents ± 1 standard deviation (Jung and Bhushan, 2010a).	196
Fig. 85	Pressure drop as a function of flow rate in the channel with flat acrylic resin and rib patterned surface using water flow. The figure in the bottom is magnified in flow rate between 0 and 500 $\mu\text{L/s}$. Data are compared with predicted pressure drop values for a hydrophilic surface obtained using the Eq. 46 for laminar and turbulent flows (solid lines) (Jung and Bhushan, 2010a).	197
Fig. 86	Pressure drop as a function of flow rate in the channel with various surfaces using air flow. The figure in the bottom is magnified in flow rate between 0 and 50 mL/s. Data are compared with predicted pressure drop values for a hydrophilic surface obtained using the Eq. 46 for laminar and turbulent flows (solid lines) (Jung and Bhushan, 2010a).	199
Fig. 87	Pressure drop as a function of flow rate in the channel with flat acrylic resin and rib patterned surface using air flow. Data are compared with predicted pressure drop values for a hydrophilic surface obtained using the Eq. 46 for laminar and turbulent flows (solid lines) (Jung and Bhushan, 2010a).	200

Fig. 88	Schematics of a droplet of liquid showing philic/phobic nature in three different phase interface on the surface – θ_w , θ_o , and θ_{ow} are static contact angles of water droplet, oil droplet, and oil droplet in water, respectively (Jung and Bhushan, 2009b).	203
Fig. 89	Schematics of a solid-water-oil interface system. A specimen is first immersed in water phase, and then an oil droplet is gently deposited using a microsyringe, and the static contact angle in the system is measured (Jung and Bhushan, 2009b).	205
Fig. 90	SEM micrographs taken at a 45° tilt angle showing two magnifications of (a) the micropatterned surface, (b) hierarchical structure and nanostructure with three-dimensional platelets on the surface fabricated with 0.2 $\mu\text{g}/\text{mm}^2$ mass of <i>n</i> -hexatriacontane, and (c) shark skin (<i>Squalus acanthias</i>) replica. The shark skin replica shows only three ribs on each scale. It is clearly visible that the V-shaped riblets' height varies between 200-500 μm and their space varies between 100-300 μm (Jung and Bhushan, 2009b).	207
Fig. 91	Optical micrographs of droplets in three different phase interfaces on flat epoxy resin and micropatterned surface without and with $\text{C}_{20}\text{F}_{42}$. Left image: a water droplet is placed on a surface in air. Middle image: an oil droplet is placed on a surface in air. Right image: an oil droplet is placed on a solid surface in water (Jung and Bhushan, 2009b).	209
Fig. 92	Static contact angle as a function of geometric parameters for water droplet (circle) and oil droplet (cross) in air, and oil droplet in water (triangle) compared with predicted static contact angle values obtained using Wenzel and Cassie-Baxter equations (solid lines) with a measured value of θ_0 for the micropatterned surfaces (Jung and Bhushan, 2009b).	211
Fig. 93	Static contact angle as a function of geometric parameters for water droplet (circle) and oil droplet (cross) in air, and oil droplet in water (triangle) compared with predicted static contact angle values obtained using Wenzel and Cassie-Baxter equations (solid lines) with a measured value of θ_0 for the micropatterned surfaces with $\text{C}_{20}\text{F}_{42}$ (Jung and Bhushan, 2009b).	214
Fig. 94	Optical micrographs of droplets in three different phase interfaces on nanostructure and hierarchical structure fabricated with 0.2 $\mu\text{g}/\text{mm}^2$ mass of <i>n</i> -hexatriacontane. Left image: a water droplet is placed on a surface in air. Middle image: an oil droplet is placed on a surface in air. Right image: an oil droplet is placed on a solid surface in water (Jung and Bhushan, 2009b).	216
Fig. 95	Optical micrographs of droplets in three different phase interfaces on shark skin replica without and with $\text{C}_{20}\text{F}_{42}$. Left image: a water droplet is placed on a surface in air. Middle image: an oil droplet is placed on a surface in air. Right image: an oil droplet is placed on a solid surface in water (Jung and Bhushan, 2009b).	217

CHAPTER 1

INTRODUCTION

Biologically inspired design, adaptation, or derivation from nature is referred to as ‘biomimetics.’ It means mimicking biology or nature. Biomimetics is derived from the Greek word biomimesis. The word was coined by polymath Otto Schmitt in 1957, who, in his doctoral research, developed a physical device that mimicked the electrical action of a nerve. Other words used include bionics (coined in 1960 by Jack Steele of Wright-Patterson Air Force Base in Dayton, OH), biomimicry, and biognosis. The field of biomimetics is highly interdisciplinary. It involves the understanding of biological functions, structures, and principles of various objects found in nature by biologists, physicists, chemists, and material scientists, and the design and fabrication of various materials and devices of commercial interest by engineers, material scientists, chemists, and others. The word biomimetics first appeared in Webster’s dictionary in 1974 and is defined as ‘the study of the formation, structure or function of biologically produced substances and materials (as enzymes or silk) and biological mechanisms and processes (as protein synthesis or photosynthesis) especially for the purpose of synthesizing similar products by artificial mechanisms which mimic natural ones’ (Bhushan, 2009).

Nature has gone through evolution over the 3.8 Gyr since life is estimated to have appeared on the Earth (Gordon, 1976). Nature has evolved objects with high performance using commonly found materials. These function on the macroscale to the nanoscale. The understanding of the functions provided by objects and processes found in nature can guide us to imitate and produce nanomaterials, nanodevices, and processes (Bhushan, 2009).

There are a large number of objects, including bacteria, plants, land and aquatic animals, and seashells, with properties of commercial interest. **Figure 1** shows a montage of some examples from nature (Bhushan, 2009). Some leaves of water-repellent plants,

Figure 1. Montage of some examples from nature: (a) Lotus effect (Bhushan et al., 2009b), (b) glands of carnivorous plant secrete adhesive to trap insects (Koch et al., 2009a), (c) pond skater walking on water (Gao and Jiang, 2004), (d) gecko foot exhibiting reversible adhesion (Gao et al., 2005), (e) scale structure of shark reducing drag (Reif, 1985), (f) wings of a bird in landing approach, (g) spiderweb made of silk material (Bar-Cohen, 2006), and (h) antireflective moth's eye (Genzer and Efimenko, 2006).

such as *Nelumbo nucifera* (Lotus), are known to be superhydrophobic and self-cleaning due to hierarchical roughness (microbumps superimposed with a nanostructure) and the presence of a hydrophobic wax coating (Neinhuis and Barthlott, 1997; Barthlott and Neinhuis, 1997; Wagner et al., 2003; Burton and Bhushan, 2006; Bhushan and Jung, 2006; Bhushan, 2009; Koch et al., 2008a, 2009a). Water droplets on these surfaces readily sit on the apex of nanostructures because air bubbles fill in the valleys of the structure under the droplet. Therefore, these leaves exhibit considerable superhydrophobicity (**Fig. 1(a)**). Two strategies used for catching insects by plants for digestion are having sticky surfaces or sliding structures. As an example, for catching insects using sticky surfaces, the glands of the carnivorous plants of the genus *Pinguicula* (butterworts) and *Drosera* (sundew), shown in **Fig. 1(b)**, secrete adhesives and enzymes to trap and digest small insects, such as mosquitoes and fruit flies (Koch et al., 2009a). Pond skaters (*Gerris remigis*) have the ability to stand and walk upon a water surface without getting wet (**Fig. 1(c)**). Even the impact of rain droplets with a size greater than the pond skater's size does not make it immerse in the water. Gao and Jiang (2004) showed that the special hierarchical structure of the pond skater's legs, which are covered by large numbers of oriented tiny hairs (microsetae) with fine nanogrooves and covered with cuticle wax, makes the leg surfaces superhydrophobic, is responsible for the water resistance, and enables them to stand and walk quickly on the water surface. A gecko is the largest animal that can produce high (dry) adhesion to support its weight with a high factor of safety. Gecko skin is comprised of a complex hierarchical structure of lamellae, setae, branches, and spatula (Autumn et al., 2000; Gao et al., 2005; Bhushan, 2007a). The attachment pads on two feet of the Tokay gecko have an area of approximately 220 mm² (**Fig. 1(d)**). Approximately 3×10^6 setae on their toes can produce a clinging ability of approximately 20 N (vertical force required to pull a lizard down a nearly vertical (85°) surface) and allow them to climb vertical surfaces at speeds of over 1 m/s, with the capability to attach or detach their toes in milliseconds (Bhushan, 2007a). Shark skin, which is a model from nature for a low drag surface, is covered by very small individual tooth-like scales called dermal denticles (little skin teeth), ribbed with longitudinal grooves (aligned parallel to the local flow direction of the water). These grooved scales reduce the formation of vortices present on a smooth surface, resulting in water moving

efficiently over their surface (Bechert et al., 2000). An example of scale structure on the right front of a Galapagos shark (*Carcharhinus galapagensis*) is shown in **Fig. 1(e)** (Reif, 1985). Birds consist of several consecutive rows of covering feathers on their wings, which are flexible (**Fig. 1(f)**). These movable flaps develop the lift. When a bird lands, a few feathers are deployed in front of the leading edges of the wings, which help to reduce the drag on the wings. The spider generates silk fiber and has a sufficient supply of raw material for its silk to span great distances (Jin and Kaplan, 2003; Bar-Cohen, 2006). Spiderweb is a structure built of a one-dimensional fiber (**Fig. 1(g)**). The fiber is very strong and continuous and is insoluble in water. The web can hold a significant amount of water droplets, and it is resistant to rain, wind, and sunlight (Sarikaya and Aksay, 1995; Bar-Cohen, 2006). The eyes of moths are antireflective to visible light and consist of hundreds of hexagonally organized nanoscopic pillars, each approximately 200 nm in diameter and height, which result in a very low reflectance for visible light (**Fig. 1(h)**) (Genzer and Efimenko, 2006; Mueller, 2008). These nanostructures' optical surfaces make the eye surface nearly antireflective in any direction.

This thesis primarily focuses on water-repellent surfaces such as the Lotus leaf (**Fig. 1(a)**), which exhibits superhydrophobicity, self-cleaning, low adhesion, and drag reduction. Aquatic animal skin, such as shark skin (**Fig. 1(e)**), is a model from nature for drag reduction, and is also explored. Furthermore, oleophobic and self-cleaning surfaces inspired from aquatic animals are discussed.

1.1. Definitions and applications

The primary parameter that characterizes wetting is the static contact angle, which is defined as the angle that a liquid makes with a solid. The contact angle depends on several factors, such as surface energy, surface roughness, and its cleanliness (Adamson, 1990; Israelachvili, 1992; Bhushan, 1999, 2002, 2008; Nosonovsky and Bhushan, 2008a). If the liquid wets the surface (referred to as wetting liquid or hydrophilic surface), the value of the static contact angle is $0 \leq \theta \leq 90^\circ$, whereas if the liquid does not wet the surface (referred to as a non-wetting liquid or hydrophobic surface), the value of the contact angle is $90^\circ < \theta \leq 180^\circ$. The term hydrophobic/philic, which was originally

applied only to water (“hydro-” means “water” in Greek), is often used to describe the contact of a solid surface with any liquid. The term “oleophobic/philic” is used with regard to wetting by oil and organic liquids. The term “amphiphobic/philic” is used for surfaces that are both hydrophobic/philic and oleophobic/philic. Surfaces with high energy, formed by polar molecules, tend to be hydrophilic, whereas those with low energy and built of non-polar molecules tend to be hydrophobic.

Surfaces with a contact angle of less than 10° are called superhydrophilic, while surfaces with a contact angle between 150° and 180° are called superhydrophobic. In fluid flow, in order to have low drag and for applications requiring the self-cleaning feature, in addition to the high contact angle, superhydrophobic surfaces should also have very low water contact angle hysteresis. Water droplets roll off (with some slip) on these surfaces and take contaminants with them, providing the self-cleaning ability known as the “Lotus effect.” The contact angle at the front of the droplet (advancing contact angle) is greater than that at the back of the droplet (receding contact angle), resulting in contact angle hysteresis (CAH), which is the difference between the advancing and receding contact angles, representing two stable values. It occurs due to surface roughness and surface heterogeneity. Contact angle hysteresis reflects the irreversibility of the wetting/dewetting cycle. It is a measure of energy dissipation during the flow of a droplet along a solid surface. At a low value of CAH, the droplets may roll in addition to slide, which facilitates removal of contaminant particles. Surfaces with low contact angle hysteresis have a low water roll-off (tilt) angle, which denotes the angle to which a surface must be tilted for roll off of water drops (Extrand, 2002; Kijlstra et al., 2002; Bhushan and Jung, 2008; Nosonovsky and Bhushan, 2007a, 2008a,b,c; Bhushan et al., 2009a). Surfaces with CAH or a low tilting angle of less than $< 10^\circ$ are generally referred to as self-cleaning surfaces. Self-cleaning surfaces are of interest in various applications, including self-cleaning windows, windshields, exterior paints for buildings and navigation ships, utensils, roof tiles, textiles, solar panels, and applications requiring antifouling and a reduction of drag in fluid flow, e.g., in micro/nanochannels.

Superhydrophobic surfaces can also be used for energy conservation and conversion (Nosonovsky and Bhushan, 2008h, 2009a,b). Recent advances in superhydrophobic surfaces make such applications possible. Several concepts can be

used. First, the hydrophobic/philic properties of a surface significantly affect the capillary adhesion force that, in turn, affects friction and energy dissipation during the sliding contact of solid surfaces. Selection of a proper superhydrophobic surface allows the reduction of energy dissipation. Second, superhydrophobic and superoleophobic surfaces can be used for fuel economy. Third, the recently discovered effect of reversible superhydrophobicity provides potential for new ways of energy conversion such as the microscale capillary engine.

Wetting may lead to the formation of concave shaped menisci at the interface between hydrophilic solid bodies during static or sliding contact. These menisci develop a negative pressure leading to an intrinsic attractive force which increases adhesion and friction (**Fig. 2**). In some cases, the wet friction force can be greater than the dry friction force, which is usually undesirable (Bhushan, 1999, 2002, 2003, 2007b, 2008). On the other hand, high adhesion is desirable in some applications, such as adhesive tapes and adhesion of cells to biomaterial surfaces; therefore, enhanced wetting would be desirable in these applications. Numerous applications, such as magnetic storage devices and micro/nanoelectromechanical systems (MEMS/NEMS), require surfaces with low adhesion and stiction (Bhushan et al., 1995; Bhushan, 1996, 1998, 2001, 2003, 2007b, 2008). As the size of these devices decreases, surface forces tend to dominate over the volume forces, and adhesion and stiction constitute a challenging problem for proper operation of these devices. This makes the development of superhydrophobic surfaces with non-adhesive characteristics crucial for many of these emerging applications.

Figure 2. A schematic diagram of condensed water vapor from the environment forming meniscus bridges at asperity contacts which lead to an intrinsic attractive force.

1.2. Natural superhydrophobic, self-cleaning, low adhesion, and drag reduction surfaces

In the 1990s, biologists and materials scientists started to study natural superhydrophobic surfaces. Among them are the leaves of water-repellent plants such as *Nelumbo nucifera* (Lotus) and *Colocasia esculenta*, which have high contact angles with water (**Fig. 3**) (Neinhuis and Barthlott, 1997; Barthlott and Neinhuis, 1997; Wagner et al., 2003; Burton and Bhushan, 2006; Bhushan and Jung, 2006; Bhushan, 2009; Koch et al., 2008a, 2009a). The leaf surface is very rough due to so-called papillose epidermal cells, which form papillae or microasperities. In addition to the microscale roughness, the surface of the papillae is also rough, with nanoscale asperities composed of three-dimensional epicuticular waxes which are long chain hydrocarbons and hydrophobic. The waxes of Lotus exist as tubules, but on other leaves, waxes exist also in the form of

Figure 3. SEM micrographs (shown at three magnifications) of Lotus (*Nelumbo nucifera*) leaf surface which consists of microstructure formed by papillose epidermal cells covered with 3-D epicuticular wax tubules on surface, which create nanostructure, and image of water droplet sitting on the Lotus leaf (Bhushan et al., 2009b).

platelets or other morphologies (Koch et al., 2008a, 2009a). The hierarchical structure of these leaves has been studied by Burton and Bhushan (2006) and Bhushan and Jung (2006). The water droplets on these surfaces readily sit on the apex of the nanostructures because air bubbles fill in the valleys of the structure under the droplet. Therefore, these leaves exhibit considerable superhydrophobicity. Static contact angle and contact angle hysteresis of a Lotus leaf are about 164° and 3° , respectively (Bhushan et al., 2009b; Koch et al., 2009b). The water droplets on the leaves remove any contaminant particles from their surfaces when they roll off, leading to self-cleaning (Neinhuis and Barthlott, 1997). It has been reported that all superhydrophobic and self-cleaning leaves consist of an intrinsic hierarchical structure (Koch et al., 2008a, 2009a). Hierarchical structure provides air pocket formation, leading to the lowest contact area of an applied water droplet (**Fig. 4**), resulting in the reduction of contact angle hysteresis, tilt angle, and adhesive force (Bhushan and Jung, 2008; Nosonovsky and Bhushan, 2008a; Bhushan et al., 2009b). Other examples of biological objects include water striders (*Gerris remigis*) (Gao and Jiang, 2004) and mosquito (*Culex pipiens*) eyes (Gao et al., 2007). Their hierarchical structures are responsible for superhydrophobicity. Duck feathers and butterfly wings also provide superhydrophobicity (Bhushan, 2009). Their corrugated surfaces provide air pockets that prevent water from completely touching the surface.

Figure 4. Schematic and wetting of the four different surfaces. The largest contact area between the droplet and the surface is given in flat and microstructured surfaces, but is reduced in nanostructured surfaces and is minimized in hierarchical structured surfaces.

1.3. Natural superoleophobic, self-cleaning, and drag reduction surfaces

A model surface for superoleophobicity and self-cleaning is provided by fish which are known to be well protected from contamination by oil pollution although they are wetted by water (Nosonovsky and Bhushan, 2009a). Fish scales have a hierarchical structure consisting of sector-like scales with diameters of 4-5 mm covered by papillae 100-300 μm in length and 30-40 μm in width (Liu et al., 2009). Shark skin, which is a model from nature for a low drag surface, is covered by very small individual tooth-like scales called dermal denticles (little skin teeth), ribbed with longitudinal grooves (aligned parallel to the local flow direction of the water). These grooved scales reduce vortices formation present on a smooth surface, resulting in water moving efficiently over their surface (Bechert et al., 2000; Bhushan, 2009; Jung and Bhushan, 2009b, 2010a). The water surrounding these complex structures can lead to protection from marine fouling and play a role in the defense against adhesion and growth of marine organisms, e.g., bacteria and algae (Genzer and Efimenko, 2006; Koch et al., 2009a). If oil is present on the surfaces in air or water, surfaces are known to be oleophobic and may provide self-cleaning and anti-fouling. The many sea animals including fish and shark are known to be oleophobic under water. Superoleophobic surfaces can also reduce significant losses of residual fuel in fuel tanks and pipes (Nosonovsky and Bhushan, 2008h).

1.4. Roughness-induced superhydrophobicity, self-cleaning, low adhesion, and drag reduction

One of the ways to increase the hydrophobic or hydrophilic properties of a surface is to increase surface roughness, so roughness-induced hydrophobicity or hydrophilicity has become the subject of extensive investigations. Wenzel (1936) suggested a simple model predicting that the contact angle of a liquid with a rough surface is different from that with a smooth surface. Cassie and Baxter (1944) showed that a gaseous phase including water vapor, commonly referred to as “air” in the literature, may be trapped in the cavities of a rough surface, resulting in a composite solid-liquid-air interface, as opposed to the homogeneous solid-liquid interface. These two models describe two possible wetting regimes or states: the homogeneous (Wenzel) and the composite

(Cassie-Baxter) regimes. Johnson and Dettre (1964) showed that the homogeneous and composite interfaces correspond to the two equilibrium states of a droplet. Many authors have investigated the stability of artificial superhydrophobic surfaces and showed that whether the interface is homogeneous or composite may depend on the history of the system, in particular whether the liquid was applied from the top or condensed at the bottom (Bico et al., 2002; Marmur, 2003, 2004; Lafuma and Qur, 2003; Patankar, 2004a; He et al., 2003). Extrand (2002) pointed out that whether the interface is homogeneous or composite depends on roughness structure and droplet size. It has also been suggested that the hierarchical roughness, composed by superposition of two roughness patterns at different length-scales (Herminghaus, 2000; Patankar, 2004b; Sun et al., 2005; Nosonovsky and Bhushan, 2007a,b,c,d, 2008a,b,c,f, 2009a,b), and fractal roughness (Shibuichi et al., 1996; Nosonovsky and Bhushan, 2008c) may enhance superhydrophobicity.

Herminghaus (2000) showed that certain self-affine profiles may result in superhydrophobic surfaces even for wetting liquids, if the local equilibrium condition for the triple line (line of contact between solid, liquid and air) is satisfied. Nosonovsky and Bhushan (2005, 2006a) pointed out that such configurations, although formally possible, are likely to be unstable. Nosonovsky and Bhushan (2006a, b) proposed a probabilistic model for wetting of rough surfaces with a certain probability associated with every equilibrium state. According to their model, the overall contact angle with a two-dimensional rough profile is calculated by assuming that the overall configuration of a droplet occurs as a result of superposition of numerous metastable states. The probability-based concept is consistent with the experimental data (Bhushan and Jung, 2007, 2008; Bhushan et al., 2007, 2008a,b, 2009b,c,d; Jung and Bhushan, 2007, 2008a,b, 2009a; Koch et al., 2009b), which suggests that the transition between the composite and homogeneous interfaces is gradual, rather than instant. Nosonovsky and Bhushan (2007a,b,d, 2008a,b,c,d,e,f,g) have identified mechanisms which lead to the destabilization of the composite interface, namely the capillary waves, condensation and accumulation of nanodroplets, and surface inhomogeneity. These mechanisms are scale-dependent, with different characteristic length scales. To effectively resist these scale-dependent mechanisms, a multiscale (hierarchical) roughness is required. High asperities

resist the capillary waves, while nanobumps prevent nanodroplets from filling the valleys between asperities and pin the triple line in case of a hydrophilic spot.

Various criteria have been formulated to predict the transitions from a metastable composite state to a wetted state. Extrand (2004) formulated the transition criterion referred to as the contact line density criterion, which was obtained by balancing the droplet weight and the surface forces along the contact line. Patankar (2004a) proposed a transition criterion based on energy balance. There is an energy barrier in going from a higher energy Cassie-Baxter droplet to a lower energy Wenzel droplet. The most probable mechanism is that the decrease in the gravitational potential energy during the transition helps in overcoming the energy barrier. This energy barrier was estimated by considering an intermediate state in which the water fills the grooves below the contact area of a Cassie-Baxter droplet but the liquid-solid contact is yet to be formed at the bottom of the valleys. These criteria were tested on selected experiments from the literature (Bico et al., 1999; Oner and McCarthy, 2000; Yoshimitsu et al., 2002; He et al., 2003). Bhushan et al. (2007) and Nosonovsky and Bhushan (2007c,d) found that the transition occurs at a critical value of the spacing factor, a non-dimensional parameter which is defined as the diameter of the pillars divided by the pitch distance between them for patterned surfaces and its ratio to the droplet size. Bhushan and Jung (2007, 2008) and Jung and Bhushan (2007, 2008a,b) proposed the transition criterion based on the pitch distance between the pillars and the curvature of the droplet governed by the Laplace equation, which relates the pressure inside the droplet to its curvature. In addition, the transition can occur by applying external pressure to the droplet, or by the impact of a droplet on the patterned surfaces (Richard et al., 2002; Lafuma and Quere, 2003; Bartolo et al., 2006; Reyssat et al., 2006; Jung and Bhushan, 2008b, 2009a; Nosonovsky and Bhushan, 2008g).

Contact angle on selected patterned surfaces has been measured to understand how the transition between the Cassie-Baxter regime and Wenzel regime occurs. Evaporation studies are useful in characterizing the wetting behavior because droplets with various sizes can be created to evaluate the transition criterion on a given patterned surface (Bourges-Monnier and Shanahan, 1995; Rowan et al., 1995; Erbil et al., 2002; McHale et al., 2005; Jung and Bhushan, 2007, 2008a; Nosonovsky and Bhushan, 2007a,c,

2008b,d,e; Bhushan et al., 2008a, 2009b,c,d). It has been reported that the wetting state changes from the Cassie-Baxter to Wenzel state as the droplet becomes smaller than a critical value on patterned surfaces during evaporation. Another important phenomenon related to wetting behavior is the bouncing of droplets. When a droplet hits a surface, it can bounce, spread, or stick. In practical applications of superhydrophobic surfaces, surfaces should maintain their ability to repel penetrating droplets under dynamic conditions. Jung and Bhushan (2008b) and Nosonovsky and Bhushan (2008g) showed that the transition can occur by the impact of a droplet on a given patterned surface at a critical velocity with a critical geometric parameter.

An environmental scanning electron microscope (ESEM) can be used to condense or evaporate water droplets on surfaces by adjusting the pressure of the water vapor in the specimen chamber and the temperature of the cooling stage. Transfer of the water droplet has been achieved by a specially designed micro-injector device on wool fibers and then imaged at room temperature in ESEM (Danilatos and Brancik, 1986). Images of water droplets show strong topographic contrast in ESEM such that reliable contact angle measurements can be made on the surfaces (Stelmashenko et al., 2001). Water condensation and evaporation studies on patterned surfaces were carried out by Jung and Bhushan (2008a) and Nosonovsky and Bhushan (2007a,c, 2008b,d,e) where the change of static contact angle and contact angle hysteresis was related with the surface roughness.

It has been demonstrated experimentally that roughness changes contact angle in accordance with the Wenzel model or Cassie-Baxter model, dependent upon whether the surface is hydrophilic or hydrophobic. Yost et al. (1995) found that roughness enhances wetting of a copper surface with Sn-Pb eutectic solder, which has a contact angle of 15-20° for a smooth surface. Shibuichi et al. (1996) measured the contact angle of various liquids (mixtures of water and 1,4-dioxane) on alkylketen dimmer (AKD) substrate (contact angle not larger than 109° for a smooth surface). They found that for wetting liquids, the contact angle decreases with increasing roughness, whereas for non-wetting liquids it increases. Semal et al. (1999) investigated the effect of surface roughness on contact angle hysteresis by studying a sessile droplet of squalane spreading dynamically on multilayer substrates (behenic acid on glass) and found an increase in microroughness slows the rate of droplet spread. Erbil et al. (2003) measured the contact angle of

polypropylene (contact angle of 104° for smooth surface) and found that the contact angle increases with increasing roughness. Burton and Bhushan (2005) measured contact angle with roughness of patterned surfaces and found that in the case of hydrophilic surfaces, it decreases with increasing roughness, and for hydrophobic surfaces, it increases with increasing roughness. Bhushan and Jung (2007, 2008), Jung and Bhushan (2006, 2007, 2008a,b), Bhushan et al. (2007, 2008a,b, 2009b,c,d), and Koch et al. (2009b) studied the influence of micro-, nano- and hierarchical structures, created by replication of micropatterns and by self assembly of hydrophobic alkanes and plant wax, on static contact angle, contact angle hysteresis, tilt angle and air pocket formation, adhesive force as well as efficiency of self-cleaning. They showed that for micro-, nano- and hierarchical structures, the introduction of roughness increased the hydrophobicity of the surfaces. A hierarchical structure composed of a microstructure with a superimposed nanostructure of hydrophobic waxes led to superhydrophobicity with static contact angles of 173° and low contact angle hysteresis of 2° . Jung and Bhushan (2010b) produced mechanically durable carbon nanotubes (CNT) composite hierarchical structures with a static contact angle of 170° and a contact angle hysteresis of 2° by replication of a micropatterned silicon surface using an epoxy resin and by deposition of the CNT composite using a spray method. They showed that the CNT composite structure had high mechanical strength and wear resistance from the uniform distribution and strong bonding of CNT on substrates.

Drag reduction in fluid flow is of interest in micro/nanofluidics based biosensor applications (Bhushan, 2007b). To reduce pressure drop and volume loss in micro/nanochannels, it is desirable to minimize the drag force in the solid-liquid interface. It is generally assumed that the relative velocity between a solid wall and liquid is zero at the solid-liquid interface, which is so called the no-slip boundary condition (**Fig. 5** left) (Stokes, 1851; Batchelor, 1970). However, this assumption has been widely debated for hydrophobic surfaces, and fluid film exhibits a phenomenon known as slip, which means that the fluid velocity near the solid surface is not equal to the velocity of the solid surface (**Fig. 5** right) (Goldstein, 1938, 1969; Lauga et al., 2005; Neto et al., 2005; Maali and Bhushan, 2008; Wang et al., 2009; Wang and Bhushan, 2010). The degree of boundary slip at the solid-liquid interface is characterized by a slip length. Slip length b is

defined as the length of the vertical intercept along the axis orthogonal to the interface when a tangent line is drawn along the velocity profile at the interface (**Fig. 5** right). Recent experiments with surface force apparatus (SFA) (Baudry et al., 2001; Zhu and Granick, 2002; Cottin-Bizonne et al., 2005), atomic force microscopy (AFM) (Vinogradova and Yakubov, 2003; Wang et al., 2009; Wang and Bhushan, 2010), and particle image velocimetry (PIV) (Tretheway and Meinhart, 2002) techniques have reported slip length on hydrophobic surfaces, and no slip was observed on hydrophilic surfaces (Baudry et al., 2001; Tretheway and Meinhart, 2002; Vinogradova and Yakubov, 2003; Cottin-Bizonne et al., 2005; Honig and Ducker, 2007; Maali et al., 2009). Theoretical studies (Watts et al., 1990; Lauga and Stone, 2003; Cottin-Bizonne et al., 2004; Sbragaglia and Prosperetti, 2007) and experimental studies (Ou et al., 2004; Choi and Kim, 2006; Joseph et al., 2006; Wang and Bhushan, 2010) suggest that the presence of nanobubbles at the solid-liquid interface is responsible for boundary slip on hydrophobic surfaces.

Figure 5. Schematic of velocity profiles of fluid flow without and with boundary slip. The definition of slip length b characterizes the degree of boundary slip at solid-liquid interface. The arrows represent directions for fluid flow.

1.5. Roughness-induced superoleophobicity

The surface tension of oil and organic liquids is lower than that of water, so to create a superoleophobic surface, the surface energy of the solid surface in air should be lower than that of oil. For underwater applications, if an oil droplet is placed on a solid surface in water, the solid-water-oil interface exists. The nature of oleophobicity/philicity of an oil droplet in water can be determined from the values of surface energies of various interfaces and contact angles of water and oil in air.

Many superoleophobic surfaces have been developed by modifying the surface chemistry with a coating of extreme low surface energy materials (Shibuichi et al., 1998; Li et al., 2001; Kiuru and Alakoski, 2004; Xie et al., 2004; Nicolas et al., 2006; Hoefnagels et al., 2007; Tuteja et al., 2007; Jung and Bhushan, 2009b). Tuteja et al. (2007) showed that surface curvature, in conjunction with chemical composition and roughened texture, can be used for liquids with low surface tension, including alkanes such as decane and octane. Liu et al. (2009) performed experiments in a solid-water-oil interface. They found that hydrophilic and oleophilic surfaces (solid-air-water interface and solid-air-oil interface) can switch to an oleophobic surface in water (solid-water-oil interface). As a result, oil contaminants are washed away when immersed in water. This effect can be employed for underwater oleophobicity and self-cleaning that can be used against marine ship fouling (Nosonovsky and Bhushan, 2009a). Jung and Bhushan (2009b) proposed a model for predicting the oleophobic/philic nature of surfaces and showed how the water and oil droplets in three phase interfaces influence the wetting behavior on micropatterned surfaces with varying pitch values as well as the shark skin replica as an example of aquatic animal.

1.6. Scope of the thesis

In this thesis, numerical models which provide relationships between roughness and contact angle and contact angle hysteresis as well as the Cassie-Baxter and Wenzel regime transition are discussed. The role of microbumps and nanobumps is examined by analyzing the surface characterization of hydrophobic and hydrophilic leaves on the micro- and nanoscale. Along with measuring and characterizing surface roughness, the contact angle and adhesion and friction properties of these leaves are also considered.

The knowledge gained by examining these properties of the leaves and by quantitatively analyzing the surface structure will help in the design of superhydrophobic and self-cleaning surfaces. Next, the techniques of producing superhydrophobic surfaces are described. Micro-, nano- and hierarchical patterned structures have been fabricated using soft lithography, photolithography, and techniques which involve the replication of micropatterns, self assembly of hydrophobic alkanes and plant waxes, and a spray coating of carbon nanotubes. They have been characterized to validate the models and to provide design guidelines for superhydrophobic and self-cleaning surfaces. To further examine the effect of meniscus force and real area of contact, scale dependence is considered with the use of AFM tips of various radii. To investigate how the effects of droplet size and impact velocity influence the transition, evaporation and bouncing studies are conducted on silicon surfaces patterned with pillars of two different diameters and heights and with varying pitch values and deposited with a hydrophobic coating. In order to generate submicron droplets, an atomic force microscopy-based technique using a modified nanoscale dispensing probe is presented. An ESEM study on the wetting behavior for a microdroplet with about 20 μm radius on the micropatterned Si surfaces is presented. For the durability of the various fabricated surfaces, the loss of superhydrophobicity as well as wear and friction is investigated.

Artificial surfaces from shark skin, which is one of the examples found in nature for drag reduction, have been created. To investigate drag reduction efficiency on biomimetic structured surfaces, pressure drop experiments in the channel are conducted using laminar and turbulent water and air flows.

A model for predicting the oleophobic/phile nature of the surfaces is discussed. To validate the model, it is investigated how the water and oil droplets in three phase interfaces influence the wetting behavior on micropatterned surfaces with varying pitch values and the nano- and hierarchical structures as well as the shark skin replica as an example of aquatic animal.

CHAPTER 2

MODELING OF CONTACT ANGLE FOR A LIQUID IN CONTACT WITH A ROUGH SURFACE

2.1. Contact angle definition

The surface atoms or molecules of liquids or solids have fewer bonds with neighboring atoms, and therefore, they have higher energy than similar atoms and molecules in the interior. This additional energy is characterized quantitatively by the surface tension or free surface energy γ , which is equal to the work that is required to create a unit area of the surface at a constant pressure and temperature. The unit of γ is J/m² or N/m, and it can be interpreted either as energy per unit surface area or as tension force per unit length of a line at the surface. When a solid is in contact with liquid, the molecular attraction will reduce the energy of the system below that for the two separated surfaces. This is expressed by the Dupré equation

$$W_{SL} = \gamma_{SA} + \gamma_{LA} - \gamma_{SL} \quad (1)$$

where W_{SL} is the work of adhesion per unit area, γ_{SA} and γ_{SL} are the surface energies of the solid against air and liquid, and γ_{LA} is the surface energy of liquid against air (Adamson, 1990; Israelachvili, 1992; Bhushan, 1999).

If a liquid droplet is placed on a solid surface, the liquid and solid surfaces come together under equilibrium at a characteristic angle called the static contact angle θ_0 (**Fig. 6**). This contact angle can be determined by minimizing the net surface free energy of the system (Adamson, 1990; Israelachvili, 1992; Bhushan, 1999). The total energy E_{tot} is given by (Nosonovsky and Bhushan, 2005, 2008a)

$$E_{tot} = \gamma_{LA}(A_{LA} + A_{SL}) - W_{SL}A_{SL} \quad (2)$$

where A_{SL} and A_{LA} are the contact areas of the liquid with the solid and air, respectively. It is assumed that the droplet of density ρ is smaller than the capillary length, $(\gamma_{LA}/\rho g)^{1/2}$,

Figure 6. Schematic of liquid droplet in contact with a smooth solid surface (contact angle, θ_0).

so that the gravitational potential energy can be neglected. It is also assumed that the volume and pressure are constant, so that the volumetric energy does not change. At the equilibrium $dE_{tot} = 0$, which yields

$$\gamma_{LA}(dA_{LA} + dA_{SL}) - W_{SL} dA_{SL} = 0 \quad (3)$$

For a droplet of constant volume, it is easy to show using geometrical considerations, that

$$dA_{LA} / dA_{SL} = \cos \theta_0 \quad (4)$$

Combining Eqs. 1, 3 and 4, the well-known Young equation for the contact angle is obtained

$$\cos \theta_0 = \frac{\gamma_{SA} - \gamma_{SL}}{\gamma_{LA}} \quad (5)$$

Eq. 5 provides an expression for the static contact angle for given surface energies. Note that although we use the term “air,” the analysis does not change in the case of another gas, such as water vapor.

2.2. Heterogeneous interfaces and the Wenzel and Cassie-Baxter equations

In this section, we introduce and discuss the equations that govern the contact angle of liquid with a rough surface and heterogeneous interface.

We first consider a water droplet on a rough surface with a homogeneous interface. The interface area increases with respect to that for a smooth surface. Using the

surface force balance and empirical considerations, the contact angle of a water droplet upon a rough solid surface, θ , is related to that upon a smooth surface, θ_0 for a homogeneous interface (**Fig. 7(a)**), through the non-dimensional surface roughness factor, $R_f > 1$, equal to the ratio of the surface area, A_{SL} , to its flat projected area, A_F (Wenzel, 1936)

$$\cos \theta = \frac{dA_{LA}}{dA_F} = \frac{A_{SL}}{A_F} \frac{dA_{LA}}{dA_{SL}} = R_f \cos \theta_0 \quad (6)$$

$$\text{where, } R_f = \frac{A_{SL}}{A_F} \quad (7)$$

This is called the Wenzel equation. The dependence of the contact angle on the roughness factor is presented in **Fig. 8(a)** for different values of θ_0 . The Wenzel model predicts that a hydrophobic surface ($\theta_0 > 90^\circ$) becomes more hydrophobic with an increase in R_f , while a hydrophilic surface ($\theta_0 < 90^\circ$) becomes more hydrophilic with an increase in R_f (Nosonovsky and Bhushan, 2005; Jung and Bhushan, 2006). As an example, **Figure 8(b)** shows a geometry with square-based hemispherically-topped pyramidal asperities with a rounded top, which has complete packing. The size and shape of the asperities can be optimized for a desired roughness factor.

In a similar manner, for a surface composed of two fractions, one with the fractional area f_1 and the contact angle θ_1 and the other with f_2 and θ_2 , respectively (so that $f_1 + f_2 = 1$), the contact angle for the heterogeneous interface is given by the Cassie equation (Cassie and Baxter, 1944)

$$\cos \theta = f_1 \cos \theta_1 + f_2 \cos \theta_2 \quad (8)$$

For the case of a composite interface (**Fig. 7(b)**), consisting of a solid-liquid fraction ($f_1 = f_{SL}$, $\theta_1 = \theta_0$) and liquid-air fraction ($f_2 = f_{LA} = 1 - f_{SL}$, $\cos \theta_2 = -1$), combining Eqs 7 and 8 yields the Cassie-Baxter equation (Cassie and Baxter, 1944)

$$\begin{aligned} \cos \theta &= R_f f_{SL} \cos \theta_0 - 1 + f_{SL} \\ \text{or } \cos \theta &= R_f \cos \theta_0 - f_{LA} (R_f \cos \theta_0 + 1) \end{aligned} \quad (9)$$

The opposite limiting case of $\cos \theta_2 = 1$ ($\theta_2 = 0^\circ$ corresponds to the water-on-water contact) yields the Cassie equation (Nosonovsky and Bhushan, 2008a,d)

Figure 7. Schematics of configurations described by the (a) Wenzel equation for the homogeneous interface (Eq. 6), (b) Cassie-Baxter equation for the composite interface with air pockets (Eq. 9), and (c) the Cassie equation for the homogeneous interface (Eq. 10) (Nosonovsky and Bhushan, 2008d).

Figure 8. (a) Contact angle for rough surface (θ) as a function of the roughness factor (R_f) for various contact angles of the smooth surface (θ_0), and (b) schematic of square-based hemispherically-topped pyramidal asperities with complete packing (Nosonovsky and Bhushan, 2005).

$$\cos \theta = 1 + f_{SL} (\cos \theta_0 - 1) \quad (10)$$

Eq. 10 is used sometimes for the homogeneous interface instead of Eq. 6, if the rough surface is covered by holes filled with water (de Gennes et al., 2003) (**Fig. 7(c)**).

Two situations in wetting of a rough surface should be distinguished: the homogeneous interface without any air pockets shown in **Fig. 7(a)** (called the Wenzel interface, since the contact angle is given by the Wenzel equation or Eq. 6), and the composite interface with air pockets trapped between the rough details as shown in **Fig.**

7(b) (called the Cassie or Cassie-Baxter interface, since the contact angle is given by Eq. 9).

Eq. 9 for the composite interface was derived using Eqs. 6 and 8, and it could also be obtained independently. For this purpose, two sets of interfaces are considered: a liquid-air interface with the ambient and a flat composite interface under the droplet, which itself involves solid-liquid, liquid-air, and solid-air interfaces. For fractional flat geometrical areas of the solid-liquid and liquid-air interfaces under the droplet, f_{SL} and f_{LA} ($f_{SL} = 1 - f_{LA}$), the flat area of the composite interface is (Nosonovsky and Bhushan, 2005, 2008a)

$$A_F = f_{SL} A_F + f_{LA} A_F = R_f A_{SL} + f_{LA} A_F \quad (11)$$

In order to calculate the contact angle in a manner similar to the derivation of Eq. 6, the differential area of the liquid-air interface under the droplet, $f_{LA} dA_F$, should be subtracted from the differential of the total liquid-air area dA_{LA} , which yields the Cassie-Baxter equation (Eq. 9),

$$\begin{aligned} \cos \theta &= \frac{dA_{LA} - f_{LA} dA_F}{dA_F} = \frac{A_{SL}}{A_F} \frac{dA_{LA}}{dA_{SL}} - f_{LA} = R_f f_{SL} \cos \theta_0 - f_{LA} \\ &= R_f \cos \theta_0 - f_{LA} (R_f \cos \theta_0 + 1) \end{aligned}$$

The dependence of the contact angle on the roughness factor and fractional liquid-air area for hydrophilic and hydrophobic surfaces with a composite interface (**Fig. 9(a)**) is presented in **Fig. 9(b)**.

According to Eq. 9, even for a hydrophilic surface, the contact angle increases with an increase of f_{LA} . At a high value of f_{LA} , a surface can become hydrophobic; however, the value required may be unachievable, or the formation of air pockets may become unstable. Using the Cassie-Baxter equation, the value of f_{LA} at which a hydrophilic surface could turn into a hydrophobic one is given as (Jung and Bhushan, 2006)

$$f_{LA} \geq \frac{R_f \cos \theta_0}{R_f \cos \theta_0 + 1} \quad \text{for } \theta_0 < 90^\circ \quad (12)$$

Figure 9(c) shows the value of f_{LA} requirement as a function of R_f for four surfaces

Figure 9. (a) Schematic of formation of a composite solid-liquid-air interface for rough surface, (b) contact angle for rough surface (θ) as a function of the roughness factor (R_f) for various f_{LA} values on the hydrophilic surface and the hydrophobic surface, and (c) f_{LA} requirement for a hydrophilic surface to be hydrophobic as a function of the roughness factor (R_f) and θ_o (Jung and Bhushan, 2006).

Figure 9 Continued

Formation of composite solid-liquid-air interface

with different contact angles, θ_0 . Hydrophobic surfaces can be achieved above a certain f_{LA} value as predicted by Eq. 12. The upper part of each contact angle line is the hydrophobic region. For the hydrophobic surface, contact angle increases with an increase in f_{LA} both for smooth and rough surfaces.

Based on Nosonovsky and Bhushan (2008a, 2009b), spreading of a liquid over a rough solid surface continues until simultaneously Eq. 5 (the Young equation) is satisfied locally at the triple line and the surface area is minimum over the entire liquid-air interface. The minimal surface area condition states that the sum of the inverse of the principal radii of curvature, R_1 and R_2 of the liquid surface, along the two mutually orthogonal planes (mean curvature), is constant at any point, which governs the shape of the liquid-air interface. The same condition is also the consequence of the Laplace equation, which relates pressure change through an interface, ΔP , with its mean curvature,

$$\frac{1}{R_1} + \frac{1}{R_2} = \frac{\Delta P}{\gamma_{LA}} \quad (13)$$

Note that at the thermodynamic equilibrium (when condensation and evaporation occurs at the same speed), ΔP is dependent on the partial vapor pressure. For contact with saturated vapor the mean curvature of the liquid-air interface is zero at equilibrium. A convex interface ($1/R_1 + 1/R_2 > 0$) results in evaporation prevailing over condensation; this is why small droplets tend to evaporate. However, a concave interface ($1/R_1 + 1/R_2 < 0$) results in condensation of saturated vapor prevailing over evaporation. Since the condensation prevails, a concave interface may be in thermodynamic equilibrium with undersaturated vapor. This is why concave menisci tend to condense even when the relative humidity is less than 100 % (Nosonovsky and Bhushan, 2008a, 2009b).

2.2.1. Limitations of the Wenzel and Cassie equations

Based on Nosonovsky and Bhushan (2008a,d), the Cassie equation (Eq. 8) is based on the assumption that the heterogeneous surface is composed of well-separated distinct patches of different material, so that the free surface energy can be averaged. It has been argued also that when the size of the chemical heterogeneities is very small (of atomic or molecular dimensions), the quantity that should be averaged is not the energy,

but the dipole moment of a macromolecule (Israelachvili and Gee, 1989), and Eq. 8 should be replaced by (Nosonovsky and Bhushan, 2008d)

$$(1 + \cos \theta)^2 = f_1(1 + \cos \theta_1)^2 + f_2(1 + \cos \theta_2)^2 \quad (14)$$

Experimental studies of polymers with different functional groups showed a good agreement with Eq. 14 (Tretinnikov, 2000).

Based on Nosonovsky and Bhushan (2008a,d), later investigations put the Wenzel and Cassie equations into a thermodynamic framework; however, they also showed that there is no one single value of the contact angle for a rough or heterogeneous surface (Johnson and Dettre, 1964; Marmur, 2003; Li and Amirfazli, 2006). The contact angle can be in a range of values between the receding contact angle, θ_{rec} , and the advancing contact angle, θ_{adv} . The system tends to achieve the receding contact angle when liquid is removed (for example, at the rear end of a moving droplet), whereas the advancing contact angle is achieved when the liquid is added (for example, at the front end of a moving droplet) (**Fig. 10(a)**). When the liquid is neither added nor removed, the system tends to have a static or “most stable” contact angle, which is given approximately by Eqs. 5, 6, 8, and 10.

The contact angle provided by Eqs. 5, 6, 8, and 10 is a macroscale parameter, so it is called sometimes “the apparent contact angle.” Based on Nosonovsky and Bhushan (2008a,c), the actual angle, under which the liquid-air interface comes in contact with the solid surface at the micro- and nanoscale, can be different. There are several reasons for that. First, water molecules tend to form a thin layer upon the surfaces of many materials. This is because of a long-distance van der Waals adhesion force that creates the so-called disjoining pressure (Derjaguin and Churaev, 1974). This pressure is dependent upon the liquid layer thickness and may lead to the formation of stable thin films. In this case, the shape of the droplet near the triple line (line of contact of the solid, liquid and air, shown later in **Fig. (12)**) transforms gradually from the spherical surface into a precursor layer, and thus the nanoscale contact angle is much smaller than the apparent contact angle. In addition, adsorbed water monolayers and multilayers are common for many materials. Second, even carefully prepared atomically smooth surfaces exhibit a certain roughness and chemical heterogeneity. Water tends first to cover the hydrophilic spots with high

Figure 10. (a) Liquid droplet in contact with rough surface with liquid is added or removed (advancing and receding contact angles are θ_{adv} and θ_{rec} , respectively) and (b) tilted surface profile (tilt angle, α) with a moving liquid droplet.

surface energy and low contact angle (Checco et al., 2003). The tilt angle due to roughness can also contribute to the apparent contact angle. Third, the very concept of the static contact angle is not well defined. For practical purposes, the contact angle, which is formed after a droplet is gently placed upon a surface and stops propagating, is considered the static contact angle. However, depositing the droplet involves adding liquid while leaving it involves evaporation, so it is difficult to avoid dynamic effects. Fourth, for small droplets and curved triple lines, the effect of the contact line tension may be significant. Molecules at the surface of a liquid or solid phase have higher energy because they are bonded to fewer molecules than those in the bulk. This leads to surface tension and surface energy. In a similar manner, molecules at the concave surface and,

especially, at the edge have fewer bonds than those at the surface, which leads to line tension and curvature dependence of the surface energy. This effect becomes important when the radius of curvature is comparable with the so-called Tolman's length, normally of the molecular size (Anisimov, 2007). However, the triple line at the nanoscale can be curved so that the line tension effects become important (Pompe et al., 2000). The contact angle, taking into account for the contact line effect, for a droplet with radius R is given by $\cos \theta = \cos \theta_0 + 2\tau/(R\gamma_{LA})$, where τ is the contact line tension, and θ_0 is the value given by the Young equation (Boruvka and Neumann, 1977). Thus while the contact angle is a convenient macroscale parameter, wetting is governed by interactions at the micro- and nanoscale, which determine the contact angle hysteresis and other wetting properties. **Table 1** shows various scale levels which affect wetting of a superhydrophobic surface.

Scale level	Characteristic length	Parameters	Phenomena	Interface
Macroscale	Droplet radius (mm)	Contact angle, droplet radius	Contact angle hysteresis	2-D
Microscale	Roughness detail (μm)	Shape of the droplet, position of the liquid-air interface (h)	Kinetic effects	3-D solid surface, 2-D liquid surface
Nanoscale	Molecular heterogeneity (nm)	Molecular description	Thermodynamic and dynamic effects	3-D

Table 1. Wetting of a superhydrophobic surface as a multiscale process (Nosonovsky and Bhushan, 2007c, 2008c).

2.2.2. Range of applicability of the Wenzel and Cassie equations

Gao and McCarthy (2007) showed experimentally that the contact angle of a droplet is defined by the triple line and does not depend upon the roughness under the bulk of the droplet. A similar result for chemically heterogeneous surfaces was obtained by Extrand (2003). Gao and McCarthy (2007) concluded that the Wenzel and Cassie-Baxter equations “should be used with the knowledge of their fault.” The question remained, however, under what circumstances the Wenzel and Cassie-Baxter equations can be safely used and under what circumstances they become irrelevant.

Based on Nosonovsky (2007c), for a liquid front propagating along a rough two-dimensional profile (**Fig. 11(a-b)**), the derivative of the free surface energy (per liquid front length), W , by the profile length, t , yields the surface tension force $\sigma = dW/dt = \gamma_{SL} - \gamma_{SA}$. The quantity of practical interest is the component of the tension force that corresponds to the advancing of the liquid front in the horizontal direction for dx . This component is given by $dW/dx = (dW/dt) (dt/dx) = (\gamma_{SL} - \gamma_{SA})dt/dx$. It is noted that the derivative dt/dx is equal to Wenzel’s roughness factor (R_f) in the case when the roughness factor is constant throughout the surface. Therefore, the Young equation Eq. 5, which relates the contact angle with solid, liquid, and air interface tensions, is modified as (Nosonovsky, 2007c)

$$\gamma_{LA} \cos \theta = R_f (\gamma_{SA} - \gamma_{SL}) \quad (15)$$

The empirical Wenzel equation (Eq. 6) is a consequence of Eq. 15 combined with the Young equation.

Nosonovsky (2007c) showed that for a more complicated case of a non-uniform roughness, given by the profile $z(x)$, the local value of derivative, $r(x) = dt/dx = (1 + (dz/dx)^2)^{1/2}$ matters. In the cases that were studied experimentally by Gao and McCarthy (2007) and Extrand (2003), the roughness was present ($r > 1$) under the bulk of the droplet, but there was no roughness ($r = 0$) at the triple line, and the contact angle was given by Eq. 6 (**Fig. 11(c)**). In the general case of a 3-D rough surface $z(x, y)$, the roughness factor can be defined as a function of the coordinates $r(x, y) = (1 + (dz/dx)^2 + (dz/dy)^2)^{1/2}$.

Figure 11. Liquid front in contact with a (a) smooth solid surface and (b) rough solid surface, propagation for a distance dt along the curved surface corresponds to the distance dx along the horizontal surface. (c) Surface roughness under the bulk of the droplet does not affect the contact angle (Nosonovsky, 2007c).

Eq. 6 is valid for uniformly rough surfaces, that is, surfaces with $r = \text{const}$, and for non-uniformly rough surfaces the generalized Wenzel equation is formulated to determine the local contact angle (a function of x and y) with rough surfaces at the triple line (Nosonovsky, 2007c; Nosonovsky and Bhushan, 2008a,b)

$$\cos \theta = r(x, y) \cos \theta_0 \quad (16)$$

The difference between the Wenzel equation (Eq. 6) and the Nosonovsky-Bhushan equation (Eq. 16) is that the latter is valid for a non-uniform roughness with the roughness factor as the function of the coordinates. Eq. 16 is consistent with the experimental results of the scholars who showed that roughness beneath the droplet does not affect the contact angle, since it predicts that only roughness at the triple line matters. It is also consistent with the results of the researchers who confirmed the Wenzel equation (for the case of the uniform roughness) and of those who reported that only the triple line matters (for non-uniform roughness). A summary of experimental results for uniform and non-uniform rough and chemically heterogeneous surfaces is shown in **Table 2**.

The Cassie equation for the composite surface can be generalized in a similar manner introducing the spatial dependence of the local densities, f_1 and f_2 of the solid-liquid interface with the contact angle, as a function of x and y , given by (Nosonovsky, 2007c)

$$\cos \theta_{composite} = f_1(x, y) \cos \theta_1 + f_2(x, y) \cos \theta_2 \quad (17)$$

where $f_1 + f_2 = 1$, θ_1 and θ_2 are contact angles of the two components.

According to Nosonovsky (2007c), the important question remains, what should be the typical size of roughness/heterogeneity details in order for the generalized Wenzel and Cassie equations (Eqs. 16-17) to be valid? Some scholars have suggested that roughness/heterogeneity details should be comparable with the thickness of the liquid-air interface and thus “the roughness would have to be of molecular dimensions to alter the equilibrium conditions” (Bartell and Shepard, 1953), whereas others have claimed that roughness/heterogeneity details should be small compared with the linear size of the droplet (Johnson and Dettre, 1964; Li and Amirfazli, 2006; Bhushan and Jung, 2007, 2008; Jung and Bhushan, 2006, 2007, 2008a,b; Bhushan et al., 2007; Barbieri et al., 2007). The interface in the analysis proposed earlier is an idealized 2-D object, which has no thickness. In reality, the triple line zone has two characteristic dimensions: the thickness (of the order of molecular dimensions) and the length (of the order of the droplet size).

Experiment	Roughness / hydropobicity at the triple line and at the rest of the surface	Roughness at the bulk (under the droplet)	Experimental contact angle (compared with that at the rest of the surface)	Theoretical contact angle, Wenzel/Cassie equations	Theoretical contact angle, generalized Wenzel-Cassie (Eqs. 16-17)
Gao and McCarthy (2007)	Hydrophobic	Hydrophilic	Not changed	Decreased	Not changed
	Rough	Smooth	Not changed	Decreased	Not changed
	Smooth	Rough	Not changed	Increased	Not changed
Extrand (2003)	Hydrophilic	Hydrophobic	Not changed	Increased	Not changed
	Hydrophobic	Hydrophilic	Not changed	Decreased	Not changed
Bhushan et al. (2007)	Rough	Rough	Increased	Increased	Increased
Barbieri et al. (2007)	Rough	Rough	Increased	Increased	Increased

Table 2. Summary of experimental results for uniform and non-uniform rough and chemically heterogeneous surfaces. For non-uniform surfaces, the results shown for droplets larger than the islands of non-uniformity. Detailed quantitative values of the contact angle in various sets of experiments can be found in the referred sources (Nosonovsky, 2007c).

According to Nosonovsky and Bhushan (2008a,b), the apparent contact angle, given by Eqs. 16-17, may be viewed as the result of averaging of the local contact angle at the triple line by its length, and thus the size of the roughness/heterogeneity details should be small compared to the length (and not the thickness) of the triple line (Nosonovsky and Bhushan, 2008b). A rigorous definition of the generalized equation requires the consideration of several length scales. The length dx needed for averaging of the energy gives the length over which the averaging is performed to obtain $r(x, y)$. This length should be larger than roughness details. However, it is still smaller than the droplet size and the length scale at which the apparent contact angle is observed (at which local variations of the contact angle level out). Since of these lengths (the roughness size, dx , the droplet size) the first and the last are of practical importance, we conclude that the roughness details should be smaller than the droplet size. When the liquid-air interface is

studied at the length scale of roughness/heterogeneity details, the local contact angle, θ_0 , is given by Eqs. 6-10. The liquid-air interface at that scale has perturbations caused by the roughness/heterogeneity, and the scale of the perturbations is the same as the scale of the roughness/heterogeneity details. However, when the same interface is studied at a larger scale, the effect of the perturbation vanishes, and apparent contact angle is given by Eqs. 16-17 (**Fig. 11(c)**). This apparent contact angle is defined at the length scale for which the small perturbations of the liquid-air interface vanish, and the interface can be treated as a smooth surface. The values of $r(x, y)$, $f_1(x, y)$, $f_2(x, y)$ in Eqs. 16-17 are average values by the area (x, y) with a size larger than a typical roughness/heterogeneity detail size. Therefore, the generalized Wenzel and Cassie equations can be used at the scale at which the effect of the interface perturbations vanish, or, in other words, when the size of the solid surface roughness/heterogeneity details is small compared with the size of the liquid-air interface, which is of the same order as the size of the droplet (Nosonovsky and Bhushan, 2008b).

Nosonovsky and Bhushan (2008a,d) used the surface energy approach to find the domain of validity of the Wenzel and Cassie equations (uniformly rough surfaces) and generalized it for a more complicated case of non-uniform surfaces. The generalized equations explain a wide range of existing experimental data, which could not be explained by the original Wenzel and Cassie equations.

2.3. Contact angle hysteresis

Contact angle hysteresis is another important characteristic of a solid-liquid interface. Contact angle hysteresis occurs due to surface roughness and heterogeneity. Although for surfaces with roughness carefully controlled on the molecular scale it is possible to achieve contact angle hysteresis as low as $< 1^\circ$ (Gupta et al., 2005), hysteresis cannot be eliminated completely, since even atomically smooth surfaces have a certain roughness and heterogeneity. Contact angle hysteresis is a measure of energy dissipation during the flow of a droplet along a solid surface. Low contact angle hysteresis results in a very low water roll-off angle, which denotes the angle to which a surface may be tilted for roll-off of water drops (i.e., very low water contact angle hysteresis) (Extrand, 2002;

Kijlstra et al., 2002; Bhushan and Jung, 2007, 2008; Jung and Bhushan, 2007, 2008a) (**Fig. 10(b)**). Low water roll-off angle is important in liquid flow applications such as in micro/nanochannels and surfaces with self-cleaning ability.

Certain conclusions about the relationship of contact angle hysteresis to roughness can be made. It is known that the energy gained for surfaces during contact is greater than the work of adhesion for separating the surfaces, due to so called adhesion hysteresis. Factors that affect contact angle hysteresis include adhesion hysteresis, surface roughness, and inhomogeneity. Bhushan et al. (2007) and Nosonovsky and Bhushan (2007b) assumed that contact angle hysteresis is equal to the adhesion hysteresis term and the term corresponding to the effect of roughness, H_r . They further noted that adhesion hysteresis can be assumed to be proportional to the fractional solid-liquid area ($1 - f_{LA}$). Using Eq. 9, the difference of cosines of the advancing and receding angles is related to the difference of those for a nominally smooth surface, θ_{adv0} and θ_{rec0} , as

$$\cos\theta_{adv} - \cos\theta_{rec} = R_f(1 - f_{LA})(\cos\theta_{adv0} - \cos\theta_{rec0}) + H_r \quad (18)$$

The first term in the right-hand part of the equation, which corresponds to the inherent contact angle hysteresis of a smooth surface, is proportional to the fraction of the solid-liquid contact area, $1 - f_{LA}$. The second term, H_r , is the effect of surface roughness, which is equal to the total perimeter of the asperity per unit area, or in other words, to the length density of the triple line (Bhushan et al., 2007). Thus Eq. 18 involves both the term proportional to the solid-liquid interface area and to the triple line length. It is observed from Eqs. 9 and 18 that increasing $f_{LA} \rightarrow 1$ results in increasing the contact angle ($\cos\theta \rightarrow -1, \theta \rightarrow \pi$) and decreasing the contact angle hysteresis ($\cos\theta_{adv} - \cos\theta_{rec} \rightarrow 0$). In the limiting case of very small solid-liquid fractional contact area under the droplet, when the contact angle is large ($\cos\theta \approx -1 + (\pi - \theta)^2 / 2$, $\sin\theta \approx \theta - \pi$) and where the contact angle hysteresis is small ($\theta_{adv} \approx \theta \approx \theta_{rec}$), based on Eqs. 9 and 18 (Nosonovsky and Bhushan, 2007b),

$$\pi - \theta = \sqrt{2(1 - f_{LA})(R_f \cos\theta_0 + 1)} \quad (19)$$

$$\theta_{adv} - \theta_{rec} = (1 - f_{LA})R_f \frac{\cos\theta_{a0} - \cos\theta_{r0}}{-\sin\theta} = (\sqrt{1 - f_{LA}})R_f \frac{\cos\theta_{r0} - \cos\theta_{a0}}{\sqrt{2(R_f \cos\theta_0 + 1)}} \quad (20)$$

For the homogeneous interface, $f_{LA} = 0$, whereas for the composite interface f_{LA} is a non-zero number. It is observed from Eqs. 19-20 that for a homogeneous interface, increasing roughness (high R_f) leads to increasing the contact angle hysteresis (high values of $\theta_{adv} - \theta_{rec}$), while for the composite interface, an approach to unity of f_{LA} provides both high contact angle and small contact angle hysteresis (Jung and Bhushan, 2006; Bhushan et al., 2007; Nosonovsky and Bhushan, 2007b,d). Therefore, the composite interface is desirable for self-cleaning.

A sharp edge can pin the line of contact of the solid, liquid, and air (also known as the “triple line”) at a position far from stable equilibrium, i.e., at contact angles different from θ_0 (Eustathopoulos et al., 1999). This effect is illustrated in the bottom sketch of **Fig. 12**, which shows a droplet propagating along a solid surface with grooves. Based on Nosonovsky and Bhushan (2005, 2008a), at the edge point, the contact angle is not defined and can have any value between the values corresponding to contact with the horizontal and inclined surfaces. For a droplet moving from left to right, the triple line will be pinned at the edge point until it will be able to proceed to the inclined plane. As it is observed from **Fig. 12**, the change of the surface slope (α) at the edge is the cause of the pinning. Because of the pinning, the value of the contact angle at the front of the droplet (dynamic maximum advancing contact angle or $\theta_{adv} = \theta_0 + \alpha$) is greater than θ_0 , whereas the value of the contact angle at the back of the droplet (dynamic minimum receding contact angle or $\theta_{rec} = \theta_0 - \alpha$) is smaller than θ_0 . A hysteresis domain of the dynamic contact angle is thus defined by the difference $\theta_{adv} - \theta_{rec}$. The liquid can travel easily along the surface if the contact angle hysteresis is small. It is noted that the static contact angle lies within the hysteresis domain; therefore, increasing the static contact angle up to the values of a superhydrophobic surface (approaching 180°) will also result in a reduction of the contact angle hysteresis. In a similar manner, contact angle hysteresis can also exist even if the surface slope changes smoothly, without sharp edges. There is an analogy between the two mechanisms leading to contact angle hysteresis (energy dissipation at the solid-liquid interface and pinning of the triple line) and dissipation mechanisms of dry friction (adhesion and deformation) (Nosonovsky, 2007b).

Figure 12. Liquid droplet in contact with a solid surface – smooth surface, contact angle θ_0 ; rough surface, contact angle θ ; and a surface with sharp edges. For a droplet moving from left to right on a sharp edge (shown by arrow), the contact angle at a sharp edge may be any value between the contact angle with the horizontal plane and with the inclined plane. This effect results in difference of advancing ($\theta_{adv} = \theta_0 + \alpha$) and receding ($\theta_{rec} = \theta_0 - \alpha$) contact angles (Nosonovsky and Bhushan, 2005).

2.4. Stability of a composite interface and role of hierarchical structure

Stability of the composite interface is an important issue. Even though it may be geometrically possible for the system to become composite, it may be energetically profitable for the liquid to penetrate into the valleys between asperities and form a homogeneous interface. Marmur (2003) formulated geometrical conditions for a surface under which the energy of the system has a local minimum and the composite interface may exist. Patankar (2004a) pointed out that whether the homogeneous or composite interface exists depends on the system's history, i.e., on whether the droplet was formed at the surface or deposited. However, the above-mentioned analyses do not provide an answer to which of the two possible configurations, homogeneous or composite, will actually form.

Based on Nosonovsky and Bhushan (2007b, 2008a), formation of a composite interface is also a multiscale phenomenon which depends upon the relative sizes of the liquid droplet and roughness details. The composite interface is fragile and can be irreversibly transformed into the homogeneous interface, thus damaging superhydrophobicity. In order to form a stable composite interface with air pockets between solid and liquid, the destabilizing factors such as capillary waves, nanodroplet condensation, surface inhomogeneity, and liquid pressure should be avoided. First, the capillary waves at the liquid-air interface may destabilize the composite interface. Due to an external perturbation, a standing capillary wave can form at the liquid-air interface. If the amplitude of the capillary wave is greater than the height of the asperity, the liquid can touch the valley between the asperities, and if the angle under which the liquid comes in contact with the solid is greater than θ_0 , it is energetically profitable for the liquid to fill the valley (Nosonovsky and Bhushan, 2005, 2006a). When the composite interface is destroyed and space between the asperities is filled with water, it is highly unlikely that the composite interface will be formed again because the transition from the non-composite solid-liquid interface to a composite interface would require a large activation energy. Such a transition has never been observed. The effect of capillary waves is more pronounced for small asperities with height comparable with wave amplitude. Second, nanodroplets may condensate and accumulate in the valleys between asperities and eventually destroy the composite interface. Cheng et al. (2005) observed condensation of

submicron sized droplets on a Lotus leaf surface and found that droplets tend to condense at areas adjacent to bumps (i.e, in the valleys) and have a contact angle of less than 90° , whereas larger droplets have higher contact angles, thus demonstrating that the contact angle is scale dependent. The scale effect is observed for small droplets or at small distances near the triple line. Scale dependence of the contact angle has been reported by Nosonovsky and Bhushan (2007b, 2008a). At nanoscale distances from the triple line the liquid touches the solid under a much lower contact angle. Third, even hydrophobic surfaces are usually not chemically homogeneous and can have hydrophilic spots. It is known from experiments that for droplets of submicron size, the value of the contact angle is usually smaller than for droplets at the macroscale (Lafuma and Quere, 2003). Checco et al. (2003) suggested that surface inhomogeneity is responsible for this scale effect, since nanodroplets tend to sit at the highest free surface energy (most hydrophilic) spots and thus have lower contact angles. Their phenomenological numerical simulations showed good agreement with experimental data.

For high f_{LA} , a nanopattern is desirable because whether a liquid-air interface is generated depends upon the ratio of distance between two adjacent asperities and droplet radius. Furthermore, asperities can pin liquid droplets and thus prevent liquid from filling the valleys between asperities. High R_f can be achieved by both micropatterns and nanopatterns. Nosonovsky and Bhushan (2007a,b,c,d, 2008a,b,c,f) have demonstrated that a combination of microroughness and nanoroughness (multiscale roughness) with convex surfaces can help resist the destabilization by pinning the interface. It also helps in preventing the gaps between the asperities from filling with liquid, even in the case of a hydrophilic material. The effect of roughness on wetting is scale dependent, and mechanisms that lead to destabilization of a composite interface are also scale-dependent. To effectively resist these scale-dependent mechanisms, it is expected that a multiscale roughness is optimum for superhydrophobicity.

Nosonovsky (2007a) considered a two-dimensional structure with rectangular pillars of height h and width a separated by distance b , covered with small semi-circular bumps (convex) and grooves (concave) of radius r (**Fig. 13(a)**). If the distance between the pillars is small in comparison with the capillary length, the effect of gravity is

negligible, it can be assumed that the liquid-air interface is a horizontal plane, and its position is characterized by the vertical coordinate z . The free energy is given by (Nosonovsky, 2007a)

$$W = A_{SL}\gamma_{SL} + A_{SA}\gamma_{SA} + A_{LA}\gamma_{LA} = rL\gamma_{LA}(\sin \alpha - \alpha \cos \theta_0), \quad 0 < z < h \quad (21)$$

where $\alpha = \arccos((r-z)/r) + 2\pi N$ is the angle corresponding to vertical position of the interface z , N is the number of ridges or grooves, and L is length of the grooves in the y -direction, which is required based on the dimensional considerations. The dependence is presented in **Fig. 13(b)**, for the cases of hydrophobic ($\theta_0 = 150^\circ$) and hydrophilic ($\theta_0 = 30^\circ$) materials for both the convex surface (with bumps) and concave surface (with grooves). It is seen that for the convex surface, there are many states of stable equilibrium (shown in **Fig. 13(a)** with dotted lines), separated by energy barriers which correspond to every ridge, whereas for the concave surface equilibrium states are unstable. Therefore, the ridges can pin the triple line and thus lead to a composite interface. In the case of a hydrophilic surface, each lower position of the equilibrium state corresponds to a lower value of W , therefore, when the liquid advances from one equilibrium state to the next, the total energy decreases, and thus liquid's advance is energetically profitable. When the liquid reaches the bottom of the valley and completely fills the space between the pillars forming a homogeneous interface, the total energy decreases dramatically by the value of (Nosonovsky, 2007a)

$$\Delta W = bL(\gamma_{SA} + \gamma_{LA} - \gamma_{SL}) = bL\gamma_{LA}(1 + \cos \theta_0) \quad (22)$$

The opposite transition from a homogeneous interface to a composite interface requires high activation energy ΔW and is thus unlikely, making the transition from composite interface to homogeneous interface irreversible. If the distance between the pillars b is much greater than r , the energy barriers which separate the equilibrium states, $2\pi rL\gamma_{LA} \cos \theta_0$, will be relatively small compared to ΔW , and low activation energy will be required for the liquid to spread and propagate from one equilibrium state to the other (Nosonovsky and Bhushan, 2007b,d).

For the interface to be stable, the value of the contact angle should decrease when the liquid-air interface advances, whereas for receding liquid the contact angle should increase. For a two-dimensional surface, the change of angle is equal to the change of the

Figure 13. Two-dimensional pillars with semi-circular bumps/grooves. (a) Schematics of the structure. The bumps may pin the triple line, because an advance of the LA interface results in decrease of the contact angle ($\theta < \theta_0$), making equilibrium stable. Grooves provide with equilibrium positions, which satisfy the Young equation, however, the equilibrium is unstable, because an advance of the LA interface results in increase of the contact angle ($\theta > \theta_0$). (b) Energy profiles for configurations in **Fig. 13(a)** with bumps and grooves for hydrophilic ($\theta_0 = 30^\circ$) and hydrophobic ($\theta_0 = 150^\circ$) materials. Energy (normalized by $Lr\gamma_{LA}$) is shown as a function of vertical position of the interface z (normalized by the radius of bumps/grooves r). Bumps result in stable equilibriums (energy minima), whereas grooves result in unstable equilibriums (energy maxima) (Nosonovsky, 2007a).

slope of the surface, and whether the configuration is stable or not depends on the sign of curvature of the surface. As indicated earlier, the convex surface (with bumps) leads to a stable interface, whereas a concave surface (with grooves) leads to an unstable interface. This approach was suggested for creating superoleophobic surfaces, since the surface tension of oil and organic liquids is much lower than that of water, and it is difficult to create a surface not wetted by oil (Tuteja et al., 2007). Since oleophilic surfaces in air (solid-oil-air system) can become superoleophobic when immersed in water (solid-oil-water system), underwater superoleophobicity has potential for self-cleaning anti-fouling surfaces for ships.

An experiment suggesting that the sign of curvature is indeed important for hydrophobicity was conducted by Sun et al. (2005). They produced both a positive and a negative replica of a Lotus leaf surface by nanocasting using poly(dimethylsiloxane), which has a contact angle with water of about 105° . This value is close to the contact angle of the wax which covers Lotus leaves (about 103° as reported by Kamusewitz et al. (1999)). The positive and negative replicas have the same roughness factor and thus should produce the same contact angle in the case of a homogeneous interface, according to Eq. 6; however, the values of surface curvature are opposite. The value of contact angle for the positive replica was found to be 160° (same as for Lotus leaf), while for the negative replica it was only 110° . This result suggests that the high contact angle for Lotus leaf is due to the composite, rather than homogeneous interface, and that the sign of surface curvature indeed plays a critical role in the formation of the composite interface.

2.5. The Cassie-Baxter and Wenzel wetting regime transition

Since superhydrophobicity requires a stable composite interface, it is important to understand the destabilization mechanisms for the Cassie-Baxter and Wenzel wetting transition. Based on Nosonovsky and Bhushan (2008a,d), it is known from experimental observations that the transition from the Cassie-Baxter to Wenzel regime can be an irreversible event. Whereas such a transition can be induced, for example, by applying pressure or force to the droplet (Jung and Bhushan, 2008b; Nosonovsky and Bhushan, 2008g), electric voltage (Krupenkin et al., 2004; Bahadur and Garimella, 2007), light for

a photocatalytic texture (Feng et al., 2004), and vibration (Bormashenko et al., 2007b), the opposite transition is rarely observed. Several approaches have been proposed for investigation of the transition between the Cassie-Baxter and Wenzel regimes, referred to as “the Cassie-Wenzel transition.” It has been suggested that the transition takes place when the net surface energy of the Wenzel regime becomes equal to that of the Cassie-Baxter regime, or, in other words, when the contact angle predicted by the Cassie-Baxter equation is equal to that predicted by the Wenzel equation. Lafuma and Quere (2003) noticed that in certain cases the transition does not occur even when it is energetically profitable, and considered such a Cassie-Baxter state metastable. Extrand (2003) suggested that the weight of the droplet is responsible for the transition and proposed the contact line density model, according to which the transition takes place when the weight exceeds the surface tension force at the triple line. Patankar (2004a) suggested that which of the two states is realized may depend upon how the droplet was formed, that is upon the history of the system. Quère (2005) also suggested that the droplet curvature (which depends upon the pressure difference between the inside and the outside of the droplet) governs the transition. Nosonovsky and Bhushan (2006a) suggested that the transition is a dynamic process of destabilization and identified possible destabilizing factors. It has been also suggested that the curvature of multiscale roughness defines the stability of the Cassie-Baxter wetting regime (Nosonovsky and Bhushan, 2007a,b,d, 2008a,b,d,e; Nosonovsky, 2007a,b) and that the transition is a stochastic gradual process (Nosonovsky and Bhushan, 2005; Ishino and Okumura, 2006; Bormashenko et al., 2007a,b). Numerous experimental results support many of these approaches, however, it is not clear which particular mechanism prevails.

Based on Nosonovsky and Bhushan (2008a,d), there is an asymmetry between the wetting and dewetting processes, since less energy is released during wetting than the amount required for dewetting due to adhesion hysteresis. Adhesion hysteresis is one of the reasons that leads to contact angle hysteresis, and it also results in the hysteresis of the Wenzel and Cassie-Baxter state transition. **Figure 14** shows the contact angle of a rough surface as a function of surface roughness parameter, given by Eq. 9. Here it is assumed that $R_f \sim 1$ for a Cassie-Baxter regime with a stable composite interface, and the liquid droplet sits flat over the surface. It is noted that at a certain point, the contact

angles given by the Wenzel and Cassie-Baxter equations are the same, and $R_f = (1 - f_{LA}) - f_{LA}/\cos\theta_0$. At this point, the lines corresponding to the Wenzel and Cassie-Baxter regimes intersect. This point corresponds to an equal net energy of the Cassie-Baxter and Wenzel regimes. For a lower roughness (e.g., larger pitch between the asperities) the Wenzel state is more energetically profitable, whereas for a higher roughness the Cassie-Baxter regime is more energetically profitable.

It is observed from **Fig. 14** that an increase of roughness may lead to the transition between the Wenzel and Cassie-Baxter regimes at the intersection point. With decreasing roughness, the system is expected to transit to the Wenzel state. However, experiments (Bhushan and Jung, 2007, 2008; Jung and Bhushan, 2007, 2008a,b; Bhushan et al., 2007; Barbieri et al., 2007) show that, despite the energy in the Wenzel regime being lower than that in the Cassie-Baxter regime, the transition does not necessarily occur, and the droplet may remain in the metastable Cassie-Baxter regime. This is because there are energy barriers associated with the transition, which occurs due to destabilization by dynamic effects (such as waves and vibration) (Nosonovsky and Bhushan, 2008a,d).

In order to understand contact angle hysteresis and the transition between the Cassie-Baxter and Wenzel regimes, Nosonovsky and Bhushan (2008a,d) analyzed the shape of the free surface energy profile. The free surface energy of a droplet upon a smooth surface as a function of the contact angle has a distinct minimum which corresponds to the most stable contact angle. As shown in **Fig. 15(a)**, the macroscale profile of the net surface energy allows us to find the contact angle (corresponding to energy minimums); however it fails to predict the contact angle hysteresis and Cassie-Baxter and Wenzel transition, which are governed by micro- and nanoscale effects. As soon as microscale substrate roughness is introduced, the droplet shape cannot be considered as an ideal truncated sphere anymore, and energy profiles have multiple energy minimums, corresponding to the location of the asperities (**Fig. 15(b)**). The microscale energy profile (solid line) has numerous energy maxima and minima due to surface asperities. While exact calculation of the energy profile for a 3-D droplet is complicated, a qualitative shape may be obtained by assuming a periodic sinusoidal dependence (Johnson and Dettre, 1964), superimposed upon the macroscale profile, as shown in **Fig. 15(b)** (Nosonovsky and Bhushan, 2008a,d). Thus the advancing and

Figure 14. Wetting hysteresis for a superhydrophobic surface. Contact angle as a function of roughness. The stable Wenzel state (i) can transform into the stable Cassie state with increasing roughness (ii). The metastable Cassie state (iii) can abruptly transform (iv) into the stable Wenzel state. The transition i-ii corresponds to equal Wenzel and Cassie states free energies, whereas the transition iv corresponds to a significant energy dissipation and thus it is irreversible (Nosonovsky and Bhushan, 2008d).

receding contact angles can be identified as the maximum and minimum possible contact angles corresponding to energy minimum points. However, the transition between the Wenzel and Cassie-Baxter branches still cannot be explained. Note also that **Figure 15(b)** explains qualitatively the hysteresis due to the kinetic effect of the asperities, but not the inherited adhesion hysteresis, which is characterized by the molecular length scale and cannot be captured by the microscale model.

Based on Nosonovsky and Bhushan (2008a,d), the energy profile as a function of the contact angle does not provide information on how the transition between the Cassie-Baxter and Wenzel regimes occurs, because their two states correspond to completely isolated branches of the energy profile in **Fig. 15(a-b)**. However, the energy may depend not only upon the contact angle, but also upon micro/nanoscale parameters, such as for example the vertical position of the liquid-air interface under the droplet, h (assuming that the interface is a horizontal plane) or similar geometrical parameters (assuming a more complicated shape of the interface). In order to investigate the Wenzel and Cassie-Baxter transition, Nosonovsky and Bhushan (2008a,d) studied the dependence of the energy upon these parameters. They assume that the liquid-air interface under the droplet is a flat horizontal plane. When such air layer thickness or the vertical position of the liquid-air interface, h , is introduced, the energy can be studied as a function of the droplet's shape, the contact angle, and h (**Fig. 15(c)**). For an ideal situation, the energy profile has an abrupt minimum at the point corresponding to the Wenzel state, which corresponds to the sudden net energy change due to the destruction of the solid-air and liquid-air interfaces ($\gamma_{SL} - \gamma_{SA} - \gamma_{LA} = -\gamma_{LA}(\cos\theta + 1)$) times the interface area) (**Fig. 15(c)**). In a more realistic case, the liquid-air interface cannot be considered horizontal due to nanoscale imperfectness or dynamic effects such as the capillary waves (Nosonovsky and Bhushan, 2006a). A typical size of the imperfectness is much smaller than the size of details of the surface texture and thus belongs to the molecular scale level. The height of the interface, h , can now be treated as an average height. The energy dependence upon h is now not as abrupt as in the idealized case. For example, for the “triangular” shape as shown in **Fig. 15(c)**, the Wenzel state may become the second attractor for the system. It is seen that there are two equilibriums which correspond to the Wenzel and Cassie-Baxter

regimes, with the Wenzel state corresponding to a much lower energy level. The energy dependence upon h governs the transition between the two states, and it is observed that a much larger energy barrier exists for the transition from Wenzel to Cassie-Baxter regime than for the opposite transition. This is why the first transition has never been observed experimentally (Nosonovsky and Bhushan, 2007c).

To summarize, the contact angle hysteresis and Cassie-Baxter and Wenzel transition cannot be determined from the macroscale equations and are governed by micro- and nanoscale phenomena (Nosonovsky and Bhushan, 2008a,d).

Figure 15. Schematics of net free energy profiles. (a) Macroscale description; energy minimums correspond to the Wenzel and Cassie states. (b) Microscale description with multiple energy minimums due to surface texture. Largest and smallest values of the energy minimum correspond to the advancing and receding contact angles. (c) Origin of the two branches (Wenzel and Cassie) is found when a dependence of energy upon h (air layer thickness or vertical position of the liquid-air interface) is considered for the microscale description (solid line) and nanoscale imperfectness (dashed line) (Nosonovsky and Bhushan, 2008d). When the nanoscale imperfectness is introduced, it is observed that the Wenzel state corresponds to an energy minimum and the energy barrier for the Wenzel-Cassie transition is much smaller than for the opposite transition.

Figure 15 Continued

CHAPTER 3

LOTUS EFFECT SURFACES IN NATURE

Many biological surfaces are known to be superhydrophobic and self-cleaning. In this section, we will discuss various plant leaves, their roughness and wax coatings in relation to their hydrophobic/hydrophilic and self-cleaning properties.

3.1. Plant leaves

Hydrophobic and water-repellent abilities of many plant leaves have been known for a long time. Scanning electron microscope (SEM) studies since the 1970s have revealed that the hydrophobicity of the leaf surface is related to its microstructure. The outer cells covering a plant, especially the leaf, are called epidermis cells. The epidermis in all plant surfaces is covered by a thin extracellular membrane, called cuticle. The plant cuticle is a composite material mainly built up of a cutin network and hydrophobic waxes (Barthlot and Neinhuis, 1997; Koch et al., 2008a, 2009a). The chemical structure of the epicuticular waxes has been studied extensively by plant scientists and lipid chemists in recent decades (Baker, 1982; Jetter et al., 2006). The epicuticular waxes can be either thin with a 2-D structure or thick with a 3-D structure or a combination thereof. It is believed that waxes diffuse through the cuticle via a lipidic pathway (Koch et al., 2009c). After diffusion of the wax, the tubular wax morphologies grow by crystallization or self-assembly. The plants are able to repair the wax layer by self-assembly.

The hydrophobicity of the leaves is related to another important effect, the ability to remain clean after being immersed in dirty water, known as self-cleaning. This ability is best known for the Lotus (*Nelumbo nucifera*) leaf that is considered by some Asian cultures as “sacred” due to its purity. Not surprisingly, the ability of Lotus-like surfaces for self-cleaning and water repellency was dubbed the “Lotus effect.” As far as the biological implications of the Lotus effect, self-cleaning plays an important role in the

defense against pathogens binding to the leaf surface. Many spores and conidia of pathogenic organisms – most fungi – require water for germination and can infect leaves only in the presence of water.

Neinhuis and Barthlott (1997) systematically studied surfaces and wetting properties of about 200 water-repellent plants (for a comprehensive review, see Koch et al., 2008a, 2009a). Among the epidermal relief features are the papillose epidermal cells either with every epidermal cell forming a single papilla or cells being divided into papillae. The scale of the epidermal relief ranged from 5 μm in multipapillate cells to 100 μm in large epidermal cells. Some cells also are convex (rather than having real papillae) and/or had hairs (trichomes). Neinhuis and Barthlott (1997) also found various types and shapes of wax crystals at the surface. Also see Koch et al. (2008a, 2009a). Interestingly, the hairy surfaces with a thin film of wax exhibited water-repellency for short periods (minutes), after which water penetrated between the hairs, whereas hairs with a thick film led to strong water-repellency. The wax crystal creates nanoroughness, in addition to the microroughness created by the papillae. Apparently, roughness plays the dominant role in the Lotus effect.

The SEM study reveals that the Lotus leaf surface is covered by “bumps,” more exactly called papillae (papillose epidermal cells), which, in turn, are covered by an additional layer of epicuticular waxes (Barthlott and Neinhuis, 1997). The wax is present in crystalline tubules, composed of a mixture of long-chain aliphatic compounds, principally nonacosanol and nonacosanediols (Koch et al., 2006a, 2008a, 2009a). The wax is hydrophobic with a water contact angle of about 95° - 110° , whereas the papillae provide the tool to magnify the contact angle based on the Wenzel model, discussed in the preceding section. The experimental value of the static water contact angle with the Lotus leaf was reported about the 164° (Bhushan et al., 2009b; Koch et al., 2009b). Indeed, taking the papillae density of 3400 per square millimeter, the average radius of the hemispherical asperities $r = 10 \mu\text{m}$ and the aspect ratio $h/r = 1$, provides, based on Eq. 6, the value of the roughness factor $R_f \approx 4$ (Nosonovsky and Bhushan, 2005).

Taking the value of the contact angle for wax, $\theta_0 = 104^\circ$ (Kamusewitz et al., 1999), the calculation with the Wenzel equation yields $\theta = 165^\circ$, which is close to the

experimentally observed values (Nosonovsky and Bhushan, 2005). However, the simple Wenzel model may be not sufficient to explain the Lotus effect, as the roughness structure forms a composite interface. Moreover, its structure has hierarchical roughness. So, a number of more sophisticated models have been developed to study the role of hierarchical roughness on contact angle (Nosonovsky and Bhushan, 2007a,b,c,d, 2008a,b,c,d,e,f). A qualitative explanation for self-cleaning is that on a smooth surface contamination particles are mainly redistributed by a water droplet; on a rough surface they adhere to the droplet and are removed from the leaves when the droplet rolls off.

3.2. Characterization of superhydrophobic and hydrophilic leaf surfaces

In order to understand the mechanisms of hydrophobicity in plant leaves, a comprehensive comparative study of superhydrophobic and hydrophilic leaf surfaces and their properties was carried out by Bhushan and Jung (2006) and Burton and Bhushan (2006). Below is a discussion of the findings of the study.

3.2.1. Experimental techniques

The static contact angles were measured using a Rame-Hart model 100 contact angle goniometer with droplets of deionized (DI) water (Burton and Bhushan, 2006; Bhushan and Jung, 2006). Droplets of about 5 μL in volume (with diameter of a spherical droplet about 2.1 mm) were gently deposited on the substrate using a microsyringe for the static contact angle. All measurements were made by five different points for each sample at 22 ± 1 °C and $50 \pm 5\%$ RH. The measurement results were reproducible within $\pm 3^\circ$.

An optical profiler (NT-3300, Wyko Corp., Tuscon, AZ) was used to measure surface roughness for different surface structures (Burton and Bhushan, 2006; Bhushan and Jung, 2006). A greater Z-range of the optical profiler of 2 mm is a distinct advantage over the surface roughness measurements with an AFM which has a Z-range of on the order of 7 μm , but it has only a maximum lateral resolution of approximately 0.6 μm (Bhushan, 1999, 2002). A commercial AFM (D3100, Nanoscope IIIa controller, Digital Instruments, Santa Barbara, CA) was used for additional surface roughness measurements with a high lateral resolution (sub nm) and for adhesion and friction

measurements (Burton and Bhushan, 2005; Bhushan and Jung, 2006). The measurements for surface roughness were performed with a square pyramidal Si(100) tip with a native oxide layer which had a nominal radius of 20 nm on a rectangular Si(100) cantilever with a spring constant of 3 N m^{-1} in the tapping mode.

Adhesion and friction force at various relative humidities (RH) were measured using a $15 \text{ }\mu\text{m}$ radius borosilicate ball (Bhushan, 1999, 2002, 2008). A large tip radius was used to measure contributions from several microbumps and a large number of nanobumps. Friction force was measured under a normal load ranging from 20 to 250 nN using a 90° scan angle at the velocity of $100 \text{ }\mu\text{m/s}$ in $50 \text{ }\mu\text{m}$ and at a velocity of $4 \text{ }\mu\text{m/s}$ in $2 \text{ }\mu\text{m}$ scans. The quantitative measurement of friction force was calibrated by the method described by Bhushan (2008). The normal load was varied (20 - 250 nN), and a friction force measurement was taken at each increment. By plotting the friction force as a function of normal load, an average coefficient of friction was obtained from the slope of the fit line of the data. The adhesive force was measured using the force distance curve approach. In this technique, the AFM tip is brought into contact with the sample by extending the piezo vertically, then retracting the piezo and calculating the force required to separate the tip from the sample. The adhesive force is obtained by multiplying the cantilever spring constant with the cantilever deflection during the retraction between zero value and the maximum negative value. The method is described in detail by Bhushan (1999, 2002, 2008).

3.2.2. SEM micrographs

Figure 16 shows the SEM micrographs of two superhydrophobic leaves – Lotus (*Nelumbo nucifera*) and elephant ear or taro plant (*Colocasia esculenta*), referred to as Lotus and Colocasia, respectively – and two hydrophilic leaves – beech (*Fagus sylvatica*) and Magnolia (*Magnolia grandiflora*), referred to as Fagus and Magnolia, respectively (Bhushan and Jung, 2006). Lotus and Colocasia are characterized by papillose epidermal cells responsible for the creation of papillae or microbumps on the surfaces, and an additional layer of 3-D epicuticular waxes which are a mixture of very long chain fatty acids molecules (compounds with chains > 20 carbon atoms) and create nanostructure on the entire surface. Fagus and Magnolia are characterized by rather flat tabular cells with a

thin wax film with a 2-D structure (Barthlott and Neinhuis, 1997). The leaves are not self-cleaning, and contaminant particles from ambient are accumulated, which make them hydrophilic.

Figure 16. Scanning electron micrographs of the relatively rough, water-repellent leaf surfaces of *Nelumbo nucifera* (*Lotus*) and *Colocasia esculenta* and the relatively smooth, wettable leaf surfaces of *Fagus sylvatica* and *Magnolia grandiflora* (Bhushan and Jung, 2006).

3.2.3. Contact angle measurements

Figure 17(a) shows the contact angles for the superhydrophobic and hydrophilic leaves before and after applying acetone. The acetone was applied in order to remove any wax present on the surface. As a result, for the superhydrophobic leaves, the contact angle dramatically reduced, whereas for the hydrophilic leaves, the contact angle was almost unchanged. It is known that there is a 2-D very thin wax layer on the hydrophilic leaves, which introduces little roughness. In contrast, superhydrophobic leaves are known to have a thin 3-D wax layer on their surface consisting of nanoscale roughness over microroughness created by the papillae, which results in a hierarchical roughness. The combination of this wax and the roughness of the leaf creates a superhydrophobic surface.

We calculated the contact angles for leaves with smooth surfaces using the Wenzel equation and the calculated R_f and the contact angle of the four leaves (Bhushan and Jung, 2006). The results are presented in **Fig. 17(a)**. The approximate values of R_f for Lotus and Colocasia are 5.6 and 8.4 and for Fagus and Magnolia are 3.4 and 3.8, respectively. Based on the calculations, the contact angles on smooth surfaces were approximately 99° for Lotus and 96° for Colocasia. For both Fagus and Magnolia, the contact angles for the smooth surfaces were found to be approximately 86° and 88° . A further discussion on the effect of R_f on the contact angle will be presented later.

Figure 17(b) shows the contact angles for both fresh and dried states for the four leaves. There is a decrease in the contact angle for all four leaves when they are dried. For Lotus and Colocasia, this decrease is present because it is found that a fresh leaf has taller bumps than a dried leaf (data to be presented later), which will give a larger contact angle, according to the Wenzel equation. When the surface area is at a maximum compared to the footprint area, as with a fresh leaf, the roughness factor will be at a maximum and will only reduce when shrinking has occurred after drying. To understand the reason for the decrease of contact angle after drying of hydrophilic leaves, dried Magnolia leaves were also measured using an AFM. It is found that the dried leaf (peak-valley (P-V) height = $7\text{ }\mu\text{m}$, mid-width = $15\text{ }\mu\text{m}$, and peak radius = $18\text{ }\mu\text{m}$) has taller bumps than a fresh leaf (P-V height = $3\text{ }\mu\text{m}$, mid-width = $12\text{ }\mu\text{m}$, and peak radius = $15\text{ }\mu\text{m}$), which increases the roughness, and the contact angle decreases, leading to a more

hydrophilic surface.

Contact angle for various leaves before and after removing surface layer and calculated values of flat leaves

Contact angle for various fresh and dried leaves

Figure 17. Contact angle measurements and calculations for the leaf surfaces, (a) before and after removing surface layer as well as calculated values, and (b) fresh and dried leaves. The contact angle on a smooth surface for the four leaves was obtained using the roughness factor calculated (Bhushan and Jung, 2006).

3.2.4. Surface characterization using an optical profiler

The use of an optical profiler allows measurements to be made on fresh leaves which have a large P-V distance. Three different surface height maps for superhydrophobic and hydrophilic leaves are shown in **Fig. 18 and 19** (Bhushan and Jung, 2006). In each figure, a 3-D map and a flat map along with a 2-D profile in a given location of the flat 3-D map are shown. A scan size of $60\ \mu\text{m} \times 50\ \mu\text{m}$ was used to obtain a sufficient amount of bumps to characterize the surface but also to maintain enough resolution to get an accurate measurement.

The structures found with the optical profiler correlate well with the SEM images shown in **Fig. 16**. The bumps on the Lotus leaf are distributed on the entire surface, but the Colocasia leaf shows a very different structure to that of the Lotus. The surface structure for Colocasia not only has bumps similar to Lotus, but also surrounding each bump is a ridge that keeps the bumps separated. With these ridges, the bumps have a hexagonal (honeycomb) packing geometry that allows for the maximum number of bumps in a given area. The bumps of Lotus and both bumps and ridges of Colocasia contribute to the superhydrophobic nature since they both increase the R_f factor and result in air pockets between the droplet of water and the surface. In Fagus and Magnolia height maps, short bumps can be seen on the surface. This means that with decreased bump height, the probability of air pocket formation decreases, and bumps have a less beneficial effect on the contact angle.

As shown in 2-D profiles of superhydrophobic and hydrophilic leaves in **Fig. 18 and 19**, a curve has been fitted to each profile to show exactly how the bump shape behaves. For each leaf a second order curve fit has been given to the profiles to show how closely the profile is followed. By using the second order curve fitting of the profiles, the radius of curvature can be found (Bhushan and Jung, 2006; Burton and Bhushan, 2006).

Using these optical surface height maps, different statistical parameters of bumps and ridges can be found to characterize the surface: P-V height, mid-width, and peak radius (Bhushan, 1999, 2002). The mid-width is defined as the width of the bump at a height equal to half of peak to mean value. **Table 3** shows these quantities found in the optical height maps for the four leaves. Comparing the superhydrophobic and hydrophilic leaves, it can be seen that the P-V height for bumps of Lotus and Colocasia is much taller

than that for the bumps of *Fagus* and *Magnolia*. The peak radius for the bumps of *Lotus* and *Colocasia* is also smaller than that for the bumps of *Fagus* and *Magnolia*. However, the values of mid-width for the bumps of the four leaves are similar.

Figure 18. Surface height maps and 2-D profiles of hydrophobic leaves using an optical profiler. For *Lotus* leaf, a microbump is defined as a single, independent microstructure protruding from the surface. For *Colocasia* leaf, a microbump is defined as the single, independent protrusion from the leaf surface, whereas a ridge is defined as the structure that surrounds each bump and is completely interconnected on the leaf. A curve has been fitted to each profile to show exactly how the bump shape behaves. The radius of curvature is calculated from the parabolic curve fit of the bump (Bhushan and Jung, 2006).

Figure 19. Surface height maps and 2-D profiles of hydrophilic leaves using an optical profiler. For *Fagus* and *Magnolia* leaves, a microbump is defined as a single, independent microstructure protruding from the surface. A curve has been fitted to each profile to show exactly how the bump shape behaves. The radius of curvature is calculated from the parabolic curve fit of the bump (Bhushan and Jung, 2006).

Leaf		Microbump (μm) Scan size (50×50 μm)			Nanobump (μm) Scan size (2×2 μm)		
		P-V height	Mid- width	Peak radius	P-V height	Mid- width	Peak radius
Lotus							
Fresh		13 [*]	10 [*]	3 [*]	0.78 ^{**}	0.40 ^{**}	0.15 ^{**}
Dried		9 ^{**}	10 ^{**}	4 ^{**}	0.67 ^{**}	0.25 ^{**}	0.10 ^{**}
Colocasia							
Fresh	Bump	9 [*]	15 [*]	5 [*]	0.53 ^{**}	0.25 ^{**}	0.07 ^{**}
	Ridge	8 [*]	7 [*]	4 [*]	0.68 ^{**}	0.30 ^{**}	0.12 ^{**}
Dried	Bump	5 ^{**}	15 ^{**}	7 ^{**}	0.48 ^{**}	0.20 ^{**}	0.06 ^{**}
	Ridge	4 ^{**}	8 ^{**}	4 ^{**}	0.57 ^{**}	0.25 ^{**}	0.11 ^{**}
Fagus							
Fresh		5 [*]	10 [*]	15 [*]	0.18 ^{**}	0.04 ^{**}	0.01 ^{**}
		4 ^{**}	5 ^{**}	10 ^{**}			
Magnolia							
Fresh		4 [*]	13 [*]	17 [*]	0.07 ^{**}	0.05 ^{**}	0.04 ^{**}
		3 ^{**}	12 ^{**}	15 ^{**}			

* Data measured using optical profiler

** Data measured using AFM

Table 3. Microbump and nanobump map statistics for hydrophobic and hydrophilic leaves, measured both fresh and dried leaves using an optical profiler and AFM (Bhushan and Jung, 2006).

3.2.5. Surface characterization, adhesion and friction using an AFM

3.2.5.1. Comparison of two AFM measurement techniques

To measure topographic images of the leaf surfaces, both the contact and tapping modes were first used (Bhushan and Jung, 2006). **Figure 20** shows surface height maps of dried Lotus obtained using the two techniques. In the contact mode, local height variation for Lotus leaf was observed in 50 μm scan size. However, little height variation was obtained in a 2 μm scan even at loads as low as 2 nN. This could be due to the substantial frictional force generated as the probe scanned over the sample. The frictional force can damage the sample. The tapping mode technique allows high-resolution topographic imaging of sample surfaces that are easily damaged, loosely held to their substrate, or difficult to image by other AFM techniques (Bhushan, 1999, 2002). As shown in **Fig. 20**, with the tapping mode technique, the soft and fragile leaves can be imaged successfully. Therefore tapping mode technique was used to examine the surface roughness of the superhydrophobic and hydrophilic leaves using an AFM.

3.2.5.2. Surface characterization

The AFM has a Z-range on the order of 7 μm , and cannot be used for measurements in a conventional way because of the high P-V distances of a Lotus leaf. Burton and Bhushan (2006) developed a new method to fully determine the bump profiles. In order to compensate for the large P-V distance, two scans were made for each height: one measurement that scans the tops of the bumps and another measurement that scans the bottom or valleys of the bumps. The total height of the bumps is embedded within the two scans. **Figure 21** shows the 50 μm surface height maps obtained using this method (Bhushan and Jung, 2006). The 2-D profiles in the right side column take the profiles from the top scan and the bottom scan for each scan size and splice them together to get the total profile of the leaf. The 2 μm surface height maps for both fresh and dried Lotus can also be seen in **Fig. 21**. This scan area was selected on the top of a microbump obtained in the 50 μm surface height map. It can be seen that nanobumps are randomly and densely distributed on the entire surface of Lotus.

We also measured the surface height maps for the hydrophilic leaves in both 50

Figure 20. Surface height maps showing the top scan and bottom scan in a 50 μm scan size and the bump peak scan selected in a 2 μm scan size for a Lotus leaf using an AFM in contact mode and tapping mode. Two methods were used to determine a suitable method to obtain high resolution of nanotopography for a Lotus leaf (Bhushan and Jung, 2006).

Figure 21. Surface height maps and 2-D profiles showing the top scan and bottom scan of a dried Lotus leaf in 50 μm scan (because the P-V distance of a dried Lotus leaf is greater than the Z-range of an AFM), and the top scan of both fresh and dried Lotus in a 2 μm scan (Bhushan and Jung, 2006). Splicing technique was used to determine the bump profiles. In order to compensate for the large P-V distance, the total height of the bumps is embedded within the top scan and bottom scan.

Figure 22. Surface height maps and 2-D profiles of Fagus and Magnolia using an AFM in both 50 μm and 2 μm scans (Bhushan and Jung, 2006).

μm and $2\ \mu\text{m}$ scan sizes as shown in **Fig. 22** (Bhushan and Jung, 2006). For *Fagus* and *Magnolia*, microbumps were found on the surface, and the P-V distance of these leaves is lower than that of *Lotus* and *Colocasia*. It can be seen in the $2\ \mu\text{m}$ surface height maps that nanobumps selected on the peak of the microbump have an extremely low P-V distance.

Using the AFM surface height maps, different statistical parameters of bumps and ridges can be obtained: P-V height, mid-width, and peak radius. These quantities for the four leaves are listed in **Table 3**. It can be seen that the values correlate well with the values obtained from optical profiler scans except for the bump height, which decreases by more than half because of leaf shrinkage.

3.2.5.3. Adhesive force and friction

Adhesive force and coefficient of friction of superhydrophobic and hydrophilic leaves using AFM are presented in **Fig. 23** (Bhushan and Jung, 2006). For each type of leaf, adhesive force measurements were made for both fresh and dried leaves using a $15\ \mu\text{m}$ radius tip. It is found that the dried leaves had a lower adhesive force than the fresh leaves. Adhesive force arises from several sources in changing the presence of a thin liquid film, such as an adsorbed water layer that causes meniscus bridges to build up around the contacting and near contacting bumps as a result of surface energy effects (Bhushan, 1999, 2002). When the leaves are fresh there is moisture within the plant material that causes the leaf to be soft, and when the tip comes into contact with the leaf sample, the sample will deform, and a larger real area of contact between the tip and sample will occur, and the adhesive force will increase. After the leaf has dried, the moisture that was in the plant material is gone, and there is not as much deformation of the leaf when the tip comes into contact with the leaf sample. Hence, the adhesive force is decreased because the real area of contact has decreased.

The adhesive force of *Fagus* and *Magnolia* is higher than that of *Lotus* and *Colocasia*. The reason is that the real area of contact between the tip and leaf surface is expected to be higher in hydrophilic leaves than in superhydrophobic leaves. In addition, the *Fagus* and *Magnolia* are hydrophilic and have a high affinity to water. The combination of high real area of contact and affinity to water are responsible for higher

Figure 23. Adhesive force for fresh and dried leaves, and the coefficient of friction for dried leaves for 50 μm and 2 μm scan sizes for hydrophobic and hydrophilic leaves. All measurements were made using an AFM with 15 μm radius borosilicate tip. Reproducibility for both adhesive force and coefficient of friction is $\pm 5\%$ for all measurements (Bhushan and Jung, 2006).

meniscus forces (Bhushan, 1999, 2002). The coefficient of friction was only measured on a dried plant surface with the same sliding velocity (10 $\mu\text{m/s}$) in different scan sizes rather than including the fresh surface because the P-V was too large to scan back and

forth with the AFM to obtain friction force. As expected, the coefficient of friction for superhydrophobic leaves is lower than that for hydrophilic leaves due to the real area of contact between the tip and leaf sample, similar to the adhesive force results. When the scan size from microscale to nanoscale decreases, the coefficient of friction also decreases in each leaf. The reason for such dependence is the scale dependent nature of the roughness of the leaf surface. **Figures 21 and 22** show AFM topography images and 2-D profiles of the surfaces for different scan sizes. The scan size dependence of the coefficient of friction has been reported previously (Poon and Bhushan, 1995; Koinkar and Bhushan, 1997; Tambe and Bhushan, 2004).

3.2.6. Role of the hierarchical roughness

The approximation of the roughness factor for the leaves on the micro- and nanoscale was made using AFM scan data (Bhushan and Jung, 2006). Roughness factors for various leaves are presented in **Table 4**. As mentioned earlier, the open space between asperities on a surface has the potential to collect air, and its probability appears to be higher in nanobumps as the distance between bumps in the nanoscale is smaller than those in microscale. Using roughness factor values, along with the contact angles (θ) from both superhydrophobic and hydrophilic surfaces, 153° and 152° in Lotus and Colocasia, and 76° and 84° in Fagus and Magnolia, respectively, the contact angles (θ_0) for the smooth surfaces can be calculated using the Wenzel equation (Eq. 6) for microbumps and the Cassie-Baxter equation (Eq. 9) for nanobumps. Contact angle ($\Delta\theta$) calculated using R_f on the smooth surface can be found in **Table 4**. It can be seen that the roughness factors and the differences ($\Delta\theta$) between θ and θ_0 on the nanoscale are higher than those in the microscale. This means that nanobumps on the top of a microbump increase contact angle more effectively than microbumps. In the case of hydrophilic leaves, the values of R_f and $\Delta\theta$ change very little on both scales.

Based on the data in **Fig. 23**, the coefficient of friction values in the nanoscale are much lower than those in the microscale. It is clearly observed that friction values are scale dependent. The height of a bump and the distance between bumps in microscale is much larger than those in nanoscale, which may be responsible for larger values of friction force on the microscale.

One difference between microbumps and nanobumps for surface enhancement of water repellency is the effect on contact angle hysteresis, in other words, the ease with which a droplet of water can roll on the surface. It has been stated earlier that contact angle hysteresis decreases and contact angle increases due to the decreased contact with the solid surface caused by the air pockets beneath the droplet. The surface with nanobumps has a high roughness factor compared with that of microbumps. With large distances between microbumps, the probability of air pocket formation decreases and is responsible for high contact angle hysteresis. Therefore, on the surface with nanobumps, the contact angle is high and contact angle hysteresis is low, and drops rebound easily and can set into a rolling motion with a small tilt angle (Bhushan and Jung, 2006).

Natural water-repellent and self-cleaning surfaces such as the Lotus leaf (Koch et al., 2008a, 2009a) or water strider leg (Gao and Jiang, 2004) have a hierarchical structure. However, the functionality of this hierarchical roughness remains a subject of discussion, and several explanations have been suggested. Nosonovsky and Bhushan (2007a,b,c,d, 2008a,b,c,d,e,f) showed that the mechanisms involved in superhydrophobicity are scale dependent, and thus the roughness must be hierarchical in order to respond to these mechanisms. The surface must be able to repel both macroscopic and microscopic droplets. Fürstner et al. (2005) pointed out that artificial surfaces with one level of roughness can well repel large “artificial rain” droplets; however, they cannot repel small “artificial fog” droplets trapped in the valleys between the bumps, so the hierarchy may have to do with the ability to repel droplets of various size ranges. According to Gao and McCarthy (2006), the large bumps allow to maintain the composite interface while the small ones enhance the contact angle in accordance to the Wenzel model. We showed that a droplet with radius of about 100 to 400 μm on micropatterned surfaces goes through transition from the composite interface to the solid-liquid interface as the pitch increases (Jung and Bhushan, 2008a), and the hierarchical structure can prevent the gaps between the pillars from filling with liquid until the droplet evaporated completely (Bhushan et al., 2008a, 2009c,d).

Leaf (Contact angle)	Scan size	State	R_f	$\Delta\theta$
Lotus (153°)	50 μm	Dried	5.6	54 [*]
	2 μm	Fresh	20	61 ^{**}
		Dried	16	60 ^{**}
Colocasia (152°)	50 μm	Dried	8.4	56 [*]
	2 μm bump	Fresh	18	60 ^{**}
		Dried	14	59 ^{**}
	2 μm ridge	Fresh	18	60 ^{**}
		Dried	15	59 ^{**}
Fagus (76°)	50 μm	Fresh	3.4	-10 [*]
	2 μm	Fresh	5.3	2 ^{**}
Magnolia (84°)	50 μm	Fresh	3.8	-4 [*]
	2 μm	Fresh	3.6	14 ^{**}

* Calculations made using Wenzel equation.

** Calculations made using Cassie–Baxter equation. We assume that the contact area between the droplet and air is the half of the whole area of the rough surface.

Table 4. Roughness factor and contact angle ($\Delta\theta = \theta - \theta_o$) calculated using R_f on the smooth surface for hydrophobic and hydrophilic leaves measured using an AFM, both microscale and nanoscale (Bhushan and Jung, 2006).

CHAPTER 4

HOW TO MAKE A SURFACE FOR SUPERHYDROPHOBICITY, SELF-CLEANING, LOW ADHESION, AND DRAG REDUCTION

Fabrication of superhydrophobic surfaces has been an area of active research since the mid-1990s. In general, the same techniques that are used for micro- and nanostructure fabrication, such as lithography, etching, deposition and self-assembly, have been utilized for producing superhydrophobic surfaces (**Fig. 24, Table 5**). Pros and cons of these techniques are summarized in **Table 6**. Among especially interesting developments is the creation of switchable surfaces that can be turned from hydrophobic to hydrophilic by surface energy modification through electrowetting, light and X-ray irradiation, dynamic effects, optical effects (e.g., the transparence, reflectivity or non-reflectivity) combined with the Lotus effect, hydrophobic interactions, and so on (Feng et al., 2004; Xu et al., 2005; Shirtcliffe et al., 2005; Wang et al., 2007; Krupenkin et al., 2007). An important requirement for potential applications for optics and self-cleaning glasses is the creation of transparent superhydrophobic surfaces. In order for the surface to be transparent, roughness details should be smaller than the wavelength of visible light (about 400-700 nm) (Nakajima et al., 1999).

Two main requirements for a superhydrophobic surface are that the surface should be rough and that it should be hydrophobic (low surface energy). These two requirements lead to two methods of producing a superhydrophobic surface: first, it is possible to make a rough surface from an initially hydrophobic material and, second, to modify a rough hydrophilic surface by modifying surface chemistry or applying a hydrophobic material upon it. Note that roughness is usually a more critical property than the low surface energy, since both moderately hydrophobic and very hydrophobic materials can exhibit similar wetting behavior when roughened.

Figure 24. Typical methods to fabricate micro/nanoroughened surfaces.

Material	Technique	Contact angle	Notes	Source
Teflon	Plasma	168		Zhang et al. (2004a); Shiu et al. (2004)
Fluorinated block polymer solution	Casting under humid environment	160	Transparent	Yabu and Shimomura (2005)
PFOS	Electro- and chemical polymerization	152	Reversible (electric potential)	Xu et al. (2005)
PDMS	Laser treatment	166		Khorasani et al. (2005)
PS-PDMS Block copolymer	Electrospining	>150		Ma et al. (2005)
PS, PC, PMMA	Evaporation	>150		Bormashenko et al. (2006)
PS nanofiber	Nanoimprint	156		Lee et al. (2004)
Polyaniline nanofiber	Chemical polymerization	175		Chiou et al. (2007)
PET	Oxygen plasma etching	>150		Teshima et al. (2005)
Organo-triethoxysilanes	Sol-gel	155	Reversible (temperature)	Shirtcliffe et al. (2005)
Al	Chemical etching	>150		Qian and Shen (2005)
Copper	Electrodeposition	160	Hierarchical	Shirtcliffe et al. (2004)
Si	Photolithography	170		Bhushan and Jung (2007)
Si	E-beam lithography	164		Martines et al. (2005)
Si	X-ray lithography	>166		Furstner et al. (2005)
PS, PMMA	AFM nanolithography			Martin et al. (2005); Cappella and Bonaccorso (2007)

Continued

Table 5. Typical materials and corresponding techniques to produce micro/nanoroughness.

Table 5 Continued

Material	Technique	Contact angle	Notes	Source
Si	Casting	158	Plant leaf replica	Sun et al. (2005); Fürstner et al. (2005)
Si (Black Si)	Plasma etching	>150	For liquid flow	Jansen et al. (1995)
Silica	Sol-gel	150		Hikita et al. (2005); Shang et al. (2005)
Silica	Layer-by-layer assembly	160	Hierarchical	Zhao et al. (2008)
Polyelectrolyte multilayer surface overcoated with silica nanoparticles	Self assembly	168		Zhai et al. (2004)
Epoxy resin with synthetic and plant waxes	Replication and self assembly	173	Hierarchical	Bhushan et al. (2008a,b; 2009c,d); Koch et al. (2009b)
Nano-silica spheres	Dip coating	105		Klein et al. (2003)
Silica colloidal particles in PDMS	Spin coated	165	Hierarchical	Ming et al. (2005)
Au clusters	Electrochemical deposition	>150		Zhang et al. (2004b)
Carbon nanotubes	Chemical vapor deposition	>165		Lau et al. (2003)
Carbon nanotubes	Chemical vapor deposition	159	Hierarchical	Huang et al. (2005)
Carbon nanotubes	Replication and spray coating	170	Hierarchical	Jung and Bhushan (2010b)
ZnO, TiO ₂ Nanorods	Sol-gel	>150	Reversible (UV irradiation)	Feng et al. (2004)

Techniques	Pros	Cons
Lithography	Accuracy, large area	Slow process, high cost
Etching	Fast	Chemical contamination, less control
Deposition	Flexibility, cheap	Can be high temperature, less control
Self assembly	Flexibility, cheap	Require suitable precursor

Table 6. Pros and cons of various fabrication techniques.

4.1. Roughening to create one-level structure

Lithography is a well-established technique, applied for creating a large area of periodic micro/nanopatterns. It includes photo, E-beam, X-ray, and soft lithography. Bhushan and Jung (2007) produced micropatterned Si using photolithography. To obtain a sample that is hydrophobic, a SAM of 1, 1, -2, 2, - tetrahydroperfluorodecyltrichlorosilane (PF_3) was deposited on the sample surfaces using a vapor phase deposition technique. They obtained a superhydrophobic surface with a contact angle up to 170° . Martines et al. (2005) fabricated ordered arrays of nanopits and nanopillars by using electron beam lithography. They obtained a superhydrophobic surface with a static contact angle of 164° and contact angle hysteresis of 1° for a surface consisting of tall pillars with cusped tops after hydrophobization with octadecyltrichlorosilane (OTS). Fürstner et al. (2005) created silicon wafers with regular patterns of spikes by X-ray lithography. The wafer was hydrophobized by sputtering a layer of gold and subsequent immersion in a hexadecanethiol solution. AFM can be used in nanolithography to produce a nanostructure with the aid of solvent (Cappella and Bonaccorso, 2007) or electro field (Martin et al., 2005) on PS and PMMA, respectively. Jung and Bhushan (2006) created low aspect ratio asperities (LAR, 1:1 height-to-diameter ratio), high aspect ratio asperities (HAR, 3:1 height-to-diameter ratio), and a Lotus pattern (replica from the Lotus leaf), all on a PMMA surface using soft lithography.

A self-assembled monolayer (SAM) of perfluorodecyltriethoxysilane (PFDTES) was deposited on the patterned surfaces using a vapor phase deposition technique.

One well-known and effective way to make rough surfaces is etching using either plasma, laser, chemical, or electrochemical techniques (Ma and Hill, 2006). Jansen et al. (1995) etched a silicon wafer using a fluorine-based plasma by utilizing the black silicon method to obtain isotropic, positively, and negatively tapered as well as vertical walls with smooth surfaces. Coulson et al. (2000) described an approach in plasma chemical roughening of poly(tetrafluoroethylene) (PTFE) substrates followed by the deposition of low surface energy plasma polymer layers, which give rise to high repellency towards polar and nonpolar probe liquids. A different approach was taken by Shiu et al. (2004), who treated a Teflon film with oxygen plasma and obtained a superhydrophobic surface with a contact angle of 168° . Fluorinated materials have a limited solubility, which makes it difficult to roughen them. However, they may be linked or blended with other materials, which are often easier to roughen, in order to make superhydrophobic surfaces. Teshima et al. (2005) obtained a transparent superhydrophobic surface from a poly(ethylene terephthalate) (PET) substrate via selective oxygen plasma etching followed by plasma-enhanced chemical vapor deposition using tetramethylsilane (TMS) as the precursor. Khorasani et al. (2005) produced porous PDMS surfaces with the contact angle of 175° using CO_2 -pulsed laser etching method as an excitation source for surface. Qian and Shen (2005) described a simple surface roughening method by dislocation selective chemical etching on polycrystalline metals such as aluminum. After treatment with fluoroalkylsilane, the etched metallic surfaces exhibited superhydrophobicity. Xu et al. (2005) fabricated a reversible superhydrophobic surface with a double-roughened perfluorooctanesulfonate (PFOS) doped conducting polypyrrole (PPy) film by a combination of electropolymerization and chemical polymerization. Reversibility was achieved by switching between superhydrophobic doped or oxidized states and superhydrophilicity dedoped or neutral states with changing the applied electrochemical potential.

Stretching method can be used to produce a superhydrophobic surface. Zhang et al. (2004a) stretched a Teflon film and converted it into fibrous crystals with a large

fraction of void space in the surface, leading to high roughness and the superhydrophobicity.

Deposition methods also make a substrate rough from the bulk properties of the material and enlarge potential applications of superhydrophobic surfaces. There are several ways to make a rough surface including adsorption, dip coating, electrospinning, anodization, electrochemical, evaporation, chemical vapor deposition (CVD), and plasma. Solidification of wax can be used to produce a superhydrophobic surface. Shibuichi et al. (1996) used alkylketene dimer (AKD) wax on a glass plate to spontaneously form a fractal structure in its surfaces. They obtained a surface with a contact angle larger than 170° without any fluorination treatments. Klein et al. (2003) obtained superhydrophobic surfaces by simply dip-coating a substrate with a slurry containing nano-silica spheres, which adhered to the substrate after a low temperature heat treatment. After reaction of the surface with a fluoroalkyltrichlorosilane, the hydrophobicity increased with a decreasing area fraction of spheres. Ma et al. (2005) produced block copolymer poly(styrene-*b*-dimethylsiloxane) fibers with submicrometer diameters in the range 150-400 nm by electrospinning from a solution in tetrahydrofuran and dimethylformamide. They obtained superhydrophobic nonwoven fibrous mats with a contact angle of 163° . Shiu et al. (2004) produced self-organized close-packed superhydrophobic surfaces by spin-coating the monodispersed polystyrene beads solution on a substrate surface. Abdelsalam et al. (2005) studied the wetting of structured gold surfaces formed by electrodeposition through a template of submicrometer spheres and discussed the role of the pore size and shape in controlling wetting. Bormashenko et al. (2006) used evaporated polymer solutions of polystyrene (PS), polycarbonate (PC) and polymethylmethacrylate (PMMA) dissolved in chlorinated solvents, dichloromethane (CH_2Cl_2), and chloroform (CHCl_3), to obtain self-assembled structure with hydrophobic properties. Chemical/physical vapor deposition (CVD/PVD) has been used for the modification of surface chemistry as well. Lau et al. (2003) created superhydrophobic carbon nanotube forests by modifying the surface of vertically aligned nanotubes with plasma enhanced chemical vapor deposition (PECVD). Superhydrophobicity was achieved down to the microscopic level where essentially spherical, micrometer-sized water droplets can be suspended on top of the nanotube forest. Zhu et al. (2005) and

Huang et al. (2005) prepared surfaces with two-scale roughness by the controlled growth of carbon nanotube (CNT) arrays by CVD. Zhao et al. (2006) also synthesized vertically aligned multiwalled carbon nanotube (MWCNT) arrays by chemical-vapor deposition on Si substrates using a thin film of iron (Fe) as catalyst layer and aluminum (Al) film.

Attempts to create superhydrophobic surfaces by casting and nanoimprint methods have been successful. Yabu and Shimomura (2005) prepared a porous superhydrophobic transparent membrane by casting a fluorinated block polymer solution under humid environment. Transparency was achieved because the honeycomb-patterned films had a sub-wavelength pore size. Sun et al. (2005) reported a nanocasting method to make a superhydrophobic PDMS surface. They first made a negative PDMS template using a Lotus leaf as an original template and then used the negative template to make a positive PDMS template – a replica of the original Lotus leaf. Zhao et al. (2005) prepared a superhydrophobic surface by casting a micellar solution of a copolymer poly(styrene-b-dimethylsiloxane) (PS-PDMS) in humid air based on the cooperation of vapor-induced phase separation and surface enrichment of PDMS block. Lee et al. (2004) produced vertically aligned PS nanofibers by using nanoporous anodic aluminum oxide as a replication template in a heat- and pressure-driven nanoimprint pattern transfer process. As the aspect ratio of the polystyrene (PS) nanofibers increased, the nanofibers could not stand upright but formed twisted bundles resulting in a three-dimensionally rough surface with a contact angle of about 155°.

4.2. Coating to create one-level hydrophobic structures

Modifying the surface chemistry with a hydrophobic coating widens the potential applications of superhydrophobic surfaces. There are several ways to modify the chemistry of a surface including sol-gel, dip coating, self-assembly, electrochemical and chemical/physical vapor deposition. Shirtcliffe et al. (2005) prepared porous sol–gel foams from organo-triethoxysilanes which exhibited switching between superhydrophobicity and superhydrophilicity when exposed to different temperatures. Hikita et al. (2005) used colloidal silica particles and fluoroalkylsilane as the starting materials and prepared a sol–gel film with superliquid-repellency by hydrolysis and condensation of alkoxysilane compounds. Feng et al. (2004) produced superhydrophobic

surfaces using ZnO nanorods by sol-gel method. They showed that superhydrophobic surfaces can be switched into hydrophilic surfaces by alternation of ultraviolet (UV) irradiation. Shang et al. (2005) did not blend low surface energy materials in the sols, but described a procedure to make transparent superhydrophobic surfaces by modifying silica based gel films with a fluorinated silane. In a similar way, Wu et al. (2005) made a microstructured ZnO-based surface via a wet chemical process and obtained superhydrophobicity after coating the surface with long-chain alkanoic acids. Chiou et al. (2007) created polyaniline nanofibers using chemical oxidative polymerization to produce uniform aligned nanofibers and then CF₄ plasma treatment was performed to create superhydrophobic surfaces with a contact angle of 175°.

Zhai et al. (2004) used a layer-by-layer (LBL) self-assembly technique to create a poly(allylamine hydrochloride)/poly(acrylic acid) (PAH/PAA) multilayer which formed a honeycomb-like structure on the surface after an appropriate combination of acidic treatments. After cross-linking the structure, they deposited silica nanoparticles on the surface via alternating dipping of the substrates into an aqueous suspension of the negatively charged nanoparticles and an aqueous PAH solution, followed by a final dipping into the nanoparticle suspension. Superhydrophobicity was obtained after the surface was modified by a chemical vapor deposition of (tridecafluoro-1,1,2,2-tetrahydrooctyl)-1-trichlorosilane followed by a thermal annealing.

Zhang et al. (2004b) showed that the surface covered with dendritic gold clusters, which was formed by electrochemical deposition onto an indium tin oxide (ITO) electrode modified with a polyelectrolyte multilayer, showed superhydrophobic properties after further deposition of a n-dodecanethiol monolayer. Han et al. (2005) described the fabrication of Lotus leaf-like superhydrophobic metal surfaces by using electrochemical reaction of Cu or Cu–Sn alloy plated on steel sheets with sulfur gas, and subsequent perfluorosilane treatment. Chemical bath deposition (CBD) has also been used to make nanostructured surfaces, thus, Hosono et al. (2005) fabricated a nanopin film of brucite-type cobalt hydroxide (BCH) and achieved the contact angle of 178° after further modification of lauric acid (LA). Shi et al. (2006) described the use of galvanic cell reaction as a facile method to chemically deposit Ag nanostructures on the *p*-silicon wafer on a large scale. When the Ag covered silicon wafer was further modified with a

self-assembled monolayer of *n*-dodecanethiol, a superhydrophobic surface was obtained with a contact angle of about 154° and a tilt angle lower than 5°.

4.3. Methods to create two-level (hierarchical) structures

Two-level (hierarchical) roughness structures are typical for superhydrophobic surfaces in nature, as was discussed above. Recently, many efforts have been devoted to fabricating these hierarchical structures in various ways. Shirtcliffe et al. (2004) prepared a hierarchical (double-roughened) copper surface by electrodeposition from acidic copper sulfate solution onto flat copper and a patterning technique of coating with a fluorocarbon hydrophobic layer. Another way to obtain a rough surface for superhydrophobicity is assembly from colloidal systems. Ming et al. (2005) prepared a hierarchical (double roughened) surface consisting of silica-based raspberry-like particles. First is the attachment of epoxy and amino groups onto the silica microparticles of about 700 nm and nanoparticles of about 70 nm, respectively, using established synthetic procedures. Two suspensions in ethanol are created, one with microparticles and another one with nanoparticles. In the next step, the suspension with the silica microparticles is added dropwise to the suspension with the nanoparticles. The nanoparticles attach to the microparticles due to the reaction between the epoxy and amino groups present on the surface of the particles. Then, the suspension is centrifuged to separate any unreacted particles. A next step involves depositing these micro/nanostructured particles into an epoxy film (on silicon). Finally, since the resulting micro/nanoparticle surface is initially hydrophilic, it is made hydrophobic by a deposition of monoepoxy-end-capped poly(dimethylsiloxane) (PDMS). Northen and Turner (2005) fabricated arrays of flexible silicon dioxide platforms supported by single high aspect ratio silicon pillars down to 1 µm in diameter and with heights up to ~50 µm. When these platforms were coated with polymeric organorods of approximately 2 µm tall and 50-200 nm in diameter, it showed that the surface is highly hydrophobic with a water contact angle of 145°. Chong et al. (2006) fabricated hierarchically ordered nanowire arrays with periodic voids at the microscale and hexagonally packed nanowires at the nanoscale. This hierarchical surface was created by selective electrodeposition using nanoporous anodic

alumina as a template and a porous gold film as a working electrode that is patterned by microsphere monolayers. Wang et al. (2006) also developed a novel precursor hydrothermal redox method with $\text{Ni}(\text{OH})_2$ as the precursor to fabricate a hierarchical structure consisting of nickel hollow microspheres with nickel nanoparticles *in situ*. The created hierarchical hollow structure exhibited enhanced coercivity and remnant magnetization as compared with hollow nickel submicrometer spheres, hollow nickel nanospheres, bulk nickel, and free Ni nanoparticles.

Kim et al. (2007) fabricated a hierarchical structure which looks like the same structures as the Lotus leaf. First, the nanoscale porosity was generated by anodic aluminum oxidation, and then, the anodized porous alumina surface was replicated by polytetrafluoroethylene. The polymer sticking phenomenon during the replication created the sub-microstructures on the negative polytetrafluoroethylene nanostructure replica. The contact angle of the created hierarchical structure was about 160° and the tilting angle is less than 1° . Del Campo and Greiner (2007) reported that SU-8 hierarchical patterns comprising of features with lateral dimensions ranging from 5 mm to 2 mm and heights from 10 to 500 μm were obtained by photolithography, which comprises of a step of layer-by-layer exposure in soft contact printed shadow masks which are embedded into the SU-8 multilayer. Bhushan et al. (2008a,b, 2009c,d) and Koch et al (2009b) produced hierarchical structures by replication of a micropatterned silicon surface and Lotus leaf microstructure using an epoxy resin and by self assembly of synthetic and plant waxes as thin hydrophobic three-dimensional crystals to create hydrophobic nanostructures. The fabrication technique used is a low cost two step process, which provides flexibility in the fabrication of a variety of hierarchical structures. They showed that a hierarchical structure has a high propensity of air pocket formation and leads to a static contact angle of 173° and contact angle hysteresis and tilt angle of $\sim 2^\circ$. Zhao et al. (2008) fabricated a hierarchical structure by using layer-by-layer assembly of silica nanoparticles on a microsphere-patterned polyimide precursor substrate combined with the fluoroalkylsilane treatment. The microstructures were created by replica molding of polyamide using two-dimensional PS microsphere arrays. They obtained a superhydrophobic surface with a static contact angle of 160° and sliding angle of less than 10° . Cortese et al. (2008) applied plasma CF_4 treatment on micropattern PDMS and obtained contact angle of 170° .

Kuan et al. (2009) produced a hierarchical structure by imprinting ZnO precursor films using gratings with 830 nm and 50 μm dimensions. They achieved a contact angle of 141° by nanostructures deposited on sawtooth patterns without modifying the surface chemistry. Jung and Bhushan (2010b) produced mechanically durable CNT composite hierarchical structures with a static contact angle of 170° and a contact angle hysteresis of 2° by replication of a micropatterned silicon surface using an epoxy resin and by deposition of the CNT composite using a spray method. They showed that CNT composite structure had high mechanical strength and wear resistance led from the uniform distribution and strong bonding of CNT on substrates.

CHAPTER 5

FABRICATION AND CHARACTERIZATION OF MICRO-, NANO- AND HIERARCHICAL STRUCTURED SURFACES

In this section, we will discuss experimental measurements of the wetting properties of micro-, nano- and hierarchical patterned surfaces.

5.1. Experimental techniques

5.1.1. Contact angle, surface roughness, and adhesion

The static and dynamic (advancing and receding) contact angles were measured using a Rame-Hart model 100 contact angle goniometer and droplets of DI water (Burton and Bhushan, 2005; Bhushan and Jung, 2007,2008; Jung and Bhushan, 2006,2007; Bhushan et al., 2008a,b, 2009c,d; Koch et al., 2009b). For measurement of the static contact angle, the droplet size should be smaller than the capillary length, but larger than the dimension of the structures present on the surfaces. Droplets of about 5 μL in volume (with the diameter of a spherical droplet about 2.1 mm) were gently deposited on the substrate using a microsyringe for measurement of the static contact angle. The advancing and receding contact angles were measured by the addition and removal of water from a DI water sessile droplet using a microsyringe. The contact angle hysteresis was calculated as the difference between the measured advancing and receding contact angles, and the tilt angle was measured by using a simple tilting stage (Bhushan and Jung, 2007, 2008; Bhushan et al., 2008a,b, 2009c,d; Koch et al., 2009b). All measurements were made at five different points for each sample at 22 ± 1 °C and $50 \pm 5\%$ RH. The measurements were reproducible to within $\pm 3^\circ$.

For surface roughness measurement, an optical profiler (NT-3300, Wyko Corp., Tuscon, AZ) was used for different surface structures (Burton and Bhushan, 2006;

Bhushan and Jung, 2006, 2007, 2008). The optical profiler has one advantage due to its greater Z-range (2 mm) over an AFM (Z-range about 7 μm), but it has a maximum lateral resolution of only approximately 0.6 μm (Bhushan, 1999, 2002). Experiments were performed using three different radii tips to study the effect of scale dependence. Large radii atomic force microscope (AFM) tips were primarily used in this study. A borosilicate ball with 15 μm radius and a silica ball with 3.8 μm radius were mounted on a gold-coated triangular Si_3N_4 cantilever with a nominal spring constant of 0.58 N m^{-1} . A square pyramidal Si_3N_4 tip with a nominal radius of 30-50 nm on a triangular Si_3N_4 cantilever with a nominal spring constant of 0.58 N m^{-1} was used for the smaller radius tip. Adhesive force was measured using the force distance curve approach described earlier (Bhushan, 1999, 2002, 2008).

5.1.2. Droplet evaporation studies

Droplet evaporation was observed and recorded by a digital camcorder (Sony, DCRSR100) with a 10 X optical and 120 X digital zoom for every run of the experiment. Then the decrease in the diameter of the droplets with time was determined (Jung and Bhushan, 2007, 2008a, Bhushan et al., 2008a, 2009c). The resolution of the camcorder was 0.03 s per frame. An objective lens placed in front of the camcorder during recording gave a total magnification of 10 to 20 times. Droplet diameter as small as a few hundred microns could be measured with this method. Droplets were gently deposited on the substrate using a microsyringe, and the whole process of evaporation was recorded. Images obtained were analyzed using Imagetool® software (University of Texas Health Science Center) for the contact angle. To find the dust trace remaining after droplet evaporation, an optical microscope with a CCD camera (Nikon, Optihot-2) was used. All measurements were made in a controlled environment at $22 \pm 1^\circ\text{C}$ and $45 \pm 5\% \text{ RH}$ (Jung and Bhushan, 2007, 2008a, Bhushan et al., 2008a, 2009c,d).

5.1.3. Bouncing droplet studies

The process of dynamic impact was recorded by a high speed camera (Kodak Ektapro HS Motion Analyzer, Model 4540) operated at 500 frames/s for each experimental run and then measuring the dynamic impact behavior of the droplet as a

function of time. The impact velocity was calculated by varying the droplet release height. The size of the droplet was the same as that of a droplet for the static contact angle. All measurements were made in a controlled environment at 22 ± 1 °C and $45 \pm 5\%$ RH (Jung and Bhushan, 2008b).

5.1.4. Vibrating droplet studies

The process of dynamic behavior was obtained by a system producing vertical vibrations (Jung and Bhushan, 2009a). The system consists of an electrodynamic shaker (Labworks Inc. Model ET-126A/B) connected with a signal generator and power amplifier, a digital camcorder (Sony, DCRSR100, Tokyo, Japan) with an objective lens, and a lamp (Digital Instruments Inc. Model F0-50) for a light source. The specimen was placed on the top of the shaker, and a droplet was gently deposited using a microsyringe. The size of the droplet was the same as that of a droplet for the static contact angle as reported earlier. The vibration frequency was controlled between 0 and 300 Hz at 0.4 mm amplitude for measurement of the resonance frequency of a droplet. For wetting behavior of a droplet on the surface, a frequency of 30 Hz, which was less than the resonance frequency, was chosen, and the vibration amplitude was controlled between 0 and 3 mm. The vibration time applied to the droplet was 1 min for each experiment. All measurements were made in a controlled environment at 22 ± 1 °C and $45 \pm 5\%$ RH (Jung and Bhushan, 2009a).

5.1.5. Microdroplet condensation and evaporation studies using ESEM

A Philips XL30 ESEM equipped with a Peltier cooling stage was used to study smaller droplets (Jung and Bhushan, 2008a). ESEM uses a gaseous secondary electron detector (GSED) for imaging. The ESEM column is equipped with a multistage differential pressure-pumping unit. The pressure in the upper part is about 10^{-6} to 10^{-7} Torr, but a pressure of about 1 to 15 Torr can be maintained in the observation chamber. When the electron beam (primary electrons) ejects secondary electrons from the surface of the sample, the secondary electrons collide with gas molecules in the ESEM chamber, which in turn acts as a cascade amplifier, delivering the secondary electron signal to the positively biased GSED. The positively charged ions are attracted toward the specimen to

neutralize the negative charge produced by the electron beam. Therefore, the ESEM can be used to examine electrically isolated specimens in their natural state. In ESEM, adjusting the pressure of the water vapor in the specimen chamber and the temperature of the cooling stage allows the water to condense on the sample in the chamber. For the measurement of the static and dynamic contact angles on patterned surfaces, video images were recorded. The voltage of the electron beam was 15 kV, and the distance of the specimen from the final aperture was about 8 mm. If the angle of observation is not parallel to the surface, the electron beam is not parallel to the surface but inclined at an angle, this will produce a distortion in the projection of the droplet profile. A mathematical model to calculate the real contact angle from the ESEM images was used to correct the tilting of the surfaces during imaging (Brugnara et al., 2006; Jung and Bhushan, 2008a).

5.1.6. Generation of submicron droplets

In order to generate submicron droplets, we developed an AFM-based technique using a modified nanoscale dispensing (NADIS) probe as shown in **Fig. 25** (Jung and Bhushan, 2008c). NADIS probe was fabricated from modifying a commercially available silicon nitride (Si_3N_4) cantilever (Olympus OMCL-RC800) with lengths of 100 and 200 μm , spring constants of 0.8 and 0.1 N/m, and resonance frequencies of 68.94 and 122.02 kHz, respectively (Swiss Center for Electronics and Microtechnology). The probe consisted of a loading area (30 μm diameter) for the liquid on the upper side of the cantilever. The loading area was produced by removing the material locally in and around the tip with a reflective gold layer using focused ion beam milling. The remaining gold was made hydrophobic using hexadecanethiol (in liquid phase) whereas the bare silicon nitride in the milling area remained hydrophilic. The hydrophilic–hydrophobic transition prevents spreading of the loaded liquid over the entire cantilever.

A droplet of a certain volume V is deposited on the surface. **Figure 26** shows an idealized spherical capped droplet. Based on the thickness of the droplet h and contact diameter d , the contact angle is obtained by the following equation for a simple spherical capped geometry of droplet (Jung and Bhushan, 2008c).

Figure 25. (a) Schematic of modified nanoscale dispensing (NADIS) probe for generation of submicron size droplets. The loaded liquid is limited to the loading area (30 μm diameter circle), (b) scanning electron micrograph of tip in side view and bottom view with different aperture sizes (500 nm and 200 nm) at its apex (Jung and Bhushan, 2008c).

Figure 26. Droplet of liquid in contact with a surface, contact angle θ . The thickness of droplet is h . The contact diameter between droplet and surface is d . The radius of curvature of droplet is r (Jung and Bhushan, 2008c).

$$\theta = \sin^{-1} \left(\frac{3d}{2\left(\frac{3V}{\pi h^2} + h\right)} \right) \quad (23)$$

For calculation of the contact angle of the droplet, we use the following three steps:

- (1) For the measurement of the volume of a droplet deposited on the surface, the change in resonance frequency of the cantilever before and after depositing the droplet on the surface is measured. The resonance frequency of the cantilever is measured by performing a frequency sweep of the voltage driven oscillations by thermal tune method (Cleveland et al., 1993).
- (2) For the measurement of the thickness of a droplet deposited on the surface, the distance between the tip snap-in and the position where the tip is in contact with the surface is measured in the force calibration mode.
- (3) For the measurement of the contact diameter between a droplet and surface, the image of the droplet after evaporation is measured using a Si tip.

For the thickness of a droplet deposited on the surface, the force distance curve was used (Bhushan, 1999, 2002, 2008). The droplet was deposited in the first approach. The

force distance curve was obtained during a second approach to measure the thickness of the droplet (Bhushan and Blackman, 1991; Chen and Bhushan, 2006; Lodge and Bhushan, 2006). The cantilever deflection is plotted on the vertical axis against the Z-position of the piezo scanner in a force distance curve as shown in **Fig. 27**. The measurement starts at a large separation (point A), where there is no deflection of the cantilever. As the piezo moves to the sample, a sudden mechanical instability occurs between point B and point C, and the droplet jumps into contact with the tip and wicks up around the tip to form a meniscus. The cantilever bends downward because of the attractive meniscus force acting on the tip. As the piezo further approaches the surface, the deflection of the cantilever increases while the tip travels the thickness of the droplet and eventually contacts the underlying surface at point D, and the cantilever starts to bend upward. Once the piezo reaches the end of its designated ramp size at point E, it is retracted to its starting position. The tip goes beyond zero deflection and enters the adhesion region. At point F, the elastic force of the cantilever becomes equivalent to the adhesive force, causing the cantilever to snap back to point G. As the tip travels in the liquid, it is deflected as well. The tip deflection occurs in the same direction as the piezo travels for the AFM used in this study. The liquid film thickness (h) is the sum of the travel distance of the piezo (described as h_1 in **Fig. 27**) and the deflection of cantilever (described as h_2 in **Fig. 27**). Though previous studies show that h overestimates the actual liquid film thickness, it still provides a good measurement of the thickness of droplet (Bhushan and Blackman, 1991; Chen and Bhushan, 2006; Lodge and Bhushan, 2006).

The resolution of volume (mass), thickness, and contact diameter was about $1 \times 10^{-4} \mu\text{m}^3$ (0.12 fg), 0.1 nm, and < 1 nm, respectively. The resolution of volume was calculated with the measured data of the shift in the resonance frequency of the cantilever from 122.01 to 122.02 kHz during the evaporation time of 10 minutes. The resolutions of thickness and contact diameter measurements were from the calibration data of the z piezo and x-y piezo by AFM vendor (Veeco), respectively. The accuracy of volume, thickness, and contact diameter measurement was about $\pm 10\%$, 10% and < 1 nm, respectively.

Figure 27. Force calibration plot for a droplet with 1.1 μm contact diameter on Si surface.

The horizontal distance between point C and point D, h , is a measure of droplet thickness on the surface.

5.1.7. Waterfall/jet tests

To investigate durability of the created surfaces in long-term exposure to water and different kinetic energies of water, a setup was constructed to provide a waterfall/jet flow as shown in **Fig. 28** (Jung and Bhushan, 2010b). The water from the laboratory faucet flowed through a pipe. Specimens were fixed on the stage by using a double-sided adhesive tape. Specimens are placed 2 mm below the four holes in the pipe. In order to minimize flow interruption on the specimens, the runoff plate was tilted to 45°.

Waterfall/jet experiments are composed of two different setups. First, water pressure was fixed at 10 kPa, and then specimens were exposed for 24 hours. Next, in order to apply different kinetic energies of the water, the water pressure was controlled between 0 and 45 kPa. The exposure time applied to the specimens was 20 min for each experiment.

During the tests, the change of static contact angle was measured using droplets of about 5 microliters in volume (with radius of a spherical droplet about 1 mm) gently deposited on the substrate using a microsyringe. For contact angle hysteresis, the advancing and receding contact angles were measured at the front and back of the droplet moving along

the tilted surface, respectively. The image of the droplet is obtained by a digital camcorder (Sony, DCRSR100, Tokyo, Japan) with a 10x optical and 120x digital zoom. Images obtained were analyzed using Imagetool® software (University of Texas Health Science Center) for the contact angle.

Figure 28. Schematics of waterfall/jet setup shown in front and side views (Jung and Bhushan, 2010b).

5.1.8. Wear and friction tests

To investigate the durability of structured surfaces, wear tests on the surfaces were performed using a commercial AFM (D3100, Nanoscope IIIa controller, Digital Instruments, Santa Barbara, CA) (Jung and Bhushan, 2010b). With the AFM in contact mode, the surfaces were worn using a 15 μm radius borosilicate ball that was mounted on a triangular Si_3N_4 cantilever with a nominal spring constant of 0.58 N m^{-1} . Wear scars with dimensions of $50 \times 50 \mu\text{m}^2$ were created and scanned for 1 cycle at two different loads of 100 nN and 10 μN . In order to analyze the changes in the morphology of structured surfaces before and after wear tests, surface height maps were obtained in dimensions of $100 \times 100 \mu\text{m}^2$ using a square pyramidal Si(100) tip with a native oxide layer which has a nominal radius of 20 nm on a rectangular Si(100) cantilever with a

spring constant of 3 N m^{-1} and at a natural frequency of 76 kHz in tapping mode.

In order to investigate durability at a high load, macroscale wear and friction tests on the structured surfaces were conducted based on an established procedure of using a ball-on-flat tribometer under reciprocating motion (Jung and Bhushan, 2010b). A sapphire ball with a diameter of 3 mm and surface finish of about 2 nm RMS was fixed on a stationary holder. A normal load of 10 mN was applied, and the frictional forces were measured with semiconductor strain gauges, which were then digitized and collected on a computer. Typical test conditions were: stroke length = 800 μm , average linear speed = 1 mm/s, temperature = $22 \pm 1 \text{ }^\circ\text{C}$, and relative humidity = $45 \pm 5\%$. Wear was characterized by imaging the resulting scar with an optical microscope with a CCD camera (Nikon, Optihot-2) before and after wear tests. The number of cycles to failure was determined by identifying the point where a sudden change in the friction force is observed.

5.2. Micro- and nanopatterned polymers

We studied two types of polymers: poly(methyl methacrylate) (PMMA) and polystyrene (PS) (Jung and Bhushan, 2006). PMMA and PS were chosen because they are widely used in MEMS/NEMS devices. Both hydrophilic and hydrophobic surfaces can be produced by using these two polymers, as PMMA has polar (hydrophilic) groups with high surface energy while PS has electrically neutral and nonpolar(hydrophobic) groups with low surface energy. Furthermore, a PMMA structure can be made hydrophobic by treating it appropriately, for example by coating with a hydrophobic self-assembled monolayer (SAM).

Four types of surface patterns were fabricated from PMMA: a flat film, low aspect ratio asperities (LAR, 1:1 height-to-diameter ratio), high aspect ratio asperities (HAR, 3:1 height-to-diameter ratio), and a replica of the Lotus leaf (the Lotus pattern). Two types of surface patterns were fabricated from PS: a flat film and the Lotus pattern. **Figure 29** shows SEM images of the two types of nanopatterned structures, LAR and HAR, and the one type of micropatterned structure, Lotus pattern, all on a PMMA surface (Burton and Bhushan, 2005; Jung and Bhushan, 2006). Both micro- and

Figure 29. Scanning electron micrographs of the two nanopatterned polymer surfaces (shown using two magnifications to see both the asperity shape and the asperity pattern on the surface) and the micropatterned polymer surface (Lotus pattern, which has only microstructures on the surface) (Burton and Bhushan, 2005; Jung and Bhushan, 2006).

nanopatterned structures were manufactured using soft lithography. For nanopatterned structures, PMMA film was spin-coated on the silicon wafer. A UV cured mold (PUA mold) with nanopatterns of interest was made which enables one to create sub-100-nm patterns with a high aspect ratio (Choi et al., 2004). The mold was placed on the PMMA film, and a slight pressure of $\sim 10 \text{ g/cm}^2$ ($\sim 1 \text{ kPa}$) was applied and annealed at 120°C . Finally, the PUA mold was removed from PMMA film. For micropatterned structures, a polydimethylsiloxane (PDMS) mold was first made by casting PDMS against a Lotus leaf, followed by heating. Then, the mold was placed on the PMMA and PS film to create a positive replica of Lotus leaf. As shown in **Fig. 29**, it can be seen that only

microstructures exist on the surface of Lotus pattern (Jung and Bhushan, 2006).

Since PMMA by itself is hydrophilic, in order to obtain a hydrophobic sample, a self-assembled monolayer (SAM) of perfluorodecyltriethoxysilane (PFDTES) was deposited on the sample surfaces using a vapor phase deposition technique. PFDTES was chosen because of its hydrophobic nature. The deposition conditions for PFDTES were 100 °C temperature, 400 Torr pressure, 20 min deposition time, and 20 min annealing time. The polymer surface was exposed to an oxygen plasma treatment (40 W, O₂ 187 Torr, 10 s) prior to coating (Bhushan et al., 2006). The oxygen plasma treatment is necessary to oxidize any organic contaminants on the polymer surface and to also alter the surface chemistry to allow for enhanced bonding between the SAM and the polymer surface.

5.2.1. Contact angle measurements

We measured the static contact angle of water with the micro- and nanopatterned PMMA and PS structures; see **Fig. 30** (Jung and Bhushan, 2006). Since the Wenzel roughness factor is the parameter that often determines wetting behavior, the roughness factor was calculated, and it is presented in **Table 7** for various samples. The data show that the contact angle of the hydrophilic materials decreases with an increase in the roughness factor, as predicted by the Wenzel model. When the polymers were coated with PFDTES, the film surface became hydrophobic. **Figure 30** also shows the contact angle for various PMMA samples coated with PFDTES. For a hydrophobic surface, the standard Wenzel model predicts an increase of contact angle with roughness factor, which is what happens in the case of patterned samples. The calculated values of the contact angle for various micro- and nanopatterned samples based on the contact angle of the smooth film and Wenzel equation are also presented. The measured contact angle values for the Lotus pattern were comparable with the calculated values, whereas for the LAR and HAR patterns they are higher. It suggests that nanopatterns benefit from air pocket formation. For the PS material, the contact angle of the Lotus pattern also increased with increased roughness factor.

Figure 30. Contact angles for various micro- and nanopatterned surfaces on PMMA and PS polymers and calculated values using Wenzel equation (Jung and Bhushan, 2006).

	LAR	HAR	Lotus
R_f	2.1	5.6	3.2

Table 7. Roughness factor for micro- and nanopatterned polymers (Jung and Bhushan, 2006).

5.2.2. Effect of submicron droplet

Wetting phenomena have been well studied and understood at the macroscale; however, micro- and nanoscale wetting mechanisms require further investigation. The actual contact angle, under which the liquid-vapor interface comes in contact with the solid surface at the micro- and nanoscale, is known to decrease with the droplet size (Pompe and Herminghaus, 2000; Checco et al., 2003). We measured the contact angle of micro- and nanodroplets on various surfaces based on the contact diameter, thickness, and volume of droplets measured using the atomic force microscopy-based technique (Jung and Bhushan, 2008c). The contact angle for different droplet sizes on various surfaces is summarized in **Fig. 31**. The data for the microdroplets with 2.4 – 8.1 μm diameter and nanodroplets with 0.22 – 1.1 μm diameter were compared with conventional contact angle measurements obtained with a droplet with 2.1 mm diameter (5 μL volume). The measured values of micro- and nanodroplets using an AFM were found to be lower than those of the macrodroplet (Pompe and Herminghaus, 2000; Checco et al., 2003). There are several reasons for the scale dependence, such as the effect of contact line tension of a three-phase system (solid-liquid-vapor), which is the excess free energy of a solid-liquid-vapor system per unit length of the contact line (Pompe and Herminghaus, 2000; Checco et al., 2003; Quere, 2004; Nosonovsky and Bhushan, 2007d). Another reason can be surface heterogeneity (Checco et al., 2003). For a thin fluid film present on a surface, disjoining pressure of a film is repulsive, analogous to the repulsive van der Waals force across a film, and it causes a film to spread on surfaces. It decreases with the liquid layer thickness (Israelachvili, 1992). This pressure may lead to a smaller contact angle at the nanoscale.

5.2.3. Scale dependence on adhesive force

We found that scale-dependence of adhesion and friction forces are important for this study because the tip/surface interface area changes with size (Jung and Bhushan, 2006). The meniscus force will change due to either changing tip radius, the hydrophobicity of the sample, or the number of contacting and near-contacting points. **Figure 32** shows the dependence of the tip radius and hydrophobicity on the adhesive

Contact angle for different droplet sizes on various surfaces

Figure 31. Contact angle measurements for different droplet sizes on various surfaces (Jung and Bhushan, 2008c).

PMMA polymers with different surface roughness patterns (22 °C, 50% RH)

Figure 32. Scale dependent adhesive force for various micro- and nanopatterned surfaces measured using AFM tips of various radii (Jung and Bhushan, 2006).

force for PMMA and PFDTES coated on PMMA (Jung and Bhushan, 2006). When the radius of the tip is changed, the contact angle of the sample is changed, and asperities are added to the sample surface, the adhesive force will change due to the change in the meniscus force and the real area of contact.

The two plots in **Fig 32** show the adhesive force on a linear scale for the different surfaces with varying tip radius. The left bar chart in **Fig 32** is for hydrophilic PMMA film, Lotus pattern, LAR, and HAR, and shows the effect of tip radius and hydrophobicity on adhesive force. For increasing radius, the adhesive force increases for each material. With a larger radius, the real area of contact and the meniscus contribution increase, resulting in increased adhesion. The right bar chart in **Fig 32** shows the results for PFDTES coated on each material. These samples show the same trends as the film samples, but the increase in adhesion is not as dramatic. The hydrophobicity of PFDTES on material reduces meniscus forces, which in turn reduces adhesion from the surface. The dominant mechanism for the hydrophobic material is real area of contact and not meniscus force, whereas with hydrophilic material there is a combination of real area of contact and meniscus forces (Jung and Bhushan, 2006).

5.3. Micropatterned Si surfaces

Micropatterned surfaces produced from single-crystal silicon (Si) by photolithography and coated with a self-assembled monolayer (SAM) were used in the study (Jung and Bhushan, 2007, 2008a,b). Silicon has traditionally been the most commonly used structural material for micro/nanocomponents. A Si surface can be made hydrophobic by coating it with a SAM. One of the purposes of this investigation was to study the transition from the Cassie-Baxter to Wenzel regime by changing the distance between the pillars. To create micropatterned Si, two series of nine samples each were fabricated using photolithography (Barbieri et al., 2007). Series 1 had 5- μm diameter and 10- μm height flat-top, cylindrical pillars with different pitch values (7, 7.5, 10, 12.5, 25, 37.5, 45, 60, and 75) μm , and series 2 had 14- μm diameter and 30- μm height flat-top, cylindrical pillars with different pitch values (21, 23, 26, 35, 70, 105, 126, 168, and 210) μm . The pitch is the spacing between the centers of two adjacent pillars. The SAM of 1, 1, -2, 2, -tetrahydroperfluorodecyltrichlorosilane (PF_3) was deposited on the Si sample

surfaces using a vapor phase deposition technique (Barbieri et al., 2007). PF_3 was chosen because of the hydrophobic nature of the surface. The thickness and rms roughness of the SAM of PF_3 were 1.8 nm and 0.14 nm, respectively (Kasai et al., 2005).

An optical profiler was used to measure the surface topography of the micropatterned surfaces (Bhushan and Jung, 2007, 2008; Jung and Bhushan, 2008a,b). One sample each from the two series was chosen to characterize the surfaces. Two different surface height maps can be seen for the micropatterned Si in **Fig. 33**. In each case, a 3-D map and a flat map along with a 2-D profile in a given location of the flat 3-D map are shown. A scan size of $100\ \mu\text{m} \times 90\ \mu\text{m}$ was used to obtain a sufficient amount of pillars to characterize the surface but also to maintain enough resolution to get an accurate measurement.

The images found with the optical profiler show the flat-top, cylindrical pillars on the Si surface are distributed on the entire surface in a square grid with different pitch values. Samples in series 1 had the same values of Wenzel roughness factors ($R_f = 1 + \pi DH/P^2$) as in series 2 in the consecutive order, so that the Cassie-Baxter and Wenzel theoretical models predict exactly the same series of contact angle values for both series of nine samples.

Let us consider the geometry of flat-top, cylindrical pillars of diameter D , height H , and pitch P , distributed in a regular square array as shown in **Fig. 33**. For the special case of a droplet size much larger than P (of interest in this study), a droplet contacts the flat-top of the pillars forming the composite interface, and the cavities are filled with air.

For this case, $f_{LA} = 1 - \frac{\pi D^2}{4P^2} = 1 - f_{SL}$. Further assume that the flat tops are smooth with $R_f = 1$. The contact angles for the Wenzel and Cassie-Baxter regimes are given by Eqs. 6 and 9 (Bhushan and Jung, 2007).

$$\text{Wenzel:} \quad \cos \theta = \left(1 + \frac{\pi DH}{P^2} \right) \cos \theta_0 \quad (24)$$

$$\text{Cassie-Baxter:} \quad \cos \theta = \frac{\pi D^2}{4P^2} (\cos \theta_0 + 1) - 1 \quad (25)$$

Figure 33. Surface height maps and 2-D profiles of the micropatterned surfaces using an optical profiler (Bhushan and Jung, 2007).

Geometrical parameters of the flat-top, cylindrical pillars in series 1 and 2 are used for calculating the contact angle for the above-mentioned two cases. **Figure 34** shows the plot of the predicted values of the contact angle as a function of pitch between the pillars for the two cases. The Wenzel and Cassie-Baxter equations present two possible equilibrium states for a water droplet on the surface. This indicates that there is a critical pitch below which the composite interface dominates and above which the homogeneous interface dominates the wetting behavior. Therefore, one needs to find the critical point that can be used to design superhydrophobic surfaces. Furthermore, even in cases where the liquid droplet does not contact the bottom of the cavities, the water droplet can be in a metastable state and can become unstable, with the transition from the Cassie-Baxter to Wenzel regime occurring if the pitch is large.

Figure 34. Calculated static contact angle as a function of geometric parameters for a given value of θ_0 using the Wenzel and Cassie-Baxter equations for two series of the micropatterned surfaces with different pitch values (Bhushan and Jung, 2007).

5.3.1. Cassie-Baxter and Wenzel transition criteria

A stable composite interface is essential for the successful design of superhydrophobic surfaces. However, the composite interface is fragile, and it may transform into the homogeneous interface. What triggers the transition between the regimes remains a subject of argument, although a number of explanations have been suggested. Nosonovsky and Bhushan (2007b) have studied destabilizing factors for the composite interface and found that a convex surface (with bumps) leads to a stable interface and high contact angle. Also, they have suggested the effects of a droplet's weight and curvature among the factors which affect the transition.

We investigated the effect of droplet curvature on the Cassie-Baxter and Wenzel

regime transition (Bhushan and Jung, 2007, 2008; Jung and Bhushan, 2007, 2008a,b). First, they considered a small water droplet suspended on a superhydrophobic surface consisting of a regular array of circular pillars with diameter D , height H , and pitch P as shown in **Fig. 35**. The local deformation for small droplets is governed by surface effects rather than gravity. The curvature of a droplet is governed by the Laplace equation, which relates the pressure inside the droplet to its curvature (Adamson, 1990). Therefore, the curvature is the same at the top and at the bottom of the droplet (Nosonovsky and Bhushan, 2007d). For the micropatterned surface considered here, the maximum droop of the droplet occurs in the center of the square formed by the four pillars as shown in **Fig. 35(a)**. Therefore, the maximum droop of the droplet (δ) in the recessed region can be found in the middle of two pillars which are diagonally across as shown in **Fig. 35(b)**, which is $(\sqrt{2}P - D)^2 / (8R)$. If the droop is greater than the depth of the cavity, then the droplet will just contact the bottom of the cavities between pillars. If it is much greater, transition from the Cassie-Baxter to Wenzel regime occurs.

$$(\sqrt{2}P - D)^2 / R \geq H \quad (26)$$

To investigate the dynamic effect of a bouncing water droplet on the Cassie-Baxter and Wenzel regime transition, we considered a water droplet hitting a superhydrophobic surface as shown in **Fig. 35** (Jung and Bhushan, 2008b). As the droplet hits the surface at velocity V , a liquid-air interface below the droplet is formed when the dynamic pressure is less than the Laplace pressure. The Laplace pressure can be written as

$$p_L = 2\gamma / R = 16\gamma\delta / (\sqrt{2}P - D)^2 \quad (27)$$

where γ is the surface tension of the liquid-air interface, and the dynamic pressure of the droplet is equal to

$$p_d = \frac{1}{2}\rho V^2 \quad (28)$$

where ρ is the mass density of the liquid droplet. If the maximum droop of the droplet (δ) is larger than the height of pillar (H), the droplet contacts the bottom of the cavities between pillars. Determination of the critical velocity at which the droplet touches the

bottom is obtained by equating the Laplace pressure to the dynamic pressure. To develop a composite interface, velocity should be smaller than the critical velocity given as

$$V < \sqrt{\frac{32\gamma H}{\rho(\sqrt{2}P - D)^2}} \quad (29)$$

Furthermore, in the case of large distances between the pillars, the liquid-air interface can easily be destabilized due to dynamic effects. This leads to the formation of the homogeneous solid-liquid interface (Nosonovsky and Bhushan, 2007b).

Figure 35. A liquid droplet suspended on a superhydrophobic surface consisting of a regular array of circular pillars. (a) Plan view. The maximum droop of droplet occurs in the center of square formed by four pillars. (b) Side view in section A-A. The maximum droop of droplet (δ) can be found in the middle of two pillars which are diagonally across (Jung and Bhushan, 2007).

Nosonovsky and Bhushan (2008g) used the energy barrier approach to study the Cassie-Baxter and Wenzel transition. The energy barrier is given by the product of height of the pillars, H , pillar perimeter, πD , pillar density, $1/P^2$, and the area, A_0 , required to initiate the transition, and the corresponding change in the surface energy

$$\Delta E = A_0 \frac{\pi H D}{P^2} (\gamma_{SL} - \gamma_{SA}) = -A_0 \frac{\pi H D}{P^2} \gamma_{LA} \cos \theta_0 \quad (30)$$

where, A_0 is $\pi(R \sin \theta)^2$.

For a short pitch, the net energy of the Cassie-Baxter state is lower than that of the Wenzel state, whereas for larger pitch values, the energy of the Wenzel state is lower (**Fig.15(c)**). However, due to the energy barriers, a metastable Cassie-Baxter state with a higher energy than the Wenzel state may be found.

The energy barrier of the Cassie-Baxter and Wenzel transition can be estimated as the kinetic energy of the droplet. The kinetic energy of a droplet of radius R_0 , mass m , and density ρ with the velocity V is given by

$$E_{kin} = \frac{(4/3)\pi \rho R^3 V^2}{2} \quad (31)$$

5.3.2. Contact angle measurements

In order to study the effect of pitch value on the transition from Cassie-Baxter to Wenzel regime, the static contact angles were measured on the micropatterned Si coated with PF_3 , and the data are plotted as a function of pitch between the pillars in **Fig. 36(a)** (Bhushan and Jung, 2007, 2008; Jung and Bhushan, 2007, 2008a,b). A dotted line represents the transition criteria range obtained using Eq. 26. The flat Si coated with PF_3 showed a static contact angle of 109° . The contact angle of selected micropatterned surfaces is much higher than that of the flat surfaces. It first increases with an increase in the pitch values, then drops rapidly to a value slightly higher than that of the flat surfaces. In the first portion, it jumps to a high value of 152° corresponding to a superhydrophobic surface and continues to increase to 170° at a pitch of $45 \mu\text{m}$ in series 1 and $126 \mu\text{m}$ in series 2 because open air space increases with an increase in pitch, responsible for

Figure 36. (a) Static contact angle (a dotted line represents the transition criteria range obtained using Eq. (26) and (b) contact angle hysteresis and tilt angle as a function of geometric parameters for two series of the micropatterned surfaces with different pitch values for a droplet with 1 mm in radius (5 μ L volume). Data at zero pitch correspond to a flat sample (Bhushan and Jung, 2007; Jung and Bhushan, 2007).

Figure 36 Continued

propensity of air pocket formation. The sudden drop at about a pitch value of 50 μm in series 1 and 150 μm in series 2 corresponds to the transition from the Cassie-Baxter to the Wenzel regime. In series 1, the value predicted from the curvature transition criteria (Eq. 26) is a little higher than the experimental observations. However, in series 2, there is a good agreement between the experimental data and the values theoretically predicted for the Cassie-Baxter and Wenzel transition (Jung and Bhushan, 2007, 2008a,b).

Figure 36(b) shows contact angle hysteresis and tilt angle as a function of pitch between the pillars (Bhushan and Jung, 2007, 2008). Both angles are comparable. The flat Si coated with PF_3 showed a contact angle hysteresis of 34° and tilt angle of 37° . The angle first increases with an increase of pitch value, which has to do with pinning of the droplet at the sharp edges of the micropillars. **Figure 37** shows droplets on micropatterned Si with 5- μm diameter and 10- μm height pillars with different pitch values. The asymmetrical shape of the droplet signifies pinning. The pinning on the micropatterned surfaces can be observed as compared to the flat surface. The micropatterned surface with low pitch (7 μm) has more pinning than the micropatterned surface with high pitch (37.5 μm), because the micropatterned surface with low pitch has more sharp edges in contact with a droplet. As the pitch increases, there is a higher propensity of air pocket formation and fewer numbers of sharp edges per unit area, which is responsible for sudden drop in the angle. The lowest contact angle hysteresis and tilt angle are 5° and 3° , respectively, which were observed on the micropatterned Si with 45 μm of series 1 and 126 μm of series 2. Above a pitch value of 50 μm in series 1 and 150 μm in series 2, the angle increases very rapidly because of transition to the Wenzel regime.

These results suggest that air pocket formation and the reduction of pinning in the micropatterned surface play an important role for a surface with both low contact angle hysteresis and tilt angle (Bhushan and Jung, 2007, 2008). Hence, to create superhydrophobic surfaces, it is important that they are able to form a stable composite interface with air pockets between solid and liquid.

Patterned surfaces with 5- μm diameter and
10- μm height pillars with different pitch values

0 μm pitch

7 μm pitch

37.5 μm pitch

75 μm pitch

Figure 37. Optical micrographs of droplets on the inclined micropatterned surfaces with different pitch values. The images were taken when the droplet started to move down. Data at zero pitch correspond to a flat sample (Bhushan and Jung, 2007).

5.3.3. Observation of transition during the droplet evaporation

In order to study the effect of droplet size on the transition from a composite state to a wetted state, we performed droplet evaporation experiments to observe the Cassie-Baxter and Wenzel transition on two different micropatterned Si surfaces coated with PF₃ (Jung and Bhushan, 2007, 2008a). The series of four images in **Fig. 38** show the successive photos of a droplet evaporating on the two micropatterned surfaces. The initial radius of the droplet was about 700 μm , and the time interval between first two photos was 180 s and between the latter was 60 s. In the first three photos, the droplet is shown in a Cassie-Baxter state, and its size gradually decreases with time. However, as the radius of the droplet reached 360 μm on the surface with 5- μm diameter, 10- μm height, and 37.5- μm pitch pillars, and 423 μm on the surface with 14- μm diameter, 30- μm height, and 105- μm pitch pillars, the transition from the Cassie-Baxter to Wenzel regime occurred, as indicated by the arrow. The light passes below the first droplet, indicating that air pockets exist, so that the droplet is in the Cassie-Baxter state. However, an air pocket is not visible below the last droplet, so it is in the Wenzel state. This could result from an impalement of the droplet in the micropatterned surface, characterized by a smaller contact angle.

To find the contact angle before and after the transition, the values of the contact angle are plotted against the theoretically predicted value, based on the Wenzel (calculated using Eq. 6) and Cassie-Baxter (calculated using Eq. 9) models. **Figure 39** shows the static contact angle as a function of geometric parameters for the experimental contact angles before (circle) and after (triangle) the transition compared to the Wenzel and Cassie-Baxter equations (solid lines) with a given value of θ_0 for two series of micropatterned Si with different pitch values coated with PF₃ (Jung and Bhushan, 2008a). The fit is good between the experimental data and the theoretically predicted values for the contact angles before and after transition.

To prove the validity of the transition criteria in terms of droplet size, the critical radius of a droplet deposited on the micropatterned Si with different pitch values coated with PF₃ is measured during the evaporation experiment (Jung and Bhushan, 2007, 2008a). **Figure 40** shows the radius of a droplet as a function of geometric parameters for

Figure 38. Evaporation of a droplet on two different micropatterned surfaces. The initial radius of the droplet is about 700 μm , and the time interval between first two photos was 180 s and between the latter was 60 s. As the radius of droplet reaches 360 μm on the surface with 5- μm diameter, 10- μm height, and 37.5- μm pitch pillars, and 420 μm on the surface with 14- μm diameter, 30- μm height, and 105- μm pitch pillars, the transition from the Cassie-Baxter regime to Wenzel regime occurs, as indicated by the arrow. Before the transition, air pocket is clearly visible at the bottom area of the droplet, but after the transition, air pocket is not found at the bottom area of the droplet (Jung and Bhushan, 2008a).

Figure 39. Receding contact angle as a function of geometric parameters before (circle) and after (triangle) transition compared with predicted static contact angle values obtained using the Wenzel and Cassie-Baxter equations (solid lines) with a given value of θ_0 for two series of the micropatterned surfaces with different pitch values (Jung and Bhushan, 2008a).

Figure 40. Radius of droplet as a function of geometric parameters for the experimental results (circle) compared with the transition criteria from the Cassie-Baxter regime to Wenzel regime (solid lines) for two series of the micropatterned surfaces with different pitch values (Jung and Bhushan, 2008a).

Dust trace after droplet evaporation
5- μm diameter, 10- μm height, and 37.5- μm pitch pillars

5- μm diameter, 10- μm height, and 7- μm pitch pillars

Figure 41. Dust trace remained after droplet evaporation for the micropatterned surface.

In the top image, the transition occurred at 360 μm radius of droplet, and in the bottom image, the transition occurred at about 20 μm radius of droplet during the process of droplet evaporation. The footprint size is about 450 and 25 μm for the top and bottom images, respectively (Jung and Bhushan, 2008a).

the experimental results (circle) compared with the transition criterion (Eq. 26) from the Cassie-Baxter regime to Wenzel regime (solid lines) for two series of micropatterned Si with different pitch values coated with PF₃. It is found that the critical radius of impalement is in good quantitative agreement with our predictions. The critical radius of the droplet increases linearly with the geometric parameter (pitch). For the surface with small pitch, the critical radius of droplet can become quite small.

To verify the transition, we used another approach using dust mixed in water (Jung and Bhushan, 2007, 2008a). **Figure 41** presents the dust trace remaining after droplet with 1 mm radius (5 μ L volume) evaporation on the two micropatterned Si surfaces. As shown in the top image, after the transition from the Cassie-Baxter regime to Wenzel regime, the dust particles remained not only at the top of the pillars but also at the bottom with a footprint size of about 450 μ m. However, as shown in the bottom image, the dust particles remained on only a few pillars with a footprint size of about 25 μ m until the end of the evaporation process. From **Fig. 40**, it is observed that the transition occurs at about 300 μ m radius of droplet on the 5- μ m diameter and 10- μ m height pillars with 37.5- μ m pitch, but the transition does not occur on the patterned Si surface with pitch of less than about 5 μ m. These experimental observations are consistent with model predictions. In the literature, it has been shown that on superhydrophobic natural Lotus, the droplet remains in the Cassie-Baxter regime during the evaporation process (Zhang et al., 2006). This indicates that the distance between the pillars should be minimized enough to improve the ability of the droplet to resist sinking.

5.3.4. Scaling of the Cassie-Baxter and Wenzel transition for different series

Nosonovsky and Bhushan (2007a,c,d, 2008b,d) studied the data for the Cassie-Baxter and Wenzel transition with the two series of surfaces using the non-dimensional spacing factor

$$S_f = \frac{D}{P} \quad (34)$$

The values of the droplet radius at which the transition occurs during the evaporation plotted against the spacing factor scale well for the two series of the

experimental results, yielding virtually the same straight line. Thus the two series of micropatterned surfaces scale well with each other, and the transition occurs at the same value of the spacing factor multiplied by the droplet radius (**Fig. 42(a)**). The physical mechanism leading to this observation remains to be determined, however, it is noted that this mechanism is different from the one suggested by Eq. 26. The observation suggests that the transition is a linear “1D” phenomenon and that neither droplet droop (that would involve P^2/H) nor droplet weight (that would involve R^3) are responsible for the transition, but rather linear geometric relations are involved. Note that the experimental values approximately correspond to the values of the ratio $RD/P = 50 \mu\text{m}$, or the total area of the pillar tops under the droplet $(\pi D^2/4)\pi R^2/P^2 = 6200 \mu\text{m}^2$.

5.3.5. Contact angle hysteresis and wetting/dewetting asymmetry

Contact angle hysteresis can be viewed as a result of two factors that act simultaneously. First, the changing contact area affects the contact angle hysteresis, since a certain value of contact angle hysteresis is inherent for even a nominally flat surface. Decreasing the contact area by increasing the pitch between the pillars leads to a proportional decrease of the contact angle hysteresis. This effect is clearly proportional to the contact area between the solid surface and the liquid droplet. Second, the edges of the pillar tops prevent the motion of the triple line. This roughness effect is proportional to the contact line density, and its contribution was, in the experiment, comparable with the contact area effect. Interestingly, the effect of the edges is much more significant for the advancing than for the receding contact angle.

Nosonovsky and Bhushan (2007a,c,d, 2008b,d) studied the wetting of two series of micropatterned Si surfaces with different pitch values coated with PF_3 based on the spacing factor (Eq. 34). They found that the contact angle hysteresis involves two terms (**Fig. 42(b)**): the term $S_f^2 (\pi/4)(\cos\theta_{\text{adv}0} - \cos\theta_{\text{rec}0})$ corresponding to the adhesion hysteresis (which is found even at a nominally flat surface and is a result of molecular-scale imperfectness), and the term $H_r \propto D/P^2$ corresponding to microscale roughness and proportional to the edge line density. Thus the contact angle hysteresis is given,

Figure 42. (a) Droplet radius, R , for the Cassie-Baxter and Wenzel transition as a function of $P/D = 1/S_f$. It is observed that the transition takes place at a constant value of $RD/P \sim 50 \mu\text{m}$ (dashed line). This shows that the transition is a linear phenomenon. (b) Contact angle hysteresis as a function of S_f for the 1st (squares) and 2nd (diamonds) series of the experiments compared with the theoretically predicted values of $\cos\theta_{\text{adv}} - \cos\theta_{\text{rec}} = (D/P)^2(\pi/4)(\cos\theta_{\text{adv}0} - \cos\theta_{\text{rec}0}) + c(D/P)^2$, where c is a proportionality constant. It is observed that when only the adhesion hysteresis/interface energy term is considered ($c = 0$), the theoretical values are underestimated by about a half, whereas $c = 0.5$ provides a good fit. Therefore, the contribution of the adhesion hysteresis is of the same order of magnitude as the contribution kinetic effects (Nosonovsky and Bhushan, 2007c).

based on Eq. 18 and 34, by using $R_f = 1 + \frac{\pi DH}{P^2}$ and $f_{LA} = 1 - \frac{\pi D^2}{4P^2} = 1 - f_{SL}$ (Bhushan et al., 2007, Nosonovsky and Bhushan, 2007b)

$$\cos \theta_{adv} - \cos \theta_{rec} = \frac{\pi}{4} S_f^2 (\cos \theta_{adv0} - \cos \theta_{rec0}) + H_r \quad (35)$$

Besides the contact angle hysteresis, the asymmetry of the Wenzel and Cassie-Baxter states is the result of the wetting/dewetting asymmetry. While the fragile metastable Cassie-Baxter state is often observed, as well as its transition to the Wenzel state, the opposite transition never happens. Using Eqs. 24 and 25, the contact angle with micropatterned surfaces is given by (Bhushan et al., 2007, Nosonovsky and Bhushan, 2007b)

$$\cos \theta = (1 + 2\pi S_f^2) \cos \theta_0 \quad (\text{Wenzel state}) \quad (36)$$

$$\cos \theta = \frac{\pi}{4} S_f^2 (\cos \theta_0 + 1) - 1 \quad (\text{Cassie-Baxter state}) \quad (37)$$

For a perfect macroscale system, the transition between the Wenzel and Cassie-Baxter states should occur only at the intersection of the two regimes (the point at which the contact angle and net energies of the two regimes are equal, corresponding to $S_f=0.51$). It is observed, however, that the transition from the metastable Cassie-Baxter to stable Wenzel occurs at much lower values of the spacing factor $0.083 < S_f < 0.111$. As shown in **Fig. 43(a)**, the stable Wenzel state (i) can transform into the stable Cassie-Baxter state with increasing S_f (ii). The metastable Cassie-Baxter state (iii) can abruptly transform (iv) into the stable Wenzel state (i). The transition point (i-ii) corresponds to equal free energies in the Wenzel and Cassie-Baxter states. Whereas the transition (iv) corresponds to the Wenzel energy much lower than the Cassie-Baxter energy and thus involves significant energy dissipation and is irreversible (Nosonovsky and Bhushan, 2007c). The solid and dashed straight lines correspond to the values of the contact angle, calculated from Eqs. 36-37 using the contact angle for a nominally flat surface, $\theta_0=109^\circ$. The two series of the experimental data are shown with squares and diamonds.

Figure 43(b) shows the values of the advancing contact angle plotted against the spacing factor (Eq. 34). The solid and dashed straight lines correspond to the values of

the contact angle for the Wenzel and Cassie-Baxter states, calculated from Eqs. 36-37 using the advancing contact angle for a nominally flat surface, $\theta_{adv0}=116^\circ$ (Nosonovsky and Bhushan, 2007c). It is observed that the calculated values underestimate the advancing contact angle, especially for big S_f (small distance between the pillars or pitch P). This is understandable, because the calculation takes into account only the effect of the contact area and ignores the effect of roughness and edge line density (it corresponds to $H_r = 0$ in Eq. 35), while this effect is more pronounced for high pillar density (big S_f). In a similar manner, the contact angle is underestimated for the Wenzel state, since the pillars constitute a barrier for the advancing droplet.

Figure 43(c) shows the values of the contact angle after the transition took place (dimmed blue squares and diamonds), as it was observed during evaporation (Nosonovsky and Bhushan, 2007c). For both series, the values almost coincide. For comparison, the values of the receding contact angle measured for millimeter-sized water droplets are also shown (squares and diamonds), since evaporation constitutes removing liquid, and thus the contact angle during evaporation should be compared with the receding contact angle. The solid and dashed straight lines correspond to the values of the contact angle, calculated from Eqs. 36-37 using the receding contact angle for a nominally flat surface, $\theta_{rec0} = 82^\circ$. **Figure 43(c)** demonstrates a good agreement between the experimental data and Eqs. 36-37.

In the analysis of the evaporation data of micropatterned surfaces, Nosonovsky and Bhushan (2008b) found several effects specific for the multiscale character of this process. First, they discussed the applicability of the Wenzel and Cassie-Baxter equations for average surface roughness and heterogeneity. These equations relate the local contact angle with the apparent contact angle of a rough/heterogeneous surface. However, it is not obvious what should be the size of roughness/heterogeneity averaging, since the triple line at which the contact angle is defined has two very different length scales: its width is of molecular size scale while its length is on the order of the size of the droplet (that is, microns or millimeters). They presented an argument that in order for the averaging to be valid, the roughness details should be small compared to the size of the droplet (and not the molecular size). They showed that while for uniform roughness/heterogeneity the

Figure 43. Theoretical (solid and dashed) and experimental (squares for the 1st series, diamonds for the 2nd series) (a) contact angle as a function of the spacing factor, (b) advancing contact angle, and (c) receding contact angle and values of the contact angle observed after the transition during evaporation (blue) (Nosonovsky and Bhushan, 2007c).

Wenzel and Cassie-Baxter equations can be applied, for a more complicated case of non-uniform heterogeneity, the generalized equations should be used. The proposed generalized Cassie-Baxter and Wenzel equations are consistent with a broad range of available experimental data. The generalized equations are valid both in the cases when the classical Wenzel and Cassie-Baxter equations can be applied as well as in the cases when the latter fail.

The macroscale contact angle hysteresis and Cassie-Baxter and Wenzel transition cannot be determined from the macroscale equations and are governed by micro- and nanoscale effects, so wetting is a multiscale phenomenon (Nosonovsky and Bhushan, 2007a,c,d, 2008b,d). The kinetic effects associated with contact angle hysteresis should be studied at the microscale, whereas the effects of adhesion hysteresis and the Cassie-Baxter and Wenzel transition involve processes at the nanoscale. Their theoretical arguments are supported by the experimental data on micropatterned surfaces. The experimental study of the contact angle hysteresis demonstrates that two different processes are involved: the changing solid-liquid area of contact and pinning of the triple line. The latter effect is more significant for the advancing than for the receding contact angle. The transition between wetting states was observed for evaporating microdroplets, and droplet radius scales well with the geometric parameters of the micropattern.

5.3.6. Observation of transition during the bouncing droplet

We performed bouncing droplet experiments to observe how impact velocity influences the Cassie-Baxter and Wenzel transition during the droplet hitting the surface on two different micropatterned Si surfaces with PF_3 (Jung and Bhushan, 2008b). **Figure 44** shows snapshots of a droplet with 1 mm radius hitting the surfaces. The impact velocity was obtained just prior to the droplet hitting the surface. As shown in images in the first row for the two sets of surfaces, the droplet hitting the surface under an impact velocity of 0.44 m/s first deformed and then retracted, and bounced off the surface. Finally, the droplet sat on the surface and had a high contact angle, which suggests the formation of a solid-air-liquid interface. Next, they repeated the impact experiment by increasing the impact velocity. The bounce off does not occur, and the wetting of the surface (and possibly pinning of droplet) occurred at an impact velocity of 0.88 m/s and

Dynamic effects of a droplet on micropatterned surfaces

5- μm diameter, 10- μm height, and 10- μm pitch pillars

Impact velocity = 0.44 m/s

Impact velocity = 0.88 m/s

14- μm diameter, 30- μm height, and 26- μm pitch pillars

Impact velocity = 0.44 m/s

Impact velocity = 0.76 m/s

Figure 44. Snapshots of a droplet with 1 mm radius hitting on two different micropatterned surfaces. The impact velocity was obtained just prior to the droplet hitting the surface. The pinning of droplet on the surface with 5- μm diameter, 10- μm height and 10- μm pitch pillars, and on the surface with 14- μm diameter, 30- μm height and 26- μm pitch pillars occurred at impact velocity of 0.88 m/s and 0.76 m/s, respectively (Jung and Bhushan, 2008b).

0.76 m/s, respectively, referred to as the critical velocity (described earlier). The second row of the two sets of images shows the images of the droplet at the critical velocity. After the droplet hit the surface, it wetted the surface (possibly the droplet was also pinned) after the deformation of the droplet. This is because air pockets do not exist below the droplet as a result of droplet impalement by the pillars, characterized by a smaller contact angle. These observations indicate the transition from a Cassie-Baxter to a Wenzel regime.

To identify whether one is in a Wenzel regime or a Cassie-Baxter regime, the contact angle data in the static condition and after bounce off were plotted (Jung and Bhushan, 2008b). **Figure 45** shows the measured static contact angle as a function of geometric parameters for the droplet with 1 mm radius gently deposited on the surface (circles) and for the droplet with 1 mm radius after hitting the surface at 0.44 m/s (triangles). The data are compared with predicted static contact angle values obtained using the Wenzel and the Cassie-Baxter equations (solid lines) with a given value of θ_0 (109°) for a smooth surface for two series of the micropatterned surfaces. In the case of the droplet gently deposited on the surface, as the pitch increases up to $45\text{ }\mu\text{m}$ of series 1 and $126\text{ }\mu\text{m}$ of series 2, the static contact angle first increases gradually from 152° to 170° . Then, the contact angle starts decreasing sharply. The increase in the contact angle occurs because of an increase in the roughness factor and the formation of composite surface (Bhushan and Jung, 2007). The decrease in contact angle at pitch values higher than $60\text{ }\mu\text{m}$ for series 1 and $168\text{ }\mu\text{m}$ for series 2 occurs due to the transition from composite interface to solid-liquid interface. In the case of the droplet hitting the surface at 0.44 m/s, it is shown that the liquid-air interface can easily be destabilized due to dynamic impact on the surface with a pitch value higher than $12.5\text{ }\mu\text{m}$ for series 1 and $70\text{ }\mu\text{m}$ for series 2, although the droplet is in the Cassie-Baxter regime when it is gently deposited on the surface. The static contact angle of the droplet after hitting at 0.44 m/s is lower than that of the droplet gently deposited. It can be interpreted that after hitting, the droplet contacts the bottom of the cavities between pillars and pushes out the entrapped air under the droplet, resulting in an abrupt increase of the solid-liquid surface area by dynamic impact. It will be shown in the following paragraph that the critical velocity at

which wetting occurs for series 1 and series 2 samples is equal to about 0.44 m/s at pitch values larger than 12.5 μm and 70 μm respectively. Thus, wetting at the velocity used here is expected.

Figure 45. Measured static contact angle as a function of geometric parameters for the droplet with 1 mm radius gently deposited on the surface (circles) and for the droplet with 1 mm radius after hitting the surface at 0.44 m/s (triangles). The data are compared with predicted static contact angle values obtained using Wenzel and Cassie-Baxter equations (solid lines) with a given value of θ_0 (109°) for a smooth surface for two series of the micropatterned Si with different pitch values (Jung and Bhushan, 2008b).

To study the validity of the transition criterion (Eq. 29), the critical impact velocity at which wetting of the surface (possibly pinning of droplet) occurs was measured (Jung and Bhushan, 2008b). For calculations, the surface tension of the water-air interface (γ) was taken at 0.073 N/m, the mass density (ρ) is 1000 kg/m³ for water, and 1 kg·m/s² = 1 N (Adamson, 1990). **Figure 46** shows the measured critical impact velocity of a droplet with 1 mm radius as a function of geometric parameters (triangles). The trends are compared with the predicted curve (solid lines). It is found that the critical impact velocity at which wetting occurs is in good quantitative agreement with our predictions. The critical impact velocity of the droplet decreases with the geometric parameter (pitch). For the surface with small pitch, the critical impact velocity of droplet can be large.

The energy barrier of the Cassie-Baxter and Wenzel transition can be estimated as the kinetic energy of the droplets (Nosonovsky and Bhushan, 2008g). **Figure 47** shows the dependence of the kinetic energy corresponding to the transition, E_{kin} , on $\Delta E/(A_0 \cos \theta_0)$ calculated from Eq. 30. It is observed that the dependence is close to linear, however, the series of smaller pillars has larger energies of transition. The value of A_0 is in the range $0.11 \text{ mm}^2 < A_0 < 0.18 \text{ mm}^2$ for series 1 and $0.05 \text{ mm}^2 < A_0 < 0.11 \text{ mm}^2$ for series 2, which is of the same order as the actual area under the droplet.

These results suggest that the energy barrier for the Cassie-Baxter and Wenzel transition is given by Eq. 30 and is proportional to the area under the droplet (Nosonovsky and Bhushan, 2008g). For droplets sitting on the surface or evaporating, the transition takes place when the size of the barrier decreases to the value of the vibrational energy, U . The vibrational energy of the droplet is the energy associated with the vibration of the droplet due to surface waves, thermal vibration etc. Assuming $U = \text{const}$, the proportionality of P/D and R suggests that the energy barrier is proportional to the RD/P . This is indeed true, since the area under the droplet $A_0 = \pi(R \sin \theta)^2$. Substitutiong $\sin^2 \theta = 0.1$, $\cos \theta_0 = \cos 109^\circ = -0.33$, $\gamma_{\text{LA}} = 0.072 \text{ J/m}^2$ in Eq. 30 and taking the observed value $RD/P = 50 \text{ }\mu\text{m}$ yields an estimated value of the vibrational energy $U = 1.2 \times 10^{-10} \text{ J}$. The transition happens because the size of the droplet is decreased or because the pitch

Figure 46. Measured critical impact velocity of droplet with 1 mm radius as a function of geometric parameters (triangles). The data are compared with the criterion of impact velocity for the pinning of droplet (solid lines) for two series of the micropatterned Si with different pitch values (Jung and Bhushan, 2008b).

between the pillars that cover the surface is increased. A different way to overcome the barrier is to hit the surface with a droplet with a certain kinetic energy.

Based on Nosonovsky and Bhushan (2008g), the vibrational energy U also plays a role in overcoming energy barriers that lead to contact angle hysteresis during liquid flow (Johnson and Dettre, 1964). To estimate the effect of the energy barriers on contact angle hysteresis, we assume, based on Eq. 5, that the difference between the advancing and receding contact angle is given by

$$\cos\theta_{\text{rec}} - \cos\theta_{\text{adv}} = \Delta W/\gamma_{\text{LA}} \quad (38)$$

where ΔW corresponds to the energy barrier associated with the wetting-dewetting cycle. Assuming that this energy barrier is of the same order as the vibrational energy per contact area, $\Delta W=U/A_0$, and taking $A_0=0.1 \text{ mm}^2$, we end up with $\Delta W=10^{-3} \text{ J/m}^2$. For water ($\gamma_{\text{LA}}=0.072 \text{ J/m}^2$), Eq. 38 leads to a realistic value of hysteresis on a superhydrophobic surface $\cos\theta_{\text{rec}} - \cos\theta_{\text{adv}} = 0.014$. This number provides an estimate for contact angle hysteresis in the limit of small energy barriers comparable with U . The actual values for a micropatterned surface are dependent upon the solid-liquid contact area (that provides energy barriers due to so-called adhesion hysteresis) and the density of the solid-air-liquid contact line (that provides additional pinning) and were found to be between 0.0144 and 0.440 (Bhushan et al., 2007), thus showing a good agreement with the value calculated based on U as the lower limit. This indicates that the value of U is relevant both for the Cassie-Baxter and Wenzel regime transition and contact angle hysteresis.

Figure 47. Bouncing droplets dependency of the kinetic energy of a droplet that provides the regime transition upon the energy barrier calculated from Eq. 30 (squares for series 1 and diamonds for series 2). The fit (solid line) is shown for $A_0=0.12 \text{ mm}^2$ (Nosonovsky and Bhushan, 2008g).

5.3.7. Observation and measurement of contact angle using ESEM

Figure 48 shows how water droplets grow and merge in an ESEM (Jung and Bhushan, 2008a) that was used as a contact angle analysis tool. Microdroplets (with a diameter less than 1 mm) were distributed on a micropatterned surface coated with PF_3 using condensation by decreasing temperature. At the beginning, some small water droplets appeared, i.e., water droplets at locations 1, 2 and 3 in the left image. During further condensation with decreasing temperature, droplets at locations 1 and 3 gradually grew while droplets at location 2 merged together. With further condensation, droplets at locations 1 and 2 gradually grew while droplets at location 3 merged together into one big droplet in the right image. In all cases, condensation was initiated at the bottom, therefore, the droplets were in the Wenzel regime.

Compared with the conventional contact angle measurement, ESEM is able to provide detailed information about the contact angle of microdroplets on micropatterned surfaces. The diameter of the water droplets used for the contact angle measurement was $10\text{ }\mu\text{m}$, so that the size limit pointed out by Stelmashenko et al. (2001) was avoided. For droplet size smaller than $1\text{ }\mu\text{m}$, substrate backscattering can distort the intensity profile such that the images are inaccurate.

As shown in **Fig. 49**, the static contact angle and contact angle hysteresis of the microdroplets on flat and micropatterned surfaces were obtained from the images using the methodology described earlier. Once the microdroplet's condensation and evaporation has reached a dynamic equilibrium, static contact angles were determined. The flat Si coated with PF_3 showed a static contact angle of 98° . The micropatterned surfaces coated with PF_3 increase the static contact angle compared to the flat surface coated with PF_3 due to the effect of roughness. Advancing and receding contact angles were measured during condensation/evaporation with decreasing/increasing the temperature of the cooling stage, and the contact angle hysteresis was then calculated (Jung and Bhushan, 2008a).

Figure 50 shows contact angle hysteresis as a function of geometric parameters for the microdroplets formed in the ESEM (triangles) for two series of micropatterned Si with different pitch values coated with PF_3 . Data at zero pitch correspond to a flat Si

sample. The droplets with about 20 μm radii, which are larger than the pitch, were selected in order to look at the effect of pillars in contact with the droplet. These data were compared with conventional contact angle measurements with the droplet with 1 mm radius (5 μL volume) (circle and solid lines) (Bhushan and Jung, 2007). When the distance between pillars increases above a certain value, the contact area between the micropatterned surface and the droplet decreases, resulting in a decrease of the contact angle hysteresis. Both droplets with 1 mm and 20 μm radii showed the same trend. The contact angle hysteresis for the micropatterned surfaces with low pitch are higher compared to the flat surface due to the effect of sharp edges on the pillars, resulting in pinning (Nosonovsky and Bhushan, 2005). Contact angle hysteresis for a flat surface can arise from roughness and surface heterogeneity. For a droplet advancing forward on the micropatterned surfaces, the line of contact of the solid, liquid, and air will be pinned at the edge point until it is able to move, resulting in increasing contact angle hysteresis. The contact angle hysteresis for the microdroplet from ESEM is lower as compared to that for the droplet with 1 mm radius. The difference of contact angle hysteresis between a microdroplet and a droplet with 1 mm radius could come from the different pinning effects, because the latter has more sharp edges in contact with a droplet compared to the former. The results show how droplet size can affect the wetting properties of micropatterned Si surfaces (Jung and Bhushan, 2008a).

Figure 48. Microdroplet (in dimension of less than 1 mm diameter) growing and merging process under ESEM during increasing condensation by decreasing temperature. Left image: Some small water droplets appear at the beginning, i.e. water droplets 1, 2, 3. Middle image: Water droplets at locations 1 and 3 increase in size and water droplets at location 2 merge together to form one big droplet. Right image: Water droplets at locations 1 and 2 increase in size and water droplets at location 3 merge together to form one big droplet (Jung and Bhushan, 2008a).

Figure 49. Microdroplets on flat and two micropatterned surfaces using ESEM. Second set of images were taken during increasing condensation, and the third set of images were taken during increasing evaporation. Static contact angle was measured when the droplet was stable. Advancing contact angle was measured after increasing condensation by decreasing the temperature of the cooling stage. Receding contact angle was measured after decreasing evaporation by increasing the temperature of the cooling stage (Jung and Bhushan, 2008a).

Figure 50. Contact angle hysteresis as a function of geometric parameters for the microdroplet with about 20 μm radius from ESEM (triangle) compared with the droplet with 1 mm radius (5 μL volume) (circle and solid lines) for two series of the micropatterned surfaces with different pitch values. Data at zero pitch correspond to a flat sample (Jung and Bhushan, 2008a).

5.4. Ideal surfaces with hierarchical structure

It has been reported earlier that a hierarchical surface is needed to develop a composite interface with high stability. The structure of an ideal hierarchical surface is shown in **Fig. 51**. The asperities should be high enough so that the droplet does not touch the valleys. As an example, for a structure with circular pillars, the following relationship should hold for a composite interface; $(\sqrt{2}P - D)^2 / R < H$, Eq. 26. As an example, for a droplet with a radius on the order of 1 mm or larger, a value of H on the order of 30 μm , D on the order of 15 μm , a P on the order of 130 μm (**Fig. 36**) is optimum. Nanoasperities can pin the liquid-air interface and thus prevent liquid from filling the valleys between asperities. They are also required to support nanodroplets, which may condense in the valleys between large asperities. Therefore, nanoasperities should have a small pitch to handle nanodroplets, less than 1 mm down to few nm radius. The values of h on the order of 10 nm and d on the order of 100 nm can be easily fabricated.

Figure 51. Schematic of structure of an ideal hierarchical surface. Microasperities consist of the circular pillars with diameter D , height H , and pitch P . Nanoasperities consist of pyramidal nanoasperities of height h and diameter d with rounded tops.

5.5. Hierarchical structured surfaces with wax platelets and tubules

A hierarchical structure is composed of at least two levels of structuring in different length scales. We fabricated surfaces with a hierarchical structure with micropatterned epoxy replicas and Lotus leaf microstructure, and created a second level of structuring with wax platelets and wax tubules (Bhushan et al., 2008a,b, 2009c,d; Koch et al., 2009b). Platelets and tubules are the most common wax morphologies found in plant surfaces and exist on superhydrophobic leaves, such as Lotus and *Colocasia esculenta* leaves. The structures developed mimic the hierarchical structures of superhydrophobic leaves. Two steps of the fabrication process include the production of microstructured surfaces by soft lithography and the subsequent development of nanostructures on top by self assembly of plant waxes and artificial wax components.

A two-step molding process was used to fabricate several structurally identical copies of micropatterned Si surface and Lotus leaves. The technique used is a fast, precise, and low cost molding process for biological and artificial surfaces (Koch et al., 2007, 2008b). The technique was used to mold a microstructured Si surface with pillars of 14 μm diameter and 30 μm height with 23 μm pitch (Bhushan et al., 2008a,b, 2009c,d; Koch et al., 2009b), fabricated by photolithography (Barbieri et al., 2007). Before replication of the Lotus leaf, the epicuticular wax tubules were removed in areas of approximately 6 cm^2 . For this purpose, a two-component fast hardening glue was applied on the upper side of the leaves and was carefully pressed onto the leaf. After hardening, the glue with the embedded waxes was removed from the leaf, and the procedure was repeated (Koch et al., 2009b). The replication is a two step molding process, in which first a negative replica of a template is generated and then a positive replica is generated, as shown in **Fig. 52(a)** (Bhushan et al., 2009d). A polyvinylsiloxane dental wax was applied to the surface and immediately pressed down with a glass plate. After complete hardening of the molding mass (at room temperature for approximately 5 minutes), the silicon master surface and the mold (negative) were separated. After a relaxation time of 30 minutes for the molding material, the negative replicas were filled with a liquid epoxy resin. Specimens were immediately transferred to a vacuum chamber at 750 mTorr (100 Pa) pressure for 10 seconds to remove trapped air and to increase resin infiltration through the structures. After hardening at room temperature (24 h at 22 $^{\circ}\text{C}$), the positive

Figure 52. (a) Schematic of two-step molding process used to fabricate microstructure, in which at first a negative is generated and then a positive, and (b) SEM micrographs of the master of micropatterned Si surface and positive replica fabricated from the master surface measured at 45° tilt angle (shown using two magnifications) (Bhushan et al., 2009d).

replica was separated from the negative replica. The second step can be repeated to generate a number of replicas. The pillars of the master surface have been replicated without any morphological changes as shown in **Fig. 52(b)** (Bhushan et al., 2009d). The nanogrooves of a couple of hundred nm in lateral dimension present on the pillars of master surface are shown to reproduce faithfully in the replica.

We created a nanostructure by self assembly of synthetic and plant waxes deposited by thermal evaporation (Bhushan et al., 2008a,b, 2009c,d; Koch et al., 2009b). The alkane *n*-hexatriacontane ($C_{36}H_{74}$) has been used for the development of platelet nanostructures. Tubule forming waxes which were isolated from leaves of *Tropaeolum majus* (L.) and *Nelumbo nucifera*, in the following referred to as *T. majus* and Lotus, were used to create tubule structures. The chemical structure of the major components of the wax forming tubule and alkane *n*-hexatriacontane are shown in **Table 8**. The complete chemistry of the plant waxes used is presented in Koch et al. (2006a). For a homogenous deposition of the waxes and alkane, a thermal evaporation system, as shown in **Fig. 53**, has been used (Bhushan et al., 2009d). Specimens of smooth surfaces (flat silicon replicas) and microstructured replicas were placed in a vacuum chamber at 30 mTorr (4 kPa), 20 mm above a heating plate loaded with waxes of *n*-hexatriacontane (300, 500 or 1000 μg), *T. majus* wax (500, 1000, 1500 or 2000 μg), and Lotus wax (2000 μg) (Bhushan et al., 2008a,b, 2009c,d; Koch et al., 2009b). The wax was evaporated by heating it up to 120 °C. In a vacuum chamber the evaporation from the point source to the substrate occurs in a straight line; thus, the amount of sublimated material is equal in a hemispherical region over the point of source (Bunshah, 1994). In order to estimate the amount of sublimated mass, the surface area of the half sphere was calculated by using the formula $2\pi r^2$, whereby the radius (r) represents the distance between the specimen to be covered and the heating plate with the substance to be evaporated. The amounts of wax deposited on the specimen surfaces were 0.12, 0.2 and 0.4 $\mu\text{g}/\text{mm}^2$ for *n*-hexatriacontane, and 0.2, 0.4, 0.6 and 0.8 $\mu\text{g}/\text{mm}^2$ for *T. majus* and 0.8 $\mu\text{g}/\text{mm}^2$ for Lotus waxes, respectively.

<i>n</i> -hexatriacontane	$C_{36}H_{74}$	
<i>Tropaeolum majus</i>	nonacosan-10-ol	$\begin{array}{c} \text{OH} \\ \\ \text{CH}_3-(\text{CH}_2)_8-\text{CH}-(\text{CH}_2)_{18}-\text{CH}_3 \end{array}$
	nonacosane-4,10-diol	$\begin{array}{c} \text{OH} \quad \text{OH} \\ \quad \\ \text{CH}_3-(\text{CH}_2)_2-\text{CH}-(\text{CH}_2)_5-\text{CH}-(\text{CH}_2)_{18}-\text{CH}_3 \end{array}$
Lotus	nonacosane-10,15-diol	$\begin{array}{c} \text{OH} \quad \text{OH} \\ \quad \\ \text{CH}_3-(\text{CH}_2)_8-\text{CH}-(\text{CH}_2)_4-\text{CH}-(\text{CH}_2)_{13}-\text{CH}_3 \end{array}$
	nonacosan-10-ol	$\begin{array}{c} \text{OH} \\ \\ \text{CH}_3-(\text{CH}_2)_8-\text{CH}-(\text{CH}_2)_{18}-\text{CH}_3 \end{array}$

Table 8. Chemical structure of the major components of *n*-hexatriacontane, *T. majus* and Lotus waxes. The major component is shown first (Bhushan et al., 2008a, 2009c; Koch et al., 2009b).

After coating, the specimens with *n*-hexatriacontane were placed in a desiccator at room temperature for three days for crystallization of the alkanes. A stable stage was indicated by no further increase of crystal sizes.

For the plant waxes which are a mixture of aliphatic components, different crystallization conditions have been chosen. It has been reported by Niemietz et al. (2009) that an increase of temperature from 21°C (room temperature) to 50°C had a positive effect on the mobilization and diffusion of wax molecules, required for separation of the tubule forming molecules. It is also known that chemical ambient has an influence on the propensity of wax crystallization, thus the specimens with evaporated plant waxes (*T. majus* and Lotus) were stored for three days at 50°C in a crystallization chamber, where they were exposed to a solvent (ethanol) in vapor phase (**Fig. 54**). Specimens were placed on metal posts and a filter paper wetted with 20 mL of the solvent was placed below the specimens. Slow diffusive loss of the solvent in the chamber was provided by placing a thin filter paper between the glass body and the lid. After evaporation of the solvent, specimens were left in the oven at 50°C in total for seven days. **Fig. 55** shows the nanostructures formed by Lotus wax, seven days after wax deposition on flat surfaces. **Fig. 55(a)** shows the nanostructure after storage at 21°C; in these no tubules were grown. **Fig. 55(b)** shows that Lotus waxes exposed to ethanol vapor for three days at 50°C formed wax tubules. A detailed description of the nanostructure sizes and nanoroughness is given in the following.

Flat films of *n*-hexatriacontane and wax tubules were made by heating the substances over their melting point and rapidly cooling down. This procedure interrupts the crystallization and leads to smooth films (Bhushan et al., 2008a,b, 2009c,d; Koch et al., 2009b).

Figure 53. Schematic of thermal evaporation system for self-assembly of a wax. Evaporation from the point source to the substrate occurs over hemispherical region (dotted line) (Bhushan et al., 2009d).

Figure 54. Schematic of a glass recrystallization chamber used for tubules formation. The filter paper placed at the bottom of the chamber was wetted with 20 mL of the solvent, and slow evaporation of the solvent was provided by placing a thin filter paper between the glass body and the cap placed above. The total volume of the chamber is about 200 cm³ (Bhushan et al., 2009b).

Lotus wax deposited on the surface

Nanostructure on flat epoxy replica

After seven days in air (21° C)

(a)

After seven days with ethanol vapor (50° C)

(b)

Figure 55. SEM micrographs of morphology of the Lotus wax deposited on the flat epoxy replica surface after two treatments of specimens measured at 45° tilt angle, (a) after seven days at 21° C (top), nanostructure on flat epoxy replica was found with no tubules, and (b) after seven days at 50° C with ethanol vapor (bottom), tubular nanostructures with random orientation were found on the surface (Koch et al., 2009b).

5.5.1. Nanostructures with various platelet crystal densities

Figure 56(a) shows the scanning electron microscope (SEM) micrographs of a flat surface and nanostructures fabricated with various masses of *n*-hexatriacontane (Bhushan et al., 2008a). The nanostructure is formed by three-dimensional platelets of *n*-hexatriacontane, as shown in detail in **Fig. 56(b)**. Platelets are flat crystals, grown perpendicular to the substrate surface. They are randomly distributed on the surface, and their shapes and sizes show some variations. Some of the single platelets are connected to their neighboring crystals at their lateral ends. This arrangement leads to a kind of cross-linking of the single platelets. As shown in **Fig. 56(b)**, and based on additional specimens, the platelet thickness varied between 50 and 100 nm, and their length varied between 500 and 1000 nm. The self-assembly of *n*-hexatriacontane used here, and most long chain hydrocarbons lead to layered structures with a lamellae order. In these structures, the molecular axis is orientated parallel to the substrate surface. The growth of these layers results in an ordered, crystalline 3-D structure (Dorset et al., 1983). The created nanostructures are comparable to the wax crystal morphology found on superhydrophobic leaves, e.g., *Colocasia esculenta* (Neinhuis and Barthlott, 1997) and *Triticum aestivum* (wheat) (Koch et al., 2006b). SEM micrographs of the nanostructures fabricated with three different masses of *n*-hexatriacontane show different densities of crystals. An atomic force microscope (AFM) was used to characterize the nanostructures. Statistical parameters of nanostructures (root mean square (RMS) height, peak to valley height, and summit density (η)) were calculated and are presented in **Table 9** (Bhushan, 1999, 2002). A summit is defined as a point whose height is greater than its four nearest neighboring points above a threshold value of 10% of RMS height to avoid measurement errors. The measurement results were reproducible within $\pm 5\%$.

To study the effect of nanostructures with different crystal density on superhydrophobicity, static contact angle, contact angle hysteresis and tilt angle, and adhesive forces were measured (Bhushan et al., 2008a). For contact angle hysteresis, the advancing and receding contact angles were measured at the front and back of the droplet moving along the tilted surface, respectively. The data are shown in **Fig. 57**. The static contact angle of a flat surface coated with a film of *n*-hexatriacontane was 91° . It showed a contact angle hysteresis of 87° , and the droplet still adhered at a tilt angle of 90° .

Continued

Figure 56. SEM micrographs taken at 45° tilt angle (shown using two magnifications) of (a) the flat surface and nanostructures fabricated with various mass of *n*-hexatriacontane and (b) three-dimensional platelets forming nanostructures on the surface fabricated with 0.2 μg/mm² mass of *n*-hexatriacontane. All samples are fabricated with epoxy resin coated with *n*-hexatriacontane (Bhushan et al., 2008a).

Figure 56 Continued

(b)

	RMS height (nm)	Peak to valley height (nm)	η (/sq. μm)
<i>n</i> -hexatriacontane			
Nanostructure ($0.12 \mu\text{g}/\text{mm}^2$)	46	522	0.78
Nanostructure ($0.2 \mu\text{g}/\text{mm}^2$)	65	663	1.39
Nanostructure ($0.4 \mu\text{g}/\text{mm}^2$)	82	856	1.73
<i>Tropaeolum majus</i> wax			
Nanostructure ($0.8 \mu\text{g}/\text{mm}^2$)	180	1570	0.57
Lotus wax			
Nanostructure ($0.8 \mu\text{g}/\text{mm}^2$)	187	1550	1.47

RMS – root mean square

η – summit density

Table 9. Roughness statistics for nanostructure surface measured using an AFM (Scan size $10 \mu\text{m} \times 10 \mu\text{m}$). Nanostructures were fabricated with *n*-hexatriacontane, *T. majus* and Lotus waxes (Bhushan et al., 2008a, 2009c; Koch et al., 2009b).

Nanostructuring of flat surfaces with *n*-hexatriacontane platelets creates superhydrophobic surfaces with high static contact angle and a reduction of contact angle hysteresis and tilt angle. The values are a function of crystal density. **Figure 58** shows a plot of static contact angle and contact angle hysteresis as a function of the mass of *n*-hexatriacontane deposited. As the mass of *n*-hexatriacontane increased, the static contact angle first increased, and the contact angle hysteresis decreased. Then, above a mass of $0.2 \mu\text{g}/\text{mm}^2$, static contact angle and contact angle hysteresis gradually decreased and increased with increasing mass, respectively. The highest static contact angle and lowest contact angle hysteresis are 158° and 23° at mass of $0.2 \mu\text{g}/\text{mm}^2$. As shown in **Fig. 57**, adhesive force measured using a $15 \mu\text{m}$ radius borosilicate tip in an AFM also shows a similar trend as the wetting properties. Adhesive forces of the nanostructured surfaces were lower than for the flat surface because the contact between the tip and surface was lower than on the flat surface, because the contact between the tip and surface was reduced by surface structuring (Bhushan, 1999, 2002).

In order to identify wetting regimes (Wenzel or Cassie-Baxter) as well as to understand the effect of crystal density on the propensity of air pocket formation for the nanostructured surfaces, roughness factor (R_f) and fractional liquid- air interface (f_{LA}) are needed. The R_f for the nanostructures was calculated using the AFM map (Burton and Bhushan, 2006; Bhushan and Jung, 2006). The calculated results were reproducible within $\pm 5\%$. The R_f for the nanostructured surfaces with masses of 0.12, 0.2 and $0.4 \mu\text{g}/\text{mm}^2$ were found to be 3.4, 4.9 and 6.8, respectively. For calculation of f_{LA} of the nanostructures, only the higher crystals are assumed to come in contact with a water droplet. The fractional geometrical area of the top surface for the nanostructures was calculated from SEM micrographs with top view (0° tilt angle). The SEM images were converted to high contrast black and white images using Adobe Photoshop. The increase of contrast in SEM image eliminates the smaller platelet structures, which were visible in the original SEM image. The higher crystals led to white signals in the SEM figure. The fractional geometrical area of the top nanostructured surfaces with masses of 0.12, 0.2 and $0.4 \mu\text{g}/\text{mm}^2$ was found to be 0.07, 0.15 and 0.24, leading to f_{LA} of 0.93, 0.85 and 0.76, respectively. The calculated results were reproducible within $\pm 5\%$. The values of static

contact angle in Wenzel and Cassie-Baxter regimes for the nanostructured surfaces were calculated using the values of R_f and f_{LA} and presented in **Fig. 57**. The values of contact angle hysteresis in Cassie-Baxter regimes for various surfaces were calculated using Eq. 20. The data are presented in **Fig. 57**.

As shown in **Fig 57**, the experimental static contact angle and contact angle hysteresis values for the two nanostructured surfaces with 0.2 and 0.4 $\mu\text{g}/\text{mm}^2$ were comparable to the calculated values in Cassie-Baxter regime. The results suggest that a droplet on two nanostructured surfaces should exist in the Cassie-Baxter regime. However, the experimental static contact angle and contact angle hysteresis values for the nanostructured surface with 0.12 $\mu\text{g}/\text{mm}^2$ were lower and higher than the calculated values in Cassie-Baxter regime, respectively. It is believed that neighboring crystals are separated at lower crystal density and any trapped air can be squeezed out. Whereas neighboring crystals are interconnected at higher densities and air remains trapped. At highest crystal density at a mass of 0.4 $\mu\text{g}/\text{mm}^2$, there is less open volume compared to that at 0.2 $\mu\text{g}/\text{mm}^2$, and that explains a droplet static contact angle going from 158° to 150° (Bhushan et al., 2008a).

Figure 57. Bar chart showing the measured static contact angle, contact angle hysteresis and tilt angle, calculated contact angles obtained using Wenzel and Cassie-Baxter equations with a given value of θ_0 , and calculated contact angle hysteresis using Cassie-Baxter equation on flat surface and nanostructures fabricated with various mass of *n*-hexatriacontane. The droplet on flat surface does not move along the surface even at tilt angle of 90° . The bar chart also shows adhesive forces for various structures, measured using a $15\text{ }\mu\text{m}$ radius borosilicate tip (Bhushan et al., 2008a).

Figure 58. Static contact angle and contact angle hysteresis as a function of mass of *n*-hexatriacontane deposited on nanostructures (Bhushan et al., 2008a).

5.5.2. The influence of hierarchical structure with wax platelets on the superhydrophobicity

We created surfaces with *n*-hexatriacontane of $0.2 \mu\text{g}/\text{mm}^2$ to study the influence of hierarchical structure on superhydrophobicity (Bhushan et al., 2008b, 2009d). **Figure 59** shows the scanning electron microscope (SEM) micrographs of a flat surface and nano-, micro- and hierarchical structures. To study the effect of structure on superhydrophobicity, static contact angle, contact angle hysteresis and tilt angle, and adhesive forces of four structures were measured. The data are shown in **Fig. 60**. The static contact angle of a flat surface coated with a film of *n*-hexatriacontane was 91° , and increased to 158° when *n*-hexatriacontane formed a nanostructure of platelets on it. The static contact angle on a flat specimen with a microstructure was 154° , but it increased to 169° for the hierarchical surface structure. Contact angle hysteresis and tilt angle for flat, micro- and nanostructured surfaces show similar trends. The flat surface showed a contact angle hysteresis of 87° , and the droplet still adhered at a tilt angle of 90° . The superhydrophobic micro- and nanostructured surfaces showed a reduction of contact

Figure 59. SEM micrographs of the flat surface, nanostructure, microstructure, and hierarchical structure measured at 45° tilt angle (shown using two magnifications). All samples are fabricated with epoxy resin coated with *n*-hexatriacontane (Bhushan et al., 2008b).

angle hysteresis and tilt angle, but a water droplet still needs a tilt angle of 26° and 51°, respectively, before sliding. Only the hierarchical surface structure with static contact angle of 169° and low contact angle hysteresis of 2° exceeds the basic criteria for superhydrophobic and self-cleaning surfaces (Bhushan and Jung, 2008). Adhesive force measured using a 15 µm radius borosilicate tip in an AFM also shows a similar trend as the wetting properties. Adhesion force of the hierarchical surface structure was lower than that of both micro- and nanostructured surfaces because the contact between the tip and surface was lower as a result of contact area being reduced (Bhushan, 1999, 2002).

In order to identify wetting regimes (Wenzel or Cassie-Baxter) for the various surfaces, roughness factor (R_f) and fractional liquid- air interface (f_{LA}) are needed. The R_f for the nanostructure was described earlier. The R_f for microstructure was calculated for the geometry of flat-top, cylindrical pillars of diameter D , height H , and pitch P distributed in a regular square array. For this case, roughness factor for the microstructure,

$(R_f)_{micro} = (1 + \frac{\pi DH}{P^2})$. The roughness factor for the hierarchical structure is the sum of $(R_f)_{micro}$ and $(R_f)_{nano}$. The values calculated for various surfaces are summarized in **Table 10**.

For calculation of f_{LA} , we make the following assumptions. For the microstructure, we consider that a droplet in size much larger than the pitch P contacts only the flat-top of the pillars in the composite interface, and the cavities are filled with air. For microstructure, fractional flat geometrical area of the liquid-air interface under the droplet,

$(f_{LA})_{micro} = (1 - \frac{\pi D^2}{4P^2})$ (Bhushan and Jung, 2008). The fractional geometrical area of the top surface for the nanostructure was described earlier. For the hierarchical structure, the fractional flat geometrical area of the liquid-air interface,

$(f_{LA})_{hierarchical} = 1 - (\frac{\pi D^2}{4P^2})[1 - (f_{LA})_{nano}]$. The values of contact angle hysteresis in Cassie-Baxter regimes for various surfaces were calculated using Eq. 20. The values are summarized in **Table 10**.

The values of static contact angle in the Wenzel and Cassie-Baxter regimes for various surfaces were calculated using the values of R_f and f_{LA} (**Table 10**). As shown in

Fig 60, the experimental static contact angle values for the three structured surfaces were larger than the calculated values in Cassie-Baxter regime. The results suggest that the droplets on three structured surfaces were in the Cassie-Baxter regime. This indicates that the microstructure and nanostructure surface induce air pocket formation. For the contact angle hysteresis, there is a good agreement between the experimental data and the theoretically predicted values for the Cassie-Baxter regime. These results show that air pocket formation in the micro- and nanostructure decreases the solid-liquid contact (Koch et al., 2009b). In hierarchical structured surfaces, the air pocket formation further decreases the solid-liquid contact and thereby reduces contact angle hysteresis and tilt angle (Bhushan et al., 2008b, 2009d).

			Static contact angle (deg)			Contact angle hysteresis (deg)	
	R_f	f_{LA}	Measured	Calculated in Wenzel regime	Calculated in Cassie-Baxter regime	Measured	Calculated in Cassie-Baxter regime
Flat			91			87*	
Nanostructure	4.9	0.85	158	95	149	23	24
Microstructure	3.5	0.71	154	94	136	36	34
Hierarchical structure	8.4	0.96	169	98	164	2	12

* Advancing and receding contact angles are 141° and 54°, respectively.

Table 10. Summary of static contact angles and contact angle hysteresis measured and calculated for droplets in Wenzel regime and Cassie-Baxter regime on the various surfaces with *n*-hexatriacontane using the calculated values of R_f and f_{LA} (Bhushan et al., 2008b, 2009d).

Figure 60 Bar chart showing the measured static contact angle, contact angle hysteresis and tilt angle, calculated contact angles obtained using Wenzel and Cassie-Baxter equations with a given value of θ_0 , and calculated contact angle hysteresis using Cassie-Baxter equation on various structures. The droplet on flat surface does not move along the surface even at tilt angle of 90° . The bar chart also shows adhesive forces for various structures, measured using a $15\text{ }\mu\text{m}$ radius borosilicate tip (Bhushan et al., 2008b).

5.5.3. The influence of hierarchical structure with wax tubules on the superhydrophobicity

5.5.3.1. Morphological characterization, wettability and adhesion forces of *T. majus* tubules

Figure 61(a) shows the SEM micrographs of the nanostructure and hierarchical structure fabricated with two different masses (0.6 and $0.8 \mu\text{g}/\text{mm}^2$) of *T. majus* (Bhushan et al., 2009c). SEM micrographs show an increase in the tubule amount on flat and microstructure surfaces after deposition of higher masses of wax. The tubules of *T. majus* wax grown in an ethanol atmosphere are comparable to the wax morphology found on the leaves of *T. majus*. Surfaces show a homogenous distribution of the wax mass on the specimen surfaces, and tubules provide the desired nanostructure of three-dimensional tubules on flat and microstructure surfaces. The tubule morphology of *T. majus* wax is shown in detail in **Fig. 61(b)**. The tubular crystals are hollow structures, randomly orientated on the surface and embedded into an amorphous wax layer. They are randomly distributed on the surface, and their shapes and sizes show some variations. As shown in **Fig. 61(b)**, and based on additional specimens, the tubular diameter varied between 100 and 300 nm, and their length varied between 300 and 1200 nm.

Atomic force microscopy (AFM) was used to characterize the nanostructure fabricated using *T. majus* wax of $0.8 \mu\text{g}/\text{mm}^2$ after storage at 50°C with ethanol vapor (Bhushan et al., 2009c). Statistical parameters of the nanostructure (root mean square (RMS) height, peak to valley height, and summit density (η)) were calculated and are presented in **Table 9** (Bhushan, 1999, 2002). A summit is defined as a point whose height is greater than of its four nearest neighboring points above a threshold value of 10% of RMS height to avoid measurement errors. The measurement results were reproducible within $\pm 5\%$.

To study the effect of structures with various length scales on superhydrophobicity, static contact angle, contact angle hysteresis and tilt angle, and adhesive forces of four structures produced using *T. majus* wax were measured (Bhushan et al., 2009c). Nanostructures formed on flat and microstructured surfaces were fabricated

Figure 61. SEM micrographs taken at 45° tilt angle (shown using two magnifications) of (a) the nanostructure and hierarchical structure fabricated with two different mass (0.6 and 0.8 $\mu\text{g}/\text{mm}^2$) of *T. majus* wax after storage at 50° C with ethanol vapor and (b) three-dimensional tubules forming nanostructures on the surface fabricated with 0.8 $\mu\text{g}/\text{mm}^2$ mass of *T. majus* wax after storage at 50°C with ethanol vapor (Bhushan et al., 2009c).

using *T. majus* wax of $0.8 \mu\text{g}/\text{mm}^2$ after storage at 50°C with ethanol vapor. The data are shown in **Fig. 62**. The static contact angle of a flat surface coated with a film of *T. majus* wax was 112° , and increased to 164° when *T. majus* wax formed a nanostructure of tubules on it. On the flat specimen with a microstructure on it, the static contact angle was 154° , but increased to 171° for the hierarchical surface structure. Contact angle hysteresis and tilt angle for flat, micro- and nanostructured surfaces show similar trends. Flat surface showed a contact angle hysteresis of 61° and a tilt angle of 86° . The microstructured surface shows a reduction of contact angle hysteresis and tilt angle, but a water droplet still needs a tilt angle of 31° before sliding. As tubules are formed on the flat and microstructured surfaces, the nanostructured and hierarchical structure surfaces have low contact angle hysteresis of 5° and 3° , respectively. These properties are superior to plant leaves, including Lotus leaves. Adhesive force measured using a $15 \mu\text{m}$ radius borosilicate tip in an AFM also show a similar trend as the wetting properties. Adhesion force of the hierarchical surface structure was lower than that of micro- and nanostructured surfaces because the contact between the tip and surface was lower as a result of contact area being reduced (Bhushan, 1999, 2002).

To further verify the effect of hierarchical structure on the propensity of air pocket formation, we performed evaporation experiments with a droplet on microstructure and hierarchical structure fabricated with $0.8 \mu\text{g}/\text{mm}^2$ mass of *T. majus* wax with ethanol vapor at 50°C (Bhushan et al., 2009c). **Figure 63** shows the successive photos of a droplet evaporating on two structured surfaces. On the microstructured surface, the light passes below the droplet and air pockets can be seen, so to start with the droplet is in the Cassie-Baxter regime. When the radius of the droplet decreased to $425 \mu\text{m}$, the air pockets are not visible anymore, and the droplet is in the Wenzel regime. This transition results from an impalement of the droplet in the patterned surface, characterized by a smaller contact angle. For the hierarchical structure, an air pocket was clearly visible at the bottom area of the droplet throughout, and the droplet was in a hydrophobic state until the droplet evaporated completely. It suggests that a hierarchical structure with nanostructures prevents liquid from filling the gaps between the pillars.

Figure 62. Bar chart showing the measured static contact angle, contact angle hysteresis and tilt angle on various structures fabricated with $0.8 \mu\text{m}/\text{mm}^2$ mass of *T. majus* wax after storage at 50°C with ethanol vapor. The bar chart also shows adhesive forces for various structures, measured using a $15 \mu\text{m}$ radius borosilicate tip (Bhushan et al., 2009c).

Figure 63. Evaporation of a droplet on a microstructured- and hierarchical structured surfaces fabricated with $0.8 \mu\text{g}/\text{mm}^2$ mass of *T. majus* wax after storage at 50°C with ethanol vapor. The initial radius of the droplet was about $950 \mu\text{m}$, and the time interval between first two photos was 180 s and between the latter was 60 s. As the radius of droplet reached $425 \mu\text{m}$ (foot print = $836 \mu\text{m}$) on the microstructured surface, the transition from Cassie-Baxter regime to Wenzel regime occurred, as indicated by the arrow. On the hierarchical structured surface air pockets, visible at the bottom area of the droplet, exist until the droplet evaporated completely (Bhushan et al., 2009b).

5.5.3.2. Morphological characterization, wettability and adhesion forces of Lotus tubules

For the development of nanostructures by tubule formation, Lotus wax was used (Koch et al., 2009b). **Figure 64(a)** shows the scanning electron microscope (SEM) micrographs of flat surfaces with the tubules nanostructure. Microstructures shown in **Fig. 64(b)** are the Lotus leaf and micropatterned Si replica covered with a Lotus wax film. Hierarchical structures were fabricated with microstructured Lotus leaf replicas and micropatterned Si replicas covered with a nanostructure of Lotus wax tubules, as shown in **Fig. 64(c)**. SEM micrographs show an overview (left column), a detail in higher magnification (middle column), and a large magnification of the created flat wax layers and tubules nanostructures (right column). The grown tubules provide the desired nanostructure on flat and microstructured surfaces. The recrystallized Lotus wax shows tubular hollow structures, with random orientation on the surfaces. Their shapes and sizes show only a few variations. The tubular diameter varied between 100 and 150 nm, and their length varied between 1500 and 2000 nm. Atomic force microscopy (AFM) was used to characterize the nanostructure of the Lotus wax tubules. The statistical parameters of the nanostructure (root mean square (RMS) height, peak to valley height, and summit density (η)) were calculated and are presented in **Table 9**.

To study the effect of Lotus wax tubule nanostructures on superhydrophobicity, static contact angle, contact angle hysteresis, and tilting angle were measured on flat, microstructured Lotus replica, micropatterned Si replica, and hierarchical surfaces. Hierarchical surfaces were made of the Lotus leaf replica and micropatterned Si replica with a nanostructure of wax tubules on top. Additionally, fresh Lotus leaves were investigated to compare the properties of the fabricated structures with the original biological model.

Figure 65 shows that the highest static contact angles of 173° , lowest contact angle hysteresis of 1° , and tilting angle varying between 1 and 2° were found for the hierarchical structured Si replica. The hierarchical structured Lotus leaf replica showed a static contact angle of 171° , and the same contact angle hysteresis (2°) and tilt angles of 1 - 2° as the hierarchical Si replica. Both artificial hierarchical structured surfaces show similar values as the fresh Lotus leaf surface investigated here with static contact angle of

164°, contact angle hysteresis of 3°, and a tilting angle of 3°. However, the artificial hierarchical surfaces showed higher static contact angle and lower contact angle hysteresis. Structural differences between the original Lotus leaf and the artificial Lotus leaf produced here are limited to a difference in wax tubules length, which are 0.5 to 1 μm longer in the artificial Lotus leaf (Koch et al., 2009b).

The melting of the wax led to a flat surface with a flat wax film with a much lower static contact angle (119°), a higher contact angle hysteresis (71°), and a high tilting angle of 66°. The data of a flat Lotus wax film on a flat replica show that the Lotus wax by itself is hydrophobic. However, it has been stated that the wax on the Lotus leaf surface, by itself, is weakly hydrophilic (Tuteja et al., 2008). We cannot confirm this. The data presented here demonstrate that the native, flat wax of Lotus leaves, with a static contact angle of 119°, is hydrophobic and can turn superhydrophobic (167°) by increasing the surface roughness after self assembly into three-dimensional wax tubules. The static contact angle of the Lotus wax film is 119°, which is higher than that of the wax film made of *T. majus* of 112°. However, films made of *n*-hexatriacontane showed static contact angles of only 91°. SEM investigations, made directly after contact angle measurements, revealed no morphological differences between these films. Based on the chemical composition, it should be assumed that the non-polar *n*-hexatriacontane molecules are more hydrophobic than the plant waxes, which contain high amounts of oxygen atoms. At this point these differences cannot be explained by structural or chemical differences of the films, but will be the interest for further studies.

Adhesive force measured using a 15 μm radius borosilicate tip in an AFM also shows a similar trend as the wetting properties for the artificial surfaces (**Fig. 65**) (Koch et al., 2009b). Adhesion force of the hierarchical surface structure was lower than that of micro- and nanostructured and flat surfaces because the contact between the tip and surface was lower as a result of the contact area being reduced. However, for the fresh Lotus leaf, there is moisture within the plant material, which causes softening of the leaf, and so when the tip comes into contact with the leaf sample, the sample deforms, and a larger area of contact between the tip and sample causes an increase in the adhesive force (Bhushan, 1999, 2002).

Figure 64. SEM micrographs taken at 45° tilt angle (shown using three magnifications) of (a) nanostructure on flat replica, (b) microstructures in Lotus replica and micropatterned Si replica, and (c) hierarchical structure using Lotus and micropatterned Si replicas. Nano- and hierarchical structures were fabricated with mass $0.8 \mu\text{g}/\text{mm}^2$ of Lotus wax after storage for seven days at 50°C with ethanol vapor (Koch et al., 2009b).

Static contact angle, contact angle hysteresis,
tilt angle and adhesive force data
Lotus wax ($0.8 \mu\text{g}/\text{mm}^2$) after seven days with ethanol vapor (50°C)

Figure 65. Bar chart showing the measured static contact angle, contact angle hysteresis and tilt angle on various structures fabricated with $0.8 \mu\text{g}/\text{mm}^2$ of Lotus wax after storage for seven days at 50°C with ethanol vapor. The bar chart also shows adhesive forces for various structures, measured using a $15 \mu\text{m}$ radius borosilicate tip. The error bar represents ± 1 standard deviation (Koch et al., 2009b).

5.5.4. Self-cleaning efficiency of hierarchical structured surfaces

For deposition of contamination on artificial surfaces, various structures were placed in a contamination glass chamber (Bhushan et al., 2009a). Silicon carbide (SiC) (Guillaume, Germany) particles in two different sizes ranges of 1-10 μm and 10-15 μm were used as the contaminants. The SiC particles have been chosen because of their similarity in shape, sizes, and hydrophilicity to natural dirt contaminations. The number of particles per area was determined by counting them from a 280 μm $\times$ 210 μm image taken by an optical microscope with a camera before and after water cleaning.

For the cleaning test, the specimens with the contaminants were subjected to water droplets of approximately 2 mm diameter, using two microsyringes (Bhushan et al., 2009a). In order to obtain a relative measure of the self-cleaning ability of hierarchical structures which exhibit the lowest contact angle hysteresis and tilt angle as compared to other structures (flat, nanostructures, and microstructures), the tilt angle chosen for the cleaning tests was slightly above the tilt angle for the hierarchical structures. Thus experiments were performed with 10° for surfaces covered with *n*-hexatriacontane and 3° for surfaces with Lotus wax. The water cleaning test was carried out for 2 min (water quantity, 10 mL) with nearly zero kinetic energy of droplets. For watering with nearly zero kinetic energy, the distance between the microsyringes and surface was set to 0.005 m (nearly zero impact velocity). The chosen impact velocity represents a low value compared to a natural rain shower, where a water droplet of 2 mm diameter can reach an impact velocity of 6 m/s (measured under controlled conditions) (van Dijk et al., 2002).

Figure 66 shows that none of the investigated surfaces was fully cleaned by water rinsing (Bhushan et al., 2009a). The data represent the average of five different investigated areas for each experiment. For Lotus wax, which forms tubule nanostructures, and *n*-hexatriacontane, which forms platelet nanostructures, the same tendency of particle removal was found. With the exception of hierarchical structure on all surfaces, larger particles were removed more than small ones. Most particles (70-80 %) remained on smooth surfaces, and 50-70 % of particles were found on microstructured surfaces. Most particles were removed from the hierarchical structured surfaces, but approximately 30 % of particles remained. A clear difference in particle removal,

Self-cleaning experiments using two different particle sizes

Figure 66. Bar charts showing the remaining particles after applying droplets with nearly zero kinetic energy on various structures fabricated using *n*-hexatriacontane and Lotus wax using 1-10 μm and 10-15 μm SiC particles. The experiments on the surfaces with *n*-hexatriacontane and Lotus wax were carried out on tilted stages with 10° and 3°, respectively. The error bars represent ± 1 standard deviation (Bhushan et al., 2009a).

independent of particle sizes, was only found in flat and nanostructured surfaces where larger particles were removed with higher efficiency. Observations of the droplet behavior during the movement on the surfaces showed that droplets were rolling only on the hierarchical structured surfaces. On flat, micro- and nanostructured surfaces, the droplets first applied were not moving, but the continuous application of water droplets increased the droplet volumes and led to a sliding of these large droplets. During this, some of the particles had been removed from the surfaces. However, the rolling droplets on hierarchical structures did not collect the dirt particles trapped in the cavities of the microstructures. The data clearly shows that hierarchical structures have superior cleaning efficiency.

5.5.5. Observation of transition during the bouncing droplet

To observe how the impact velocity influences the transition from the composite solid-air-liquid interface to the homogeneous solid-liquid interface during droplet impact, we performed bouncing droplet experiments on various surfaces with *n*-hexatriacontane and *T. majus* and Lotus waxes (Jung and Bhushan, 2009a). **Figure 67** shows snapshots of a droplet with 1 mm radius hitting various surfaces fabricated with 0.2 and 0.4 $\mu\text{m}/\text{mm}^2$ of *n*-hexatriacontane after storage at room temperature. The impact velocity was obtained just prior to the droplet hitting the surface. First, on the flat surface, it was found that the droplet did not bounce off even though the impact velocity applied was up to 1.5 m/s. As shown in the images in the first row for each nano-, micro- and hierarchical structured surface, the droplet hitting the surface under an impact velocity of 0.44 m/s first deformed and then retracted, and bounced off the surface. Finally, the droplet sat on the surface and had a high contact angle, which suggests the formation of a solid-air-liquid interface. Next, we repeated the impact experiment by increasing the impact velocity. As shown in the second row of images for nanostructure (0.4 $\mu\text{g}/\text{mm}^2$) and microstructure, bounce off did not occur, and the wetting of the surface (and possibly pinning of droplet) occurred at impact velocities of 1.2 m/s and 0.77 m/s, respectively, referred to as the critical impact velocity. This is because air pockets do not exist below the droplet as a result of droplet impalement by the structures, characterized by a smaller contact angle.

Figure 67. Snapshots of a droplet with 1 mm radius hitting various surfaces fabricated with 0.2 and 0.4 $\mu\text{g}/\text{mm}^2$ of *n*-hexatriacontane after storage at room temperature. The impact velocity was obtained just prior to the droplet hitting the surface. The pinning of droplet on the nanostructure with 0.4 $\mu\text{g}/\text{mm}^2$ mass, and on the microstructure occurred at impact velocities of 1.2 m/s and 0.77 m/s, respectively (Jung and Bhushan, 2009a).

Figure 67 Continued

Dynamic effects of a droplet on various surfaces with *n*-hexatriacontane

These observations indicate the transition from the composite interface to the homogenous interface. However, as shown in the second row of images for nanostructure ($0.2 \mu\text{g}/\text{mm}^2$) and hierarchical structure, during applying impact velocity of up to 1.5 m/s, the bounce off always occurred and the wetting of the surface did not occur.

As shown in **Fig. 68**, the critical impact velocity of a droplet with 1 mm radius on various structures at which wetting of the surface (possibly pinning of droplet) occurs was measured (Jung and Bhushan, 2009a). The arrow indicates that the critical impact velocity can possibly be more than 1.5 m/s, or the transition has not occurred. As mentioned earlier, when the mass of *n*-hexatriacontane increased, the static contact angle of nanostructure first increased followed by a decrease at a mass of $0.2 \mu\text{g}/\text{mm}^2$. For the critical impact velocity, the same trends were found. It is believed that if neighboring crystals are separated on a sample with lower crystal density, any trapped air can be squeezed out whereas if the neighboring crystals are interconnected on a sample with higher density, air remains trapped. At highest crystal density at a mass of $0.4 \mu\text{g}/\text{mm}^2$, there is less open volume compared to that at $0.2 \mu\text{g}/\text{mm}^2$. For all microstructures with *n*-hexatriacontane and Lotus wax, the critical impact velocities of the droplet are lower than those on nano- and hierarchical structures due to the larger distance between the pillars, and the solid-air-liquid interface can easily be destabilized from dynamic impact on the surface. Based on Eq. 29, the critical impact velocity of the droplet decreases with the geometric parameter (pitch). The theoretical critical impact velocity for microstructure using Eq. 29 is 0.5 m/s. This value is lower than the experimental values of critical impact velocity for microstructures about 30~50% depending on the structured surfaces. In our experiments, during applying impact velocity of up to 1.5 m/s on nano- and hierarchical structures with *n*-hexatriacontane ($0.2 \mu\text{g}/\text{mm}^2$ for nanostructure) and Lotus wax, the wetting of the surface did not occur. The data clearly shows that nano- and hierarchical structures are superior to microstructure in maintaining stable composite solid-air-liquid interface.

To identify whether one is in a homogeneous solid-liquid interface or a composite solid-air-liquid interface, the contact angle data in the static condition and after bounce off were measured on various surfaces, as shown in **Fig. 69** (Jung and Bhushan, 2009a).

Figure 68. Bar chart showing the measured critical impact velocity of a droplet with 1 mm radius at which transition occurs on various structures. The arrow indicates that the critical impact velocity can possibly be more than 1.5 m/s or the transition is not occurred (Jung and Bhushan, 2009a).

The contact angles of the left bar for each sample were measured using the droplet with 1 mm radius gently deposited on the surface. The contact angles of the middle and right bars for each sample were measured using the droplet after hitting the surface at 0.44 m/s and critical or highest impact velocity. Missing bars mean that the droplet, after hitting the surface, bounced off without coming to sit on the surface. The static contact angle of the droplet after impact at 0.44 m/s is lower than that of the droplet gently deposited for all of the surfaces with *n*-hexatriacontane and Lotus wax. It can be interpreted that after hitting, the droplet pushes out the entrapped air of the cavities between the pillars under the droplet, resulting in an abrupt increase of the solid-liquid surface area by dynamic impact. As mentioned earlier, after hitting the surface at a critical impact velocity, the

contact angles were close to 90° and much lower than that of the droplet gently deposited for nanostructures with *n*-hexatriacontane (0.12 and $0.4 \mu\text{g}/\text{mm}^2$) and microstructures with *n*-hexatriacontane and Lotus wax. Even though the droplet is in the composite interface when it is gently deposited on the surface, these observations indicate that the composite solid-air-liquid interface was destroyed due to dynamic impact on the surface.

Figure 69. Bar chart showing the measured static contact angle of a droplet on various surfaces. The contact angles of the left bar for each sample were measured using a droplet with 1 mm radius gently deposited on the surface. The contact angles of the middle and right bars for each sample were measured using the droplet after hitting the surface at 0.44 m/s , and critical or highest impact velocity (Jung and Bhushan, 2009a).

5.5.6. Observation of transition during the vibrating droplet

5.5.6.1. Model for the adhesion and inertia forces of the vibrating droplet

We presented a model for vibration (Jung and Bhushan, 2009a). In this model, they calculate expressions for adhesion force and inertia force as a function of droplet properties and operating conditions. Consider a small droplet of liquid deposited on a surface. The liquid and surface come together under equilibrium at a characteristic angle, called the static contact angle θ , as shown in **Fig. 70**. When a droplet on a surface is vibrated, based on Lamb (1932), a general expression for the resonance frequency f_r of a free oscillating liquid droplet is given as

$$f_r = \sqrt{\frac{n(n-1)(n+2)\gamma}{3\pi\rho V}} \quad (39)$$

where V is the volume of the droplet, and n represents the number of modes, with 2 being the 1st mode etc. For a spherical droplet with a radius R with the distance between the center of droplet and the solid H , the volume of droplet V is given by

$$\begin{aligned} V &= \frac{1}{3}\pi(R+H)^2(2R-H) \\ &= \frac{1}{3}\pi R^3(1-\cos\theta)^2(2+\cos\theta) \end{aligned} \quad (40)$$

Recent experimental studies were carried out by Noblin et al. (2004) and Celestini and Kofman (2006). They showed that the frequency decreases with the volume of the droplet, and the trends are compared with a theoretical model.

When liquid comes in contact with a surface, the energy gained for surfaces coming into contact is greater than the energy required for their separation (or the work of adhesion) by the quantity ΔW , which constitutes the adhesion hysteresis (Bhushan, 2003). For a surface, the difference between the two values of the interface energy (measured during loading and unloading) is given by ΔW . These two values are related to the advancing contact angle, θ_a , and receding contact angle, θ_r , of the surface. For example, a model based on Young's equation has been used to calculate the work of adhesion from contact angle hysteresis (Good, 1952; Chen et al., 1991; Nosonovsky and Bhushan, 2008a).

Figure 70. Droplet of liquid in contact with a solid surface – contact angle θ ; radius of droplet R ; distance between the center of droplet and the solid H (Jung and Bhushan, 2009a).

$$\cos \theta_a - \cos \theta_r = \frac{\Delta W}{\gamma} \quad (41)$$

From Eq. 41, the dominant force (adhesion force) responsible for the separation between the droplet and surface is given by (Joanny and de Gennes, 1984; Lee and Laibinis, 2000)

$$\begin{aligned} F_A &= L\gamma(\cos \theta_a - \cos \theta_r) \\ &= 2R \sin \theta \gamma(\cos \theta_a - \cos \theta_r) \end{aligned} \quad (42)$$

where L is the length of the triple contact line, referred to as line of contact of the solid, liquid, and air. The radius of a spherical droplet, R , depends on the contact angle and can be obtained from Eq. 40.

From applying vertical vibration of a droplet on a surface, the inertia force of droplet F_I is given by

$$F_I = \rho V A \omega^2 \quad (43)$$

where A and ω are the amplitude and frequency of vibration, respectively. Bormeashenko et al. (2007b) showed that the transition occurred at a critical value of inertia force acting on the length of a triple line. However, if the inertia force of the droplet vibrated on the surface can overcome the adhesion force between the droplet and surface, which ΔF is positive value (Jung and Bhushan, 2009a),

$$\Delta F = F_I - F_A \quad (44)$$

the droplet can be vertically separated from the surface (bouncing off) before the composite solid-liquid-air interface is destroyed.

5.5.6.2. Vibration study results

To estimate the resonance frequency of a droplet, a droplet on various surfaces was vibrated by varying the frequency with a sinusoidal excitation of relatively low amplitude (0.4 mm) (Jung and Bhushan, 2009a). Based on Eq. 39, the experiments were performed in the 1st and 2nd modes ($n = 2$ and 3). **Figure 71** shows the optical micrographs of droplets on the microstructured surface with *n*-hexatriacontane before and after vibration at an amplitude of 0.4 mm for 1st mode ($n = 2$) and 2nd mode ($n = 3$) of vibration. The frequencies for the 1st mode and 2nd mode were measured to be 86 Hz and 208 Hz, respectively. The resonance frequencies on various surfaces were measured, and the data are summarized in **Table 11**. For comparison, the theoretical values for the two modes were calculated using Eq. 39. For calculations, the surface tension of the water-air interface (γ) was taken to be 0.073 N/m, the mass density (ρ) was 1000 kg/m³ for water, and the volume of droplet (V) was 5 μ L. The theoretical values for 1st mode ($n = 2$) and 2nd mode ($n = 3$) from Eq. 39 are 110 and 214 Hz, respectively. These values are similar to those of flat surfaces with *n*-hexatriacontane and Lotus wax. However, with the same volume, the resonance frequencies of the structured surfaces are lower than those of flat surfaces. Celestini and Kofman (2006) showed that the resonance frequency depends on the contact angle of the structured surfaces, and it decreases with increasing contact angle. The hierarchical structures with highest contact angle have the lowest resonance frequency, consistent with the results by Celestini and Kofman (2006).

To observe how the vibration of the droplet influences the transition from the composite solid-air-liquid interface to the homogeneous solid-liquid interface, we performed vibrating droplet experiments on various surfaces with *n*-hexatriacontane and Lotus wax (Jung and Bhushan, 2009a). **Figure 72** shows optical micrographs of droplets on various surfaces with *n*-hexatriacontane before and after vibrating at a frequency of 30 Hz, which is less than the resonance frequency for 1st mode ($n = 2$). The vibration amplitude was increased until transition or until the droplet bounced off. First, on the flat

Vibration of a droplet on microstructured surface with *n*-hexatriacontane

Figure 71. Optical micrographs of droplets on the microstructured surface with *n*-hexatriacontane before and after vibration at amplitude of 0.4 mm for 1st mode ($n = 2$) and 2nd mode ($n = 3$) of vibration. The frequencies for 1st mode and 2nd mode were measured to be 86 Hz and 208 Hz, respectively (Jung and Bhushan, 2009a).

surface, it was found that the droplet did not change much after applying vibration at amplitudes ranging from 0 to 3 mm. As shown in the images for nanostructure ($0.12 \mu\text{g}/\text{mm}^2$) and microstructure, the static contact angles of the droplet before vibrating were 152° and 154° , respectively. After vibrating at amplitudes of 0.4 and 1.4 mm, the contact angles still have similar values (151° for nanostructure and 149° for microstructure), which suggests the formation of a solid-air-liquid interface. However, after vibrating at amplitudes of 2.4 mm for nanostructure ($0.12 \mu\text{g}/\text{mm}^2$) and 2.0 mm for microstructures, the static contact angles became 125° and 121° , respectively. This is because air pockets do not exist below the droplet as a result of droplet impalement by the structures, characterized by a smaller contact angle. These observations indicate the transition from the composite interface to the homogenous interface. Observations of vibration on two nanostructures (0.2 and $0.4 \mu\text{g}/\text{mm}^2$) and a hierarchical structure showed that the transition did not occur, but the droplet started to bounce off the surface from amplitudes of 2.2, 2.4, and 0.8 mm, respectively.

To study the validity of the proposed model (Eq. 44), the adhesive force responsible for the separation between the droplet and surface and the inertia force of a droplet vibrated on various structures were calculated (Jung and Bhushan, 2009a). The

Figure 72. Optical micrographs of droplets on various surfaces with *n*-hexatriacontane before and after vibrating at frequency of 30 Hz. The transition of a droplet on the nanostructure with $0.12 \mu\text{g}/\text{mm}^2$ mass of *n*-hexatriacontane and on the microstructure occurred at amplitudes of 2.4 mm and 2.0 mm, respectively (Jung and Bhushan, 2009a).

	Resonance frequency (Hz)		F _A (μN)	F _I (μN) at transition or bouncing off	ΔF = F _I - F _A
	1 st mode (n = 2)	2 nd mode (n = 3)			
<i>n</i> -Hexatriacontane					
Flat	103	271	260 ±3.7		
Nanostructure (0.12 μg/mm ²)	63	169	45±2.2	11	-34±2.2 (T)
Nanostructure (0.2 μg/mm ²)	50	147	10±1.6	10	0±1.6 (B)
Nanostructure (0.4 μg/mm ²)	54	149	13±2.0	11	-2±2.0 (B)
Microstructure	86	208	21±1.7	9	-12±1.7 (T)
Hierarchical structure	49	144	0.2±0.06	3.6	3.4±0.06 (B)
Lotus wax					
Flat	92	243	133±3.3		
Nanostructure	47	138	0.8±0.08	3.2	2.4±0.08 (B)
Microstructure (Lotus replica)	63	179	14±1.8	11	-3±1.8 (T and B)
Microstructure (Micropatterned Si replica)	66	183	10±1.6	10	0±1.6 (B)
Hierarchical structure (Lotus replica)	40	139	0.1±0.04	3.6	3.5±0.04 (B)
Hierarchical structure (Micropatterned Si replica)	38	137	0.04±0.01	2.7	2.6±0.01 (B)

B – Bouncing off

T – Transition

Table 11. Summary of the measured resonance frequency at the fixed amplitude value of 0.4 mm, the calculated inertia force of a vibrated droplet, and adhesive force between the droplet and surface on the various surfaces fabricated with *n*-hexatriacontane and Lotus wax. Positive value of ΔF means that the droplet bounced off before the transition occurs. The variation represents ± 1 standard deviation (Jung and Bhushan, 2009a).

Figure 73. Bar chart showing the calculated adhesive force responsible for the separation between the droplet and surface and inertia force of a droplet vibrated on various structures. The inertia forces were obtained as the transition or droplet bounce off occurred. If the inertia force of the droplet vibrated on the surface can overcome the adhesion force between the droplet and surface (ΔF is positive), the droplet can be vertically separated from the surface (bouncing off) before the composite solid-liquid-air interface is destroyed (Jung and Bhushan, 2009a).

adhesive force was obtained from Eq. 42 using static contact angle and contact angle hysteresis. The inertia forces were obtained from Eq. 43 using the amplitude and frequency of vibration as the transition or droplet bounce off occurred. The data are presented in **Fig. 73** and summarized in **Table 11**. As shown in **Fig. 72**, it was observed that the transition occurred as a result of droplet impalement by the structures by increasing the inertia force of droplet on the surfaces. However, if the inertia force of the droplet vibrated on the surface can overcome the adhesion force between the droplet and surface (ΔF is positive), the droplet can be vertically separated from the surface (bouncing off) before the composite solid-liquid-air interface is destroyed. The experimental results for bouncing off of the droplet appear to have the same trend as the proposed model (Eq. 44). It is shown that hierarchical structures have the positive value of the difference between the inertia force and adhesive force for droplet bounce off responsible for superior resistance to the dynamic effects and maintain stable composite solid-air-liquid interface.

5.6. Mechanically durable CNT-composite hierarchical structured surfaces

To create nano- and hierarchical structures with a high mechanical strength, multi-walled CNT were fabricated using catalyst-assisted chemical vapor deposition (CCVD) (Sun Nanotech Co Ltd, China). Iron catalyst was used to initiate growth of nanotubes using natural gas as carbon source and Ar/H₂ as buffer gas at 750° C. The contact angle of individual carbon nanotubes has been reported as 60° and higher. The multi-walled CNT composites were deposited on flat epoxy resin and microstructure using a spray method as shown in **Fig. 74** (Jung and Bhushan, 2010b). Microstructures were fabricated using a microstructured Si surface with pillars of 14 µm diameter and 30 µm height with 23 µm pitch by soft lithography (Bhushan et al., 2009b; Jung and Bhushan, 2010b). The first step of deposition of CNT composite using the spray method was to disperse the CNT into a solvent in order to maintain a uniform distribution. Acetone was used as a solvent because it does not affect surface modification and is easily vaporized in ambient conditions. The dispersion process consisted of the sonification of 200 mg CNT in 100 mL of acetone for 4 minutes using a Branson Digital Sonifier with a frequency of 20 kHz at amplitude of 80%. During this process, the mixture was exposed to ultrasonic pressure

waves in a sonifier in order to disperse the CNT into smaller aggregates. To provide strong bonding between CNT and the substrate, 200 mg EPON epoxy resin 1002F was added to the mixture of CNT and acetone, and then the mixture was sonificated for 4 more minutes. Next, the sonified mixture was poured into a spray gun and sprayed onto the specimen surfaces. The conditions for uniform deposition of the CNT on the surfaces were optimized by adjusting the concentration of CNT in the solvent. After spraying the CNT on the surfaces, the CNT composite structures were then annealed at 120 °C for 3 hours in order to improve the mechanical properties. This temperature, above the melting point (80 ~ 88 °C) and below the burning point (180 °C) of EPON epoxy resin 1002F, was selected to increase strong bonding between CNT and substrates. At this temperature, the epoxy which initially covered the CNT was melted and moved to the interface between the CNT and substrates, resulting in exposed CNTs which lead to high contact angle.

Figure 74. Schematic of spray method to deposit a mixture of CNT, epoxy, and acetone on surfaces (Jung and Bhushan, 2010b).

Figure 75 shows the SEM micrographs of nano- and hierarchical structures fabricated with CNT (Jung and Bhushan, 2010b). SEM micrographs show an overview (left column), a detail in higher magnification (middle column), and a large magnification of the nanostructures with CNT (right column). All surfaces show a homogenous distribution of CNT on the specimen. The CNT were well dispersed and embedded on flat and microstructured surfaces for the desired nanostructure. The CNT diameter varied between 10 and 30 nm, and an aspect ratio varied between 160 and 200.

Lotus leaves have been the inspiration for the development of superhydrophobic and self-cleaning products. Therefore, as a benchmark for mechanical durability studies, we used nano-, micro-, and hierarchical structures created by the self-assembly of Lotus wax with the amounts of $0.8 \mu\text{g}/\text{mm}^2$ deposited on flat epoxy resin and microstructure by thermal evaporation as shown in **Fig. 64** (Jung and Bhushan, 2010b).

Figure 75. SEM micrographs taken at 45° tilt angle, show three magnifications of nano- and hierarchical structures fabricated with CNT after three hours at 120°C (Jung and Bhushan, 2010b).

5.6.1. The influence of CNT-Composite hierarchical structure on the superhydrophobicity

To study the effect of CNT composite structures for superhydrophobicity, we measured the static contact angle and contact angle hysteresis on nano- and hierarchical structures with CNT (Jung and Bhushan, 2010b). For static contact angle and contact angle hysteresis, droplets of about 5 μL in volume (with the diameter of a spherical droplet about 2.1 mm) were gently deposited on the surface using a microsyringe. For contact angle hysteresis, the advancing and receding contact angles were measured at the front and back of the droplet moving along the tilted surface, respectively. **Figure 76(a)** shows that superhydrophobicity with a static contact angle of 166° and a contact angle hysteresis of 4° was found in the nanostructured surface with CNT. After introducing CNT nanostructure on top of the micropatterned Si replica, the higher static contact angle of 170° and lower contact angle hysteresis of 2° were found for the hierarchical structures with CNT. Both nano- and hierarchical structures created with CNT showed superhydrophobic and self-cleaning surface, which has a static contact angle of more than 150° and contact angle hysteresis of less than 10° (Jung and Bhushan, 2010b).

Figure 76(b) shows that for the hierarchical structure with Lotus wax, the highest static contact angles of 173° and lowest contact angle hysteresis of 1° were found. The recrystallized wax tubules are very similar to those of the original Lotus leaf, but are 0.5 to 1 μm longer, the static contact angle is higher, and the contact angle hysteresis is lower than reported for the original Lotus leaf (static contact angle of 164° and contact angle hysteresis of 3°) (Koch et al., 2009b). Superhydrophobicity with a static contact angle of 167° and a contact angle hysteresis of 5° was also found in the nanostructured surface with Lotus wax. The microstructured surface with Lotus wax layer has a static contact angle of 160° , but shows a much higher contact angle hysteresis of 29° than found in hierarchical structures. Melting of the Lotus wax led to a flat surface with a flat wax film and a much lower static contact angle of 119° and higher contact angle hysteresis of 71° . The data of a flat Lotus wax film on a flat replica show that the Lotus wax by itself is hydrophobic (Jung and Bhushan, 2010b).

Figure 76. Bar chart showing the measured static contact angle and contact angle hysteresis on (a) nano- and hierarchical structures fabricated with CNT after three hours at 120°C, and (b) various structures fabricated with 0.8 $\mu\text{g}/\text{mm}^2$ of Lotus wax after storage for seven days at 50°C with ethanol vapor. The error bar represents ± 1 standard deviation (Jung and Bhushan, 2010b).

5.6.2. Durability of various surfaces in waterfall/jet tests

To investigate the durability of the created surfaces in long-term exposure to water, and how different kinetic energies of the water hitting the surface affect wetting properties, we conducted waterfall/jet tests on the surfaces created with CNT and Lotus wax (Jung and Bhushan, 2010b). First, the nano- and hierarchical structures with CNT were continuously exposed to water pressure of 10 kPa for 24 h. **Figure 77(a)** (left side) shows static contact angle and contact angle hysteresis as a function of exposure time. In the case of nano- and hierarchical structures with CNT, it was observed that the static contact angles decreased slightly but remained more than 150° , and the contact angle hysteresis increased slightly but remained less than 15° . Next, the nano- and hierarchical structures with CNT were exposed to water with pressure ranging from 0 to 45 kPa for 20 min. **Figure 77(a)** (right side) shows static contact angle and contact angle hysteresis as a function of water pressure. As water pressure hitting the surfaces increased, the static contact angle and contact angle hysteresis decreased and increased slightly, respectively, but a significant change was not found on both nano- and hierarchical structures for superhydrophobicity. It can be interpreted that there was no deformation of CNT structures due to strong bonding with the substrate. As a result, superhydrophobic CNT composite structures showed good stability of wetting properties not only from long-term exposure to water but also high water pressure.

In order to compare durability of the created surfaces with CNT and Lotus wax, we also conducted waterfall/jet tests on the flat, nano-, micro-, and hierarchical structures with Lotus wax (Jung and Bhushan, 2010b). First, the surfaces with Lotus wax were continuously exposed to water pressure of 10 kPa for 24 h. **Figure 77(b)** (left side) shows static contact angle and contact angle hysteresis as a function of exposure time. As the exposure time increases up to 24 h, the static contact angle of all samples decreased slightly but remained more than 150° . However, based on contact angle hysteresis data, it was found that after an exposure time of 10 h, the values of nano- and hierarchical structures with Lotus wax increased rapidly to 27° and 12° and continued to increase to 49° and 24° at the exposure time of 24 h, respectively. This indicates that a portion of the wax nanostructured area started to be damaged, resulting in inducing the pinning of the droplet at the damaged area and then increasing contact angle hysteresis. Next, the

Figure 77. Static contact angle and contact angle hysteresis as a function of exposure time at water pressure of 10 kPa and water pressure of exposure for 20 min for the droplet with a 1 mm radius (5 μ L volume) gently deposited on the surfaces with (a) CNT and (b) Lotus wax. The data are reproducible within $\pm 5\%$ (Jung and Bhushan, 2010b).

surfaces with Lotus wax were exposed to the water with pressure ranging from 0 to 45 kPa for 20 min. **Figure 77(b)** (right side) shows static contact angle and contact angle hysteresis as a function of water pressure of exposure. As the water pressure increased up to 45 kPa, static contact angle and contact angle hysteresis of flat and microstructure with Lotus wax layer remained almost constant. However, as the water pressure increased up to 34 kPa, the static contact angle of nano- and hierarchical structures with Lotus wax first decreased slightly, and then the contact angle started decreasing sharply. It was also observed that the corresponding large change in contact angle hysteresis was found above 34 kPa. It is usually known that wax structures on the leaves can easily be induced by touching the leaf surface or by mechanical wear during transport of the leaves. As expected, it is observed that the nanostructure with Lotus wax can be damaged by water with high pressure, resulting in loss of superhydrophobicity.

5.6.3. Durability of various surfaces in AFM and ball-on-flat tribometer tests

To investigate the durability of the nanostructure fabricated using CNT, we conducted wear tests by creating $50 \times 50 \mu\text{m}^2$ wear scars with a $15 \mu\text{m}$ radius borosilicate ball for 1 cycle at two normal loads of 100 nN and 10 μN using AFM (Jung and Bhushan, 2010b). **Figure 78(a)** shows surface height maps before and after wear tests for nanostructures with CNT. As the normal load of 100 nN was applied on the nanostructure with CNT, the wear scar induced on the surface after the 100 nN normal load tests was not found or very low, and it was also hard to quantify a wear depth on the nanostructure with CNT scanned with a borosilicate ball. With increasing the normal load to 10 μN , it was found that the wear depth on the nanostructure with CNT was not significantly changed, but the morphology of the CNT differs slightly from that before wear test. It can be interpreted that the individual CNT might be expected to slide or bend by the borosilicate ball applied by high normal load of 10 μN during the test process.

For comparison, we also investigated the durability of the nanostructure fabricated using Lotus wax by applying two normal loads of 100 nN and 10 μN using AFM (Jung and Bhushan, 2010b). **Figure 78(b)** shows surface height maps before and after wear tests for nanostructures with Lotus wax. As the normal load of 100 nN was

Figure 78. Surface height maps before and after wear tests with a 15 μm radius borosilicate ball at 100 nN and 10 μN for nanostructures with (a) CNT and (b) Lotus wax using an AFM (Jung and Bhushan, 2010b).

applied on the nanostructure with Lotus wax, the change in the morphology of the structured surface was observed, and a small amount of debris was generated compared to the surface before wear test, indicating that the wax nanostructure has weak mechanical strength at even small load. With increasing the normal load to 10 μN , it was found that the depth of wear mark increased, and the nanostructure with Lotus wax was fully removed from the substrate. As expected, the nanostructure with Lotus wax exhibited the greater amount of wear compared to the nanostructure with CNT as evidenced by debris build-up around the edge of the wear test region. The damage of the structured surface can cause the sticking of water droplets in the wear region, resulting in low static contact angle and high contact angle hysteresis.

In order to investigate the durability of structured surfaces at a high load, we conducted conventional ball-on-flat tribometer experiments for the surfaces with CNT (Jung and Bhushan, 2010b). **Figure 79(a)** shows the coefficient of friction as a function of number of cycles for the nano- and hierarchical structures with CNT. The data are reproducible within $\pm 5\%$ based on three measurements. The coefficients of friction on both nano- and hierarchical structures with CNT first increased slightly for 20 cycles. Such a trend can be due to the elastic bending or buckling of CNT by contacting with a sapphire ball during the beginning of scan, resulting in an increase of the contact area. During the entire experiment, the coefficient of friction value of the nano- and hierarchical structures with CNT changed minimally, which indicates that the CNT was not being worn after 100 cycles. To investigate the change in the morphology of the surfaces after wear test, optical microscope images were obtained before and after wear test as shown in **Fig. 80(a)**. As expected, it was observed that there is no or low wear on nano- and hierarchical structures after wear tests. No or low wear on the CNT composite structure can possibly be due to the significant increase in the mechanical strength and wear resistance led from the uniform distribution and strong bonding of CNT on flat epoxy resin and microstructure. The elastic bending or buckling exhibited by CNT make them exceedingly tough materials and may be absorbing some of the force at contact acting as a compliant spring moderating the impact of the ball on the surface (Dresselhaus et al., 2000; Meyyappan, 2005; Chen et al., 2006).

Contact diameters and contact stresses of CNT at three loads used in AFM and ball-on-flat tribometer tests were calculated (Jung and Bhushan, 2010b). **Table 12** lists the physical properties of various specimens. It is assumed that contacts are single-asperity elastic contacts. For this case, the contact diameter (Bhushan, 1999, 2002),

$$d = 2 \left(\frac{3WR}{4E^*} \right)^{1/3} \quad (45)$$

where W is the total normal load, R is the asperity radius, and E^* is the effective elastic modulus. It should be noted that contact occurs on multiple asperities, and Eq. 45 gives an approximate value. The calculated contact diameter and contact stress are presented in **Table 12**. The deformation of CNT appears to be elastic at the three loads applied by borosilicate ball and sapphire ball.

In order to compare the durability of the created surfaces with CNT and Lotus wax at a high load, we conducted a wear study on the surfaces with Lotus wax using a conventional ball-on-flat tribometer (Jung and Bhushan, 2010b). As shown in **Fig. 79(b)**, the coefficient of friction value of the surfaces with Lotus wax exhibited a gradual increase when the sliding cycle increases up to about 70 cycles, and then remains constant. This indicates that the wax nanostructure and flat wax layer could be undergoing some wear due to weak bonding between them and the substrates. The change in the morphology of the surfaces with Lotus wax was observed in optical microscope images as shown in **Fig. 80(b)**. As shown in the AFM study at low loads (**Fig. 78(b)**), it is clearly observed that the flat wax layer and wax nanostructure on flat and microstructure were fully removed from the surfaces. As a result, superhydrophobic CNT composite structures showed better mechanical durability than the structured surfaces with Lotus wax to best withstand real world applications.

Figure 79. Coefficient of friction as a function of number of cycles using a ball-on-flat tribometer for the surfaces with (a) CNT and (b) Lotus wax at room temperature (22 ± 1 °C) and ambient air ($45 \pm 5\%$ RH). The data are reproducible within $\pm 5\%$ based on three measurements (Jung and Bhushan, 2010b).

Figure 80. Optical micrographs before and after wear test at 10 mN (100 cycles) using a ball-on-flat tribometer for the surfaces with (a) CNT and (b) Lotus wax (Jung and Bhushan, 2010b).

	Borosilicate ball with a 15 μm radius	Sapphire ball with a 1.5 mm radius	Carbon nanotube			
Elastic modulus (GPa)	70 ^a	390 ^b	1200 ^c			
Poisson's ratio	0.2 ^a	0.23 ^b	0.2 ^d			
Bending strength (GPa)			14.2 ^c			
	Contact diameter (μm)			Mean contact pressure (GPa)		
	Borosilicate ball at 100 nN	Borosilicate ball at 10 μN	Sapphire ball at 10 mN	Borosilicate ball at 100 nN	Borosilicate ball at 10 μN	Sapphire ball at 10 mN
Carbon nanotube	0.05	0.24	6.62	0.076	0.33	0.44

^aCallister, 2000

^bBhushan and Gupta, 1991

^cWong et al., 1997

^dZhang et al., 2008

Table 12. Typical physical properties of various specimens and calculated contact diameters and contact stresses at three loads used in AFM and ball-on-flat tribometer measurements. It is assumed that contacts are single-asperity contact (Jung and Bhushan, 2010b).

CHAPTER 6

FABRICATION AND CHARACTERIZATION OF BIOMIMETIC STRUCTURES FOR FLUID DRAG REDUCTION

Biomimetics allows one to mimic nature to develop materials and devices of commercial interest by engineers. Drag reduction in fluid flow is one of the examples found in nature. In this section, we discuss drag reduction efficiency on biomimetic structured surfaces in channels.

6.1. Experimental techniques

For the measurement of pressure drop using water and air flows, an experimental flow channel with a rectangular channel was designed and fabricated as shown in **Fig. 81** (Jung and Bhushan, 2010a). The fabricated surfaces were used for the upper and lower walls of the flow channel. Two pieces of plastic were glued between the upper and lower samples and at each end to prevent flow leak. For the measurement of pressure drop, the upper sample has two opening holes connected with a differential manometer (Model A 1000-13, Differential Pressure Plus Inc., USA). The thickness, width, and length of the resulting channel are designated as H , W , and L , respectively.

The inlet and outlet ports are machined and connected with the plastic tubes. To introduce water into the channel in laminar flow, a syringe pump (Model NE-300, New Era Pump Systems Inc., USA) was used at a range of flow rates between 50 $\mu\text{L/s}$ and 400 $\mu\text{L/s}$ (a range of flow velocity between 0.03 m/s and 0.23 m/s). The Reynolds number of the flow applied by the syringe pump is less than 300, which is the laminar flow. To create a turbulent flow, a larger flow rate is needed than can be accomplished with the syringe pump. To accomplish high fluid flow, a separate plastic chamber filled with a measured amount of water was set to allow flow through the channel under the force of

gravity. From measuring the amount of water and time to flow the water from a starting fluid level to an ending fluid level, the Reynolds number was calculated as 4200 (flow velocity of 3.8 m/s), which indicates that the flow is turbulent using this setup. In order to make air flow, laboratory air outlet was connected to the channel. A flowmeter (Model FL-1478-G, Omega Engineering, Inc., USA) was used to measure air flow rate between laboratory air outlet and channel. For the experimental measurements of air flow, the calculated range of Reynolds number was between 200 and 4600, which indicates both laminar and turbulent flows (Jung and Bhushan, 2010a).

Figure 81. Schematic of the experimental flow channel connected with a differential manometer. The thickness, width, and length of the channel are H , W , and L , respectively (Jung and Bhushan, 2010a).

6.2. Model for calculation of pressure drop and slip length

The pressure drop, Δp , of an incompressible fluid flow between two points along the channel of thickness, H , width, W , and length, L , for a hydrophilic flat surface can be calculated by (Blevins, 1984)

$$\Delta p = \frac{\rho V^2 f L}{2 D_H} \quad (46)$$

where ρ is the fluid density, V is the flow velocity obtained from flow rate (Q) divided by cross section area of the channel, and f is the friction factor which specifies the loss in

pressure required to impel a flow over the surface or through the channel. The friction factor is generally a function of Reynolds number, surface roughness, and the geometry of the surface. D_H is the hydraulic diameter which is proportional to four times the flow area divided by the perimeter of the surface containing the flow. For the rectangular channel, the hydraulic diameter is

$$D_H = \frac{2WH}{W + H} \quad (47)$$

The friction factor for laminar flow is inversely proportional to the Reynolds number as (Blevins, 1984)

$$f = \frac{k}{\text{Re}} \quad \text{for laminar flow} \quad (48)$$

$$\text{Re} = \frac{\rho V D_H}{\eta} \quad (49)$$

where η is the dynamic fluid viscosity. The Reynolds number can be used to determine whether the fluid flow will be within the laminar, turbulent, or transitional flow regimes. Since the Reynolds number is proportional to flow velocity, the pressure drop in laminar flow increases with flow velocity. k is the friction coefficient which can be found by the solution of Poisson's equation over the cross section as (Blevins, 1984)

$$k = \frac{64}{\frac{2}{3} + \frac{11}{23} \frac{H}{W} (2 - \frac{H}{W})} \quad (50)$$

From Eq. 50, the friction coefficient is dependent only on the shapes of the cross section but it is independent of surface roughness.

To improve in the calculation of the friction factor for turbulent flow in a rectangular channel, Jones (1976) developed an improved equivalent diameter, $D_e = 64D_H/k$, and the friction factor for turbulent flow can be modified as

$$f = \frac{64}{\text{Re}} \quad \text{for turbulent flow} \quad (51)$$

Next, we present an analysis to calculate slip length in the laminar flow. Using the Navier slip boundary condition, the slip length b of the two infinite parallel and smooth plates can be obtained as (Blevins, 1984; Ou et al., 2004)

$$b = \frac{4\eta QL}{\Delta p WH^2} - \frac{H}{3} \quad (52)$$

For a rectangular channel, the slip length would have the following general form (Ou et al., 2004)

$$b = \frac{c\eta QL}{\Delta p WH^2} - \frac{H}{3} \quad (53)$$

where c is a constant which needs to be obtained empirically. In order to obtain it, pressure drop measurement on a hydrophilic channel needs to be made. The Eq. 53 is then fitted under the assumption of zero slip length with the measured pressure drop data to obtain c . It was equal to 5 for the channel ($H = 0.7$ mm, $W = 2.5$ mm, $L = 60$ mm) used in this study. Now this equation is used to calculate the slip length for hydrophobic surfaces (Jung and Bhushan, 2010a).

6.3. Fabrication and characterization of biomimetic structures

A shark (*Squalus acanthias*, L. Squalidae) was used for creating a shark skin replica (Jung and Bhushan, 2010a). A shark is an aquatic animal, and its skin is permanently exposed to contamination from marine organisms, e.g., bacteria and algae. The shark was conserved in FAA (formaldehyde – acetic acid – ethanol) solution. The detailed structure varies from one location to another for the shark. The scales are present over most of the shark's body. To create a replica, the right front of shark body was selected. Before replicating the conserved shark skin, the selected area was first cleaned with acetone and then washed with deionized water. This process was repeated twice. The cleaned skin was placed in air for 1 hour for drying. For the negative replica, a polyvinylsiloxane dental wax was applied via a dispenser on the upper side of the shark skin and immediately pressed down with a glass plate. After complete hardening of the molding mass (at room temperature 3-5 minutes), the master surface and the mold (negative) were separated. The first negative replica was made only to remove any remaining contaminations from the shark surface by embedding the dirt into the replica material. A second and third replica of the same area was made to obtain negatives without contamination. For the positive replica, a liquid epoxy resin was used in the molding process.

To simulate a shark skin structure, a rib patterned surface was created using a FlashCut CNC milling machine (Jung and Bhushan, 2010a). Bechert et al. (1997) have reported that optimal groove depth for the rib surface should be about half of the lateral rib spacing for low drag. In the rib pattern design selected here, multiple stacks of ribs oriented along an axis were fabricated. For the fabrication, first a model of a rib patterned surface was designed in SolidWorks, and then the code for the rib's height, width, spacing and lengths, and channel dimensions was written using FeatureCAM in order to fabricate structures using the CNC milling machine. An acrylic resin was clamped onto the table of the CNC mill, and a fly cutter was used to make the top of the surface flat. The code was opened with FlashCut CNC and then the rib patterns were milled using an endmill with 130 μm bit.

Figure 82(a) shows the SEM micrographs of the shark skin (*Squalus acanthias*) replica taken at a top view, a 45° tilt angle side view, and a 45° tilt angle top view. The shark skin replica shows that scales are lifted up at the end, and there are only three ribs on each scale. It is clearly visible that the V-shaped riblets' height varies between 200-500 μm , and their space varies between 100-300 μm . The ribs are oriented nearly parallel to swimming direction of the sharks. **Figure 82(b)** shows the optical microscope images of the rib patterned surface fabricated as a model of artificial shark skin surfaces. The height, width, and length of the created ribs are 90, 38, and 850 μm , respectively. The spacing between the ribs is 180 μm .

To investigate drag reduction efficiency on the surfaces with superhydrophobicity, self-cleaning, and low adhesion described earlier, we used nano-, micro-, and hierarchical structures created by the self-assembly of Lotus wax with the amounts of 0.8 $\mu\text{g}/\text{mm}^2$ as shown in **Fig. 64**.

Table 13 summarizes the static contact angle and contact angle hysteresis measured on shark skin replica, rib patterned surface, and the structured surfaces with Lotus wax. The shark skin replica had a static contact angle of 89° and a contact angle hysteresis of 66° for a water droplet. For acrylic resin material, a static contact angle of 82° was found for flat acrylic resin. Introduction of the rib patterns on the flat surface led to a much higher static contact angle of 146° and lower contact angle hysteresis of 43°.

Figure 82. (a) SEM micrographs taken at top view, 45° tilt angle side view and 45° tilt angle top view, show shark skin (*Squalus acanthias*) replica. The shark skin replica show only three ribs on each scale. It is clearly visible that the V-shaped riblets' height varies between 200-500 μm and their space varies between 100-300 μm , and (b) optical microscope images (shown using two magnifications) show the rib patterned surface fabricated as a model of artificial shark skin surfaces (Jung and Bhushan, 2010a).

	Static contact angle (deg)	Contact angle hysteresis (deg)
(a) Epoxy resin		
Flat epoxy resin	76±0.9	67±2.9 (151*, 84**)
Flat with thin wax layer	119±2.4	56±3.2 (148*, 92**)
Nanostructure	167±0.7	6±1.1 (170*, 164**)
Microstructure	160±1.8	27±2.1 (169*, 142**)
Hierarchical structure	173±0.8	1±0.6 (174*, 173**)
Shark skin replica	89±1.7	66±3.4 (155*, 89**)
(b) Acrylic resin		
Flat acrylic resin	82±1.8	71±2.6 (122*, 51**)
Rib patterned surface	146±1.2	43±1.2 (158*, 115**)

Table 13. Summary of the static contact angles and contact angle hysteresis measured on the various surfaces. Nanostructures and hierarchical structures were fabricated with $0.8 \mu\text{g}/\text{mm}^2$ of Lotus wax after storage at 50°C with ethanol vapor. The variation represents ± 1 standard deviation (Jung and Bhushan, 2010a).

6.3.1. Pressure drop in the channel using water flow and calculated slip length

To observe the fluid drag reduction in the channel using water flow, experiments on flat epoxy resin, flat with thin wax layer, nanostructure, microstructure, hierarchical structure, and shark skin replica were performed (Jung and Bhushan, 2010a). In **Fig. 81**, the rectangular channels with these surfaces have dimensions of thickness of $H = 0.7 \text{ mm}$, width of $W = 2.5 \text{ mm}$, and length of $L = 60 \text{ mm}$. For calculation of the pressure drop using the Eq. 46, the mass density (ρ) and viscosity (η) for water are taken to be $1000 \text{ kg}/\text{m}^3$ and $0.001 \text{ Pa}\cdot\text{s}$ for water, respectively (Lide, 2009). **Figure 83** shows the pressure drop as a function of flow rate in the channel with various surfaces using water flow. The measured data are compared with the predicted pressure drop values for a hydrophilic surface obtained using Eq. 46 for laminar and turbulent flows (solid lines). The figure in the bottom is magnified in flow rate between 0 and $500 \mu\text{L}/\text{s}$. In both laminar and turbulent flows, the pressure drop increased linearly with flow rate for all samples. It was found that the pressure drop for the flat epoxy resin was similar to the value predicted by Eq. 46, while structured surfaces had values lower than the predicted. As mentioned

earlier and showed in **Table 13**, the introduction of roughness increases the hydrophobicity of the surfaces responsible for reduction in drag or pressure drop. The hierarchical structure with highest contact angle and lowest static contact angle hysteresis provided the highest reduction of pressure drop. It is believed that air pockets inside the grooves underneath the fluid reduce the contact area between fluid and surface, resulting in reduction of pressure drop. These results indicate that superhydrophobicity can lead to drag reduction in fluid flow (Jung and Bhushan, 2010a).

As shown in **Fig. 83**, for shark skin replica, it was found that the pressure drop in laminar flow was higher than those of the nanostructure and hierarchical structure and the reduction of pressure drop was about 12% as compared to the theoretical pressure drop. However, in turbulent flow, the reduction of pressure drop was similar to those of nanostructure and hierarchical structure. Bechert et al. (2000) showed that a turbulent boundary layer on the shark skin surface with ribs can help to reduce turbulent shear stress. The results of experimental measurements on shark skin replica showed that a reduction of pressure drop was obtained up to 30% in turbulent flow. It can be concluded that the surfaces with ribs are more benefit to produce a drag reduction in turbulent flow than that in laminar flow.

Based on a preliminary inspection of the pressure drop data, the slip length on the surfaces with different wettabilities was calculated using Eq. 53. For calculations, it is assume that there is a no-slip boundary condition on flat epoxy resin as verified from the experiments (Maali et al., 2009). **Figure 84** shows the bar chart showing the slip length in the channel with various surfaces using water flow in laminar flow ($0 < Re < 300$). The average values of slip length on the surfaces were calculated over all the experimental flow rates. A slip length of 24 μm was found for the flat surface with thin wax layer. The microstructure (covered with a Lotus wax film) and shark skin replica had slip lengths of 56 and 35 μm , but the nanostructure and hierarchical structures show much higher slip lengths of 91 and 103 μm , respectively, which implies the boundary slip increases with increasing hydrophobicity of solid surfaces. Zhu and Granick (2001) have reported that the slip length increases from nanometer range to micrometer range as the flow rate increases.

Figure 83. Pressure drop as a function of flow rate in the channel with various surfaces using water flow. The figure in the bottom is magnified in flow rate between 0 and 500 $\mu\text{L/s}$. Data are compared with predicted pressure drop values for a hydrophilic surface obtained using the Eq. 46 for laminar and turbulent flows (solid lines) (Jung and Bhushan, 2010a).

Figure 84. Bar chart showing the slip length in the channel with various surfaces using water flow in laminar flow ($0 < Re < 300$). The slip length was calculated using the Eq. 53 and the pressure drop measured on various surfaces. The error bar represents ± 1 standard deviation (Jung and Bhushan, 2010a).

To observe the fluid drag reduction in the channel using water flow, experiments on flat acrylic resin and rib patterned surfaces fabricated as a model of artificial shark skin were also performed (Jung and Bhushan, 2010a). In **Fig. 81**, the rectangular channels with these surfaces have dimensions of thickness of $H = 1$ mm, width of $W = 2$ mm, and length of $L = 100$ mm. **Figure 85** shows the pressure drop as a function of flow rate in the channel using water flow. The measured data are compared with predicted pressure drop values for a hydrophilic surface obtained using Eq. 46 for laminar and turbulent flows (solid lines). The figure in the bottom is magnified in flow rate between 0 and $500 \mu\text{L/s}$. In laminar flow, it was found that the pressure drop increased linearly with flow rate and was similar to the value predicted by Eq. 46. However, in turbulent flow, the reduction of pressure drop was obtained up to 23% as compared to the theoretical pressure drop. This result shows a similar trend to that of the shark skin replica.

Figure 85. Pressure drop as a function of flow rate in the channel with flat acrylic resin and rib patterned surface using water flow. The figure in the bottom is magnified in flow rate between 0 and 500 $\mu\text{L/s}$. Data are compared with predicted pressure drop values for a hydrophilic surface obtained using the Eq. 46 for laminar and turbulent flows (solid lines) (Jung and Bhushan, 2010a).

6.3.2. Pressure drop in the channel using air flow

To investigate the effect of air flow in the channel and compare them to water drag reduction, experiments with air flow on various surfaces were performed (Jung and Bhushan, 2010a). In **Fig. 81**, the rectangular channels have dimensions of thickness of $H = 0.7$ mm, width of $W = 2.5$ mm, and length of $L = 60$ mm. For calculation of pressure drop using Eq. 46, the mass density (ρ) and viscosity (η) for water are taken to be 1.204 kg/m^3 and $1.837 \times 10^{-5} \text{ Pa}\cdot\text{s}$ for air, respectively (Lide, 2009). **Figure 86** shows the pressure drop as a function of flow rate in the channel with various surfaces using air flow. The measured data are compared with predicted pressure drop values for a hydrophilic surface obtained using Eq. 46 for laminar and turbulent flows (solid lines). The figure in the bottom is magnified in flow rate between 0 and 50 mL/s. The pressure drop of the structured surfaces is higher than that of the hydrophilic surface in the turbulent flow which is opposite to that in liquid flow. In both laminar and turbulent flows, the pressure drop increased linearly with flow rate for all samples. As mentioned earlier, in the case of water flow, air pockets between the structures reduce the contact area between liquid and surface, resulting in reduction of the flow drag. The data shows that the structures are not beneficial for drag reduction in air flow. The introduction of roughness on the surfaces increases the pressure drop in the channel in the turbulent flow. It is generally known that the surfaces with a streamlined body can produce dramatic reductions of the fluid pressure drag with only a slight increase in shear stress in air flow (Bertin, 1979). It is also known that as the Reynolds number increases, the pressure drop becomes very large, resulting in larger pressure drag. The roughness structures on the surfaces may cause air to move around them, resulting in the formation of vortices and large fluid drag.

To observe the fluid drag reduction in the channel using air flow, experiments on flat acrylic resin and fabricated rib patterned surface were also performed (Jung and Bhushan, 2010a). The rectangular channels with these surfaces have dimensions of thickness of $H = 1$ mm, width of $W = 2$ mm, and length of $L = 100$ mm. **Figure 87** shows the pressure drop as a function of flow rate in the channel with flat acrylic resin and rib patterned surface using air flow. The measured data are compared with predicted pressure drop values for a hydrophilic surface obtained using the Eq. 46 for laminar and turbulent

flows (solid lines). The experimental results show a similar trend to the data as shown in **Fig. 86**. It was found that the pressure drop of the rib patterned surface slightly increased due to the vortices formed at the end of the ribs in turbulent flow as compared to the theoretical pressure drop.

Figure 86. Pressure drop as a function of flow rate in the channel with various surfaces using air flow. The figure in the bottom is magnified in flow rate between 0 and 50 mL/s. Data are compared with predicted pressure drop values for a hydrophilic surface obtained using the Eq. 46 for laminar and turbulent flows (solid lines) (Jung and Bhushan, 2010a).

Figure 87. Pressure drop as a function of flow rate in the channel with flat acrylic resin and rib patterned surface using air flow. Data are compared with predicted pressure drop values for a hydrophilic surface obtained using the Eq. 46 for laminar and turbulent flows (solid lines) (Jung and Bhushan, 2010a).

CHAPTER 7

MODELING, FABRICATION AND CHARACTERIZATION OF OLEOPHOBIC/PHILIC SURFACES

Oleophobic surfaces have the potential for self-cleaning and anti-fouling from biological and organic contaminants both in air and underwater applications. In this section, we discuss a model for predicting the oleophobic/philic nature and experimental measurements of the wetting properties of the surfaces.

7.1. Modeling of contact angle for various interfaces

If a water droplet is placed on a solid surface in air, the solid-air and water-air interfaces come together with a static contact angle, θ_w . The value of θ_w can be determined from the condition of the total energy of the system being minimized (Adamson, 1990; Israelachvili, 1992) and is given by the Young's equation for the contact angle, θ_w .

$$\cos \theta_w = \frac{\gamma_{SA} - \gamma_{SW}}{\gamma_{WA}} \quad (54)$$

where γ_{SW} , γ_{SA} , and γ_{WA} are surface tensions of the solid-water, solid-air, and water-air interfaces, respectively. If an oil droplet is placed on a solid surface in air, the Young's equation for the contact angle, θ_o , can be expressed by

$$\cos \theta_o = \frac{\gamma_{SA} - \gamma_{SO}}{\gamma_{OA}} \quad (55)$$

where γ_{SO} , γ_{SA} , and γ_{OA} are surface tensions of the solid-oil, solid-air, and oil-air interfaces, respectively. As predicted by Eq. 55, if γ_{SO} is higher than γ_{SA} , an oleophobic surface can be achieved.

To create an oleophobic surface in water, let us consider the solid-water-oil interface. If an oil droplet is placed on a solid surface in water, the contact angle of an oil droplet in water, θ_{OW} , is given by the Young's equation

$$\cos \theta_{OW} = \frac{\gamma_{SW} - \gamma_{SO}}{\gamma_{OW}} \quad (56)$$

where γ_{SO} , γ_{SW} , and γ_{OW} are surface tensions of the solid-oil, solid-water, and oil-water interfaces, respectively. Combining Eqs. 54, 55 and 56, the equation for the contact angle, θ_{OW} , of an oil droplet in water is given as

$$\cos \theta_{OW} = \frac{\gamma_{OA} \cos \theta_O - \gamma_{WA} \cos \theta_W}{\gamma_{OW}} \quad (57)$$

As predicted by Eq. 57, for a hydrophilic surface ($\gamma_{SA} > \gamma_{SW}$), an oleophobic surface in the solid-water-oil interface can be created if $\gamma_{OA} \cos \theta_O$ is lower than $\gamma_{WA} \cos \theta_W$. Since the surface tension of oil and organic liquids is much lower than that of water, most hydrophilic surfaces can be made oleophobic in a solid-water-oil interface. For a hydrophobic surface ($\gamma_{SA} < \gamma_{SW}$) and an oleophobic surface in a solid-air-oil interface ($\gamma_{SA} < \gamma_{SO}$), an oleophobic surface in a solid-water-oil interface can be created if $\gamma_{OA} \cos \theta_O$ is higher than $\gamma_{WA} \cos \theta_W$ and vice versa. For a hydrophobic and an oleophilic surface in solid-air-oil interface, an oleophobic surface in solid-water-oil interface cannot be created. Schematics are shown in **Fig. 88**, and the summary of philic/phobic nature in various interfaces is shown in **Table 14**. For an oleophobic surface, oil contaminants are washed away when immersed in water. This effect leads to self-cleaning that can be used against marine ship fouling (Jung and Bhushan, 2009b).

7.2. Experimental techniques

For the measurement of static contact angle, deionized water was used for water droplet and hexadecane was used for oil droplets (Jung and Bhushan, 2009b). The surface tensions of the water-air interface (γ_{WA}), oil-air interface (γ_{OA}), and oil-water interface (γ_{OW}) are 73 (Lide, 2009), 27.5 (Lide, 2009), and 51.4 (Tajima et al., 1980) mN/m, respectively. The mass densities are 1000 and 773 kg/m³ for water and hexadecane, respectively. Water and oil droplets of about 5 μ L in volume (with radius of a spherical

Figure 88. Schematics of a droplet of liquid showing philic/phobic nature in three different phase interface on the surface – θ_w , θ_O , and θ_{OW} are static contact angles of water droplet, oil droplet, and oil droplet in water, respectively (Jung and Bhushan, 2009b).

<u>Solid-air-water interface</u>		<u>Solid-water-oil interface</u>
Hydrophilic ($\gamma_{SA} > \gamma_{SW}$)	→	Oleophobic if $\gamma_{OA}\cos\theta_O < \gamma_{WA}\cos\theta_W$ Oleophilic if $\gamma_{OA}\cos\theta_O > \gamma_{WA}\cos\theta_W$
<u>Solid-air-water interface</u>	<u>Solid-air-oil interface</u>	<u>Solid-water-oil interface</u>
Hydrophobic ($\gamma_{SA} < \gamma_{SW}$)	→	<div style="display: flex; align-items: center;"> <div style="margin-right: 10px;"> Oleophobic if $\gamma_{SA} < \gamma_{SO}$ Oleophilic if $\gamma_{SA} > \gamma_{SO}$ </div> <div style="margin-right: 10px;">→</div> <div> Oleophobic if $\gamma_{OA}\cos\theta_O > \gamma_{WA}\cos\theta_W$ Oleophilic if $\gamma_{OA}\cos\theta_O < \gamma_{WA}\cos\theta_W$ </div> </div>
		Oleophilic

Table 14. Summary of philic/phobic nature in various interfaces (Jung and Bhushan, 2009b).

droplet about 1 mm) in air environment were gently deposited on the specimen using a microsyringe. The process of wetting behavior of an oil droplet in water was obtained in a solid-water-oil interface system as shown in **Fig. 89** (Jung and Bhushan, 2009b). A specimen was first immersed in water phase. Then an oil droplet was gently deposited using a microsyringe from the bottom of the system because the density of oil (hexadecane) is lower than that of water. The image of the droplet was obtained by a digital camcorder (Sony, DCRSR100, Tokyo, Japan) with a 10x optical and 120x digital zoom. Images obtained were analyzed for the contact angle using Imagetool® software (University of Texas Health Science Center). The measurements were reproducible to within $\pm 2^\circ$.

7.3. Fabrication and characterization of oleophobic surfaces

A two-step molding process was used to replicate microstructures with varying pitch values. In this technique first a negative is generated and then a positive. As a master template for the flat and micropatterned surfaces, a flat Si surface and micropatterned Si surfaces with pillars of 14 μm diameter and 30 μm height with different pitch values (21, 23, 26, 35, 70, 105, 126, 168 and 210 μm), fabricated by photolithography, were used (Jung and Bhushan, 2009b). A polyvinylsiloxane dental wax

Figure 89. Schematics of a solid-water-oil interface system. A specimen is first immersed in water phase, and then an oil droplet is gently deposited using a microsyringe, and the static contact angle in the system is measured (Jung and Bhushan, 2009b).

(President Light Body[®] Gel, ISO 4823, Polyvinylsiloxan (PLB), Coltene Whaledent, Hamburg, Germany) was applied via a dispenser on the surface and immediately pressed down with a glass plate. After complete hardening of the molding mass (3-5 minutes at room temperature), the silicon master surface and the mold (negative) were separated. After a relaxation time of 30 minutes for the molding material, the negative replicas were filled with a liquid epoxy resin (Epoxydharz L[®], No. 236349, Conrad Electronics, Hirschau, Germany) with hardener (Harter S, Nr 236365, Conrad Electronics, Hirschau, Germany). Specimens with microstructures were immediately transferred into a vacuum chamber at 750 mTorr (100 Pa) pressure for 10 seconds to remove trapped air and to increase the resin infiltration through the structures. After hardening at room temperature (24 h at 22 °C), the positive replica was separated from the negative replica. To generate several replicas the second step of replication was repeated twenty times for each surface type.

To study surfaces with some oleophobicity, a surface coating which has a lower surface tension than that of oil is needed. For this purpose, we deposited *n*-perfluoroeicosane (C₂₀F₄₂) (268828, Sigma-Aldrich, USA) on the specimen surfaces by thermal evaporation (Jung and Bhushan, 2009b). The surface energy of *n*-

perfluoroeicosane is 6.7 mJ/m^2 (6.7 mN/m) (Nishino et al., 1999). The specimens were mounted on a specimen holder with double-sided tape and placed in a vacuum chamber at 30 mTorr (4 kPa pressure), 2 cm above a heating plate loaded with $6000 \text{ }\mu\text{g}$ *n*-perfluoroeicosane (Bhushan et al., 2009b). The *n*-perfluoroeicosane was evaporated by heating it up to $170 \text{ }^\circ\text{C}$. In a vacuum chamber the evaporation from the point source to the substrate occurs in straight line; thus, the amount of sublimated material is equal in a hemispherical region over the point of source (Bunshah, 1994). In order to estimate the amount of sublimated mass, the surface area of the half sphere was calculated by using the formula $2\pi r^2$, whereby the radius (*r*) represents the distance between the specimen to be covered and the heating plate with the substance to be evaporated. The calculated amount of *n*-perfluoroeicosane deposited on the surfaces was $2.4 \text{ }\mu\text{g/mm}^2$ (amount of *n*-perfluoroeicosane loaded on a heating plate divided by surface area).

Hierarchical structures were fabricated using a two step fabrication process, including the production of microstructured surfaces by soft lithography and the subsequent development of nanostructures on top by self assembly of *n*-hexatriacontane with the amounts of $0.2 \text{ }\mu\text{g/mm}^2$ deposited by thermal evaporation, as described above (Bhushan et al., 2008a, 2009b).

We created a shark skin replica using a shark (*Squalus acanthias*, L., Squalidae) (Jung and Bhushan, 2009b). The shark was conserved in FAA (formaldehyde – acetic acid – ethanol) solution. Before replicating the conserved shark skin, the area of interest was first cleaned with acetone and then washed with deionized water. This process was repeated twice. The cleaned skin was placed in air for 1 hour for drying. For the negative replica, a polyvinylsiloxane dental wax was applied via a dispenser on the upper side of the shark skin and immediately pressed down with a glass plate. After complete hardening of the molding mass (at room temperature 3-5 minutes), the master surface and the mold (negative) were separated. The first negative replica was made only to remove any remaining contaminations from the shark surface by embedding the dirt into the replica material. A second and third replica of the same area was made to obtain negatives without contamination. For the positive replica, the process was followed as described above, and epoxy was used.

Figure 90. SEM micrographs taken at a 45° tilt angle showing two magnifications of (a) the micropatterned surface, (b) hierarchical structure and nanostructure with three-dimensional platelets on the surface fabricated with 0.2 $\mu\text{g}/\text{mm}^2$ mass of *n*-hexatriacontane, and (c) shark skin (*Squalus acanthias*) replica. The shark skin replica shows only three ribs on each scale. It is clearly visible that the V-shaped riblets' height varies between 200-500 μm and their space varies between 100-300 μm (Jung and Bhushan, 2009b).

Figure 90(a) shows the SEM micrographs taken at a 45° tilt angle, showing two magnifications of the micropatterned surface. **Figure 90(b)** shows the hierarchical structures and nanostructures covered with *n*-hexatriacontane platelets. The nanostructure is formed by three-dimensional platelets of *n*-hexatriacontane. Platelets are flat crystals, grown perpendicular to the substrate surface. The platelet thickness varied between 50 and 100 nm, and their length varied between 500 and 1000 nm. As shown in **Fig. 90(c)**, the shark skin replica shows only three ribs on each scale. It is clearly visible that the V-shaped riblets' height varies between 200-500 μm , and their space varies between 100-300 μm (Jung and Bhushan, 2009b).

7.3.1. Wetting behavior on flat and micropatterned surfaces

To observe the wetting behavior of water and oil droplets for philic/phobic nature in three phase interfaces, we performed experiments with droplets on both hydrophilic and hydrophobic and oleophilic surfaces in air (Jung and Bhushan, 2009b). **Figure 91** shows the optical micrographs of droplets in three different phase interfaces on flat epoxy resin and micropatterned surfaces. In a solid-air-water interface, the water droplet was hydrophilic for the flat epoxy resin and was superhydrophobic for the micropatterned surface with 23 μm pitch. It is known that air pocket formation between the pillars makes a high static contact angle for micropatterned surface. However, in a solid-air-oil interface, the oil droplet was oleophilic for both surfaces. In the solid-water-oil interface system, in which the oil droplet sits on water trapped in the pillars, it is observed that the oil droplet in water was oleophobic and had contact angles of 109° and 151° for flat epoxy resin and micropatterned surface with 23 μm pitch, respectively.

To study optimization of oleophobicity in the two solid-air-water and solid-air-oil interfaces, the static contact angles for water and oil droplets were measured on the micropatterned surfaces (Jung and Bhushan, 2009b). **Figure 92** shows the measured static contact angle as a function of pitch between the pillars for a water droplet (circle) and an oil droplet (cross) in air. The data are compared with predicted static contact angle values obtained using Wenzel and Cassie-Baxter equations (Eqs. 24 and 25) (solid lines) with a measured value of θ_0 for the micropatterned surfaces. In a solid-air-water interface

Figure 91. Optical micrographs of droplets in three different phase interfaces on flat epoxy resin and micropatterned surface without and with C₂₀F₄₂. Left image: a water droplet is placed on a surface in air. Middle image: an oil droplet is placed on a surface in air. Right image: an oil droplet is placed on a solid surface in water (Jung and Bhushan, 2009b).

for a water droplet, the flat epoxy resin showed a static contact angle of 76° . The static contact angle on micropatterned surfaces is higher than that of the flat surfaces. It first increases with an increase in the pitch values, then starts to drop rapidly to a value slightly higher than that of the flat surfaces. In the first portion, it jumps to a high value of 150° corresponding to a superhydrophobic surface and continues to increase to 160° at a pitch of $26\text{ }\mu\text{m}$ because open air space increases with an increase in pitch responsible for propensity of air pocket formation. The sudden drop at a pitch value of about $30\text{ }\mu\text{m}$ corresponds to the transition from the Cassie-Baxter to the Wenzel regime. The experimental observations for the transition are comparable to the value predicted from Wenzel and Cassie-Baxter equations.

In a solid-air-oil interface for an oil droplet, the flat epoxy resin showed a static contact angle of 13° . As shown in **Fig. 92**, the oil droplets on all micropatterned surfaces were oleophilic, and the contact angle was lower than that of the flat surfaces. It increases with an increase in the pitch values as predicted from Wenzel equation. As mentioned earlier, the surface tension of the oil-air interface is very low for hexadecane. Therefore, it is observed that from Eq. 55 the surface tension of solid-oil interface (γ_{SO}) is lower than that of solid-water interface (γ_{SA}), resulting in oleophilic state for all micropatterned surfaces.

To study optimization of oleophobicity in a solid-water-oil interface, the static contact angles for oil droplets in water were measured on the micropatterned surfaces (Jung and Bhushan, 2009b). **Figure 92** shows the measured static contact angle as a function of pitch between the pillars for an oil droplet in water (triangle). The data are compared with the predicted static contact angle values obtained using the Wenzel and Cassie-Baxter equations (Eqs. 24 and 25) (solid lines), with a measured value of θ_0 for the micropatterned surfaces. In a solid- water-oil interface, the oil droplet on the flat epoxy resin was oleophobic and had a static contact angle of 109° . The static contact angle of micropatterned surfaces in the solid-water-oil interface showed a similar trend to that in the solid-air-water interface. As the pitch increases up to $26\text{ }\mu\text{m}$, the static contact angle first increases gradually from 146° to 155° because the oil droplet sits on water trapped in the pillars, and open space increases with an increase in pitch. Then, the

contact angle starts decreasing rapidly due to the transition from the Cassie-Baxter to the Wenzel regime. The experimental observations for the transition are comparable to the values predicted from Wenzel and Cassie-Baxter equations. The micropatterned surfaces studied here were either hydrophilic or hydrophobic and both were oleophilic. In the solid-water-oil interface, they were oleophobic. As shown in **Fig. 88** and **Table 14**, it is observed that the data are not consistent with the model for hydrophobic surfaces. However, hydrophilic surfaces became oleophobic in the solid-water-oil interface because $\gamma_{OA}\cos\theta_O$ is higher than $\gamma_{WA}\cos\theta_W$.

Figure 92. Static contact angle as a function of geometric parameters for water droplet (circle) and oil droplet (cross) in air, and oil droplet in water (triangle) compared with predicted static contact angle values obtained using Wenzel and Cassie-Baxter equations (solid lines) with a measured value of θ_0 for the micropatterned surfaces (Jung and Bhushan, 2009b).

7.3.2. Wetting behavior on flat and micropatterned surfaces with $C_{20}F_{42}$

To study surfaces with some oleophobicity, *n*-perfluoroeicosane ($C_{20}F_{42}$), which has lower surface tension than that of oil, was deposited on the surfaces, and experiments with droplets on hydrophobic and both oleophilic and oleophobic surfaces in air were performed (Jung and Bhushan, 2009b). **Figure 91** shows the optical micrographs of droplets in three different phase interfaces on a flat epoxy resin and a micropatterned surface with $C_{20}F_{42}$. In a solid-air-water interface and a solid-air-oil interface, the water droplet and oil droplet showed contact angles of 122° and 76° for the flat epoxy resin with $C_{20}F_{42}$ and contact angles of 162° and 133° for the micropatterned surface with $23\ \mu\text{m}$ pitch with $C_{20}F_{42}$, respectively. However, in a solid-water-oil interface, the oil droplet in water was oleophilic and had contact angles of 4° and 9° for both surfaces, respectively. To explain why the oleophobic surfaces in air became oleophilic in water, the theoretical values for both surfaces were calculated using Eq. 57. For calculations, the surface tensions of the water-air interface (γ_{WA}), oil-air interface (γ_{OA}), and oil-water interface (γ_{OW}) were taken to be 73, 27.5, and 51.4 mN/m, and the contact angles for water and oil droplets in air were taken from the measured values. The theoretical values for the flat epoxy resin and the micropatterned surface with $23\ \mu\text{m}$ pitch with $C_{20}F_{42}$ are 28° and 10° , respectively. These values are similar to those from the experiments. This indicates that the oleophobic surfaces become oleophilic in water.

To study optimization of oleophobicity in two solid-air-water and solid-air-oil interfaces, the static contact angles for water and oil droplets were measured on the micropatterned surfaces with different pitch values and with $C_{20}F_{42}$ (Jung and Bhushan, 2009b). **Figure 93** shows the measured static contact angle as a function of pitch between the pillars for a water droplet (circle) and an oil droplet (cross) in air. The data are compared with the predicted static contact angle values obtained using the Wenzel and Cassie-Baxter equations (Eqs. 24 and 25) (solid lines) with a measured value of θ_0 for the micropatterned surfaces with $C_{20}F_{42}$. In a solid-air-water interface for the water droplet, the flat epoxy resin with $C_{20}F_{42}$ showed a static contact angle of 122° . The static contact angle of micropatterned surfaces with $C_{20}F_{42}$ first increases from 158° to 169° with an increase in the pitch values, then starts to drop rapidly at a pitch value of $110\ \mu\text{m}$. From

comparison of the experimental data to the Wenzel and Cassie-Baxter equations, this corresponds to the transition from Cassie-Baxter to Wenzel regime. All surfaces with $C_{20}F_{42}$ had an increase in contact angle, and the transition took place at higher pitch value than that of the micropatterned surfaces (**Fig. 92**).

In a solid-air-oil interface for an oil droplet, the flat epoxy resin with $C_{20}F_{42}$ showed a static contact angle of 76° . As shown in **Fig. 93**, the highest contact angle of micropatterned surfaces with $C_{20}F_{42}$ was 133° at a pitch value of $23\ \mu\text{m}$. Then, it decreases with an increase in the pitch values, and these values are comparable with the values predicted Wenzel equations. The contact angles of all micropatterned surfaces with $C_{20}F_{42}$ are higher than that of the flat surfaces.

To study optimization of oleophobicity in a solid-water-oil interface, the static contact angles for oil droplets in water were measured on the micropatterned surfaces with different pitch values and with $C_{20}F_{42}$ (Jung and Bhushan, 2009b). **Figure 93** shows the measured static contact angle as a function of pitch between the pillars for an oil droplet in water (triangle). The data are compared with the predicted static contact angle values obtained using the Wenzel and Cassie-Baxter equations (Eqs. 24 and 25) (solid lines) with a measured value of θ_0 for the micropatterned surfaces with $C_{20}F_{42}$. In a solid-water-oil interface, the flat epoxy resin with $C_{20}F_{42}$ was oleophilic and had a static contact angle of 4° . All micropatterned surfaces with $C_{20}F_{42}$ were oleophilic and had contact angle lower than 10° . The reason why hydrophobic and oleophobic surfaces in air became oleophilic in water can be explained from **Fig. 88** and **Table 14**. The contact angle for a water droplet is higher than that for an oil droplet on all surfaces with $C_{20}F_{42}$, and the surface tension of the water-air interface (γ_{WA}) is higher than that of the oil-air interface (γ_{OA}). Therefore, it is observed that $\gamma_{WA}\cos\theta_W$ is higher than $\gamma_{OA}\cos\theta_O$, and then the surfaces become oleophilic in the solid-water-oil interface.

Figure 93. Static contact angle as a function of geometric parameters for water droplet (circle) and oil droplet (cross) in air, and oil droplet in water (triangle) compared with predicted static contact angle values obtained using Wenzel and Cassie-Baxter equations (solid lines) with a measured value of θ_0 for the micropatterned surfaces with $C_{20}F_{42}$ (Jung and Bhushan, 2009b).

7.3.3. Wetting behavior on nano- and hierarchical structures and shark skin replica

To observe the wetting behavior of water and oil droplets for nano- and hierarchical structures found from Lotus plant surfaces, experiments with the droplets on the surfaces were performed in the three phase interface (Jung and Bhushan, 2009b).

Figure 94 shows the optical micrographs of droplets in three different phase interfaces on a nanostructure and a hierarchical structure fabricated with $0.2 \mu\text{g}/\text{mm}^2$ mass of *n*-hexatriacontane. Both nano- and hierarchical structures were superhydrophobic and had a static contact angle of 158° and 169° in the solid-air-water interface, respectively. However, they are oleophilic in the solid-air-oil interface because the surface energy of *n*-hexatriacontane is $31.4 \text{ mJ}/\text{m}^2$ ($31.4 \text{ mN}/\text{m}$) (Wu, 1979), and this value is higher than that of an oil droplet (hexadecane). In the solid-water-oil interface, nano- and hierarchical structures had a static contact angle of 10° and 5° , respectively. As shown in **Fig. 88** and **Table 14**, it is observed that both surfaces are oleophilic in solid-water-oil interface.

To study the surface structure on an aquatic animal, experiments with water and oil droplets on the shark skin replica were performed in a three phase interface (Jung and Bhushan, 2009b). **Figure 95** shows the optical micrographs of droplets in three different phase interfaces on a shark skin replica without and with $\text{C}_{20}\text{F}_{42}$. First, the shark skin replica had contact angles of 89° and $\sim 0^\circ$ for water and oil droplets, respectively. After the surface was coated with $\text{C}_{20}\text{F}_{42}$, the contact angles of water and oil droplets became 142° and 115° , respectively. In the solid-water-oil interface, the oil droplet in water on the shark skin replica became oleophobic and had a contact angle of 109° . Based on Eq. 57, the calculated value was 59° for the oil droplet in water on a shark skin replica. This difference may come from the open space under the scales of the shark skin replica responsible for the propensity of trapped water pocket formation as shown in **Fig. 69**. Shark skin replica with $\text{C}_{20}\text{F}_{42}$ was oleophilic and had a contact angle of $\sim 0^\circ$. This state is the same as the micropatterned surfaces with $\text{C}_{20}\text{F}_{42}$ as shown in **Fig. 88** and **Table 14**.

Figure 94. Optical micrographs of droplets in three different phase interfaces on nanostructure and hierarchical structure fabricated with $0.2 \mu\text{g}/\text{mm}^2$ mass of *n*-hexatriacontane. Left image: a water droplet is placed on a surface in air. Middle image: an oil droplet is placed on a surface in air. Right image: an oil droplet is placed on a solid surface in water (Jung and Bhushan, 2009b).

Figure 95. Optical micrographs of droplets in three different phase interfaces on shark skin replica without and with $C_{20}F_{42}$. Left image: a water droplet is placed on a surface in air. Middle image: an oil droplet is placed on a surface in air. Right image: an oil droplet is placed on a solid surface in water (Jung and Bhushan, 2009b).

CHAPTER 8

CLOSURE

Biomimetics allows one to mimic biology or nature to develop materials and devices of commercial interest by engineers. Properties of biological materials and surfaces result from a complex interplay between surface morphology and physical and chemical properties. Hierarchical structures with dimensions of features ranging from the macroscale to the nanoscale are extremely common in nature to provide properties of interest. There are a large number of objects including bacteria, plants, land and aquatic animals and seashells, with properties of commercial interest. This thesis has focused on surfaces with superhydrophobicity, self-cleaning, low adhesion, and drag reduction, such as Lotus leaf and shark skin. The development of superhydrophobic and self-cleaning surfaces is important for basic research as well as various applications, including self-cleaning windows, exterior paints for buildings, navigation ships, textiles, solar panels, and applications requiring antifouling and a reduction in fluid flow, e.g., in micro/nanochannels. These surfaces can also be used in energy conversion and conservation.

In this thesis, the theoretical mechanisms of wetting of rough surfaces and characterization of natural and artificial surfaces with superhydrophobicity, self-cleaning, low adhesion and drag reduction has been presented. Theoretical approaches have been presented to understand these phenomena such as the transition between the Wenzel and Cassie-Baxter wetting regimes, contact angle hysteresis, the role of hierarchical roughness, and the possibility of the creation of reversible hydrophobicity. Based on learning from the theoretical background, various leaf surfaces on the micro- and nanoscale have been characterized and attempts are made to separate out the effects of the micro- and nanobumps and the wax on the hydrophobicity. The next logical step in realizing superhydrophobic surfaces is to design surfaces based on understanding of the

leaves. Artificial superhydrophobic surfaces have been fabricated using various fabrication techniques. The influence of micro-, nano- and hierarchical structures on superhydrophobicity have been discussed by the investigation of static contact angle, contact angle hysteresis, evaporation, bouncing and vibration of a water droplet, and propensity of air pocket formation. In addition, their influence on adhesive force as well as efficiency of self-cleaning have been discussed. The models for the transition from Cassie-Baxter regime to Wenzel regime have been presented. Furthermore, the durability of the various fabricated surfaces has been discussed by the investigation of the loss of superhydrophobicity as well as wear and friction.

An aquatic animal, such as a shark, is another model from nature. Shark skin is covered by very small individual tooth-like scales called dermal denticles (little skin teeth), ribbed with longitudinal grooves (aligned parallel to the local flow direction of the water). These grooved scales reduce vortices formation present on a smooth surface, resulting in water moving efficiently over their surface. The artificial surfaces from the shark skin have been created and the influence of structure has been discussed on measurement of pressure drop and fluid drag for drag reduction efficiency.

Oleophobic surfaces have the potential for self-cleaning and anti-fouling from biological and organic contaminants both in air and underwater applications. A model for predicting the contact angle of water and oil droplets has been presented. The surface tension of oil and organic liquids is lower than that of water. So to make the surface oleophobic in a solid-air-oil interface, a material with surface energy lower than that of oil should be used. The wetting behavior of water and oil droplets for hydrophobic/philic and oleophobic/philic surfaces in three phase interfaces has been investigated. For underwater applications, we have presented oleophobicity/philicity of oil droplet in water on the surfaces with different surface energies of various interfaces and contact angles of water and oil droplets in air.

This thesis provides a useful guide for the development of biomimetic artificial surfaces. Hierarchical structures are typical for surfaces with superhydrophobic, self-cleaning, low adhesion and drag reduction in nature. The flexible and low-cost technique demonstrates that hierarchical surfaces can be produced in the laboratory for further investigations of the properties of hierarchical structured materials. A proper control of

roughness constitutes the main challenge in producing a reliable hierarchical surface and furthermore the mechanisms that trigger the Cassie-Baxter and Wenzel regime transitions still remain to be further investigated.

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