

UNDERSTANDING DEWETTING TRANSITIONS ON NANOTEXTURED
SURFACES: IMPLICATIONS FOR DESIGNING SURFACES WITH IMPROVED
WETTABILITY

Suruchi Fialoke

A DISSERTATION

in

Chemical and Biomolecular Engineering

Presented to the Faculties of the University of Pennsylvania

in

Partial Fulfillment of the Requirements for the

Degree of Doctor of Philosophy

2017

Supervisor of Dissertation

Amish J. Patel,
Reliance Industries Term Assistant Professor of Chemical and Biomolecular Engineering

Graduate Group Chairperson

John C. Crocker,
Professor of Chemical and Biomolecular Engineering

Dissertation Committee

Kathleen J. Stebe, Richer & Elizabeth Goodwin Professor of Chemical and Biomolecular Engineering

Robert Riggleman, Associate Professor of Chemical and Biomolecular Engineering

Shu Yang, Professor of Materials Science and Engineering (MSE) Chemical and Biomolecular Engineering (CBE)

UNDERSTANDING DEWETTING TRANSITIONS ON NANOTEXTURED
SURFACES: IMPLICATIONS FOR DESIGNING SURFACES WITH IMPROVED
WETTABILITY

© COPYRIGHT

2017

Suruchi Fialoke

This work is licensed under the
Creative Commons Attribution
NonCommercial-ShareAlike 3.0
License

To view a copy of this license, visit

<http://creativecommons.org/licenses/by-nc-sa/3.0/>

To Chirag

ACKNOWLEDGEMENT

I must begin by thanking my advisor, Dr. Amish Patel, for his guidance in my research endeavors over the last five years. His open-door policy, often involving debugging of my codes, valuable feedback in various aspects of research, and stimulating discussions are much appreciated. I am also very grateful for all the help Professor Shu Yang has provided, for her insightful comments and encouragement, but also for the hard questions that motivated me to widen my research area. I would also like to thank Professors Kate Stebe, and Rob Riggelman for serving on my committee and providing their valuable inputs and comments. Their effort and time is much appreciated.

It has been a privilege to be a part of the Patel group, and I would to thank the current and past members for the many scientific discussions in which we have participated. My time in the group overlapped most with Erte Xi, and I truly enjoyed working with him and collaborating on multiple projects, over the years. I have enjoyed working on several projects with current Patel group member Zhitong Ziang, and I very much look forward to continuing this work with him. I would also like to acknowledge my undergraduate research advisor at IIT Kharagpur, Dr. Rabibrata Mukherjee, for introducing me to research in the field of superhydrophobic surfaces and for being an excellent mentor in my formative years as a researcher.

I am extremely grateful to my family, especially my mom Sunita Prakash and my dad Shashi Prakash. They have always been a strong source of support throughout my life, and their diligence in their own professions and relationships has been a constant source of inspiration. I would also like to acknowledge my sister Dr. Surabhi Sangal and my younger brother Dr. Swapnil Prakash and my closest friends Deepika Bajaj and Nivedita Patnaik, for being the constant source of love, encouragement, and motivation. I am also thankful to my husband's family, my second set of parents, Vimal and Mitra Fialoke, for visiting me multiple times from India and for loving me as their own daughter.

Finally, I would like to dedicate my thesis to my best friend and loving husband, Chirag Fialoke, for being the biggest source of positivity and happiness in my life for the last 8 years we have known each other. His unconditional love, positivity, inconceivable intelligence, and humor have made this journey unbelievably easier, and I could not have done it without him.

Thank you!

ABSTRACT

UNDERSTANDING DEWETTING TRANSITIONS ON NANOTEXTURED SURFACES: IMPLICATIONS FOR DESIGNING SURFACES WITH IMPROVED WETTABILITY

Suruchi Fialoke

Amish J. Patel

Despite the early promise of superhydrophobic surfaces, their widespread technological adoption has been dawdled by the ease with which water can penetrate the surface texture, resulting in a breakdown of superhydrophobicity. Furthermore, this breakdown is believed to be irreversible, because large adhesion barriers impede the dewetting of the surface texture and the concomitant recovery of superhydrophobicity. Using molecular dynamics simulations in conjunction with advanced sampling techniques, in this thesis, we challenge this conventional argument. We show that while large barriers do typically impede the recovery of superhydrophobicity, it can nevertheless be recovered spontaneously on nanotextured surfaces, wherein collective water density fluctuations lead to non-classical dewetting pathways and reduced dewetting barriers. An understanding of the complex dewetting pathways further enables us to uncover principles for the design of novel surface textures on which dewetting barriers vanish and superhydrophobicity can be spontaneously recovered. Our results thus promise to pave the way for robust superhydrophobic surfaces with widespread applicability under the most challenging conditions from applications involving sustained underwater operation to enabling drop-wise condensation in heat exchangers. Along with recent advances in the synthesis of surfaces with nanoscale texture, work in this thesis promises to revitalize the field of superhydrophobicity and its class of problems, from its prevalent trial-and-error approach to the rational design of surface textures.

TABLE OF CONTENTS

ACKNOWLEDGEMENT	i
ABSTRACT	iii
LIST OF TABLES	ix
LIST OF ILLUSTRATIONS	xv
CHAPTER 1 : Introduction	1
1.1 Theoretical Background	1
1.1.1 Wetting on flat surfaces and Young’s equation	1
1.1.2 Wetting on rough surfaces and superhydrophobicity	2
1.1.3 Contact Angle Hysteresis (CAH)	4
1.2 Challenges	5
1.3 Molecular Dynamics Simulation Method	6
1.4 Results	7
CHAPTER 2 : Dewetting on Superhydrophobic Surfaces: Characterizing Free En- ergetics, Pathways, and Pressure Dependence	9
2.1 Introduction	10
2.2 Materials and Methods	11
2.2.1 Simulation Setup	11
2.2.2 Simulation Details	12
2.3 Free Energetics of Cassie-Wenzel Transitions	12
2.3.1 Macroscopic Theory	13
2.4 Comparison between Molecular Simulations and Macroscopic Theory	15
2.4.1 Average Interface Heights	17

2.4.2	Obtaining offsets in geometric parameters	18
2.4.3	Obtaining γ and $\cos \theta$	18
2.5	Fluctuations Facilitate Non-classical Dewetting Pathways with Reduced Barriers	19
2.6	How Pressure Influences Barriers to Wetting and Dewetting	20
2.7	Outlook	24
CHAPTER 3 : Spontaneous Recovery of Superhydrophobicity in Nanotextured Sur-		
	faces	26
3.1	Introduction	27
3.2	Materials and Methods	28
3.3	Spontaneously Recovering Superhydrophobicity on a Novel Surface Texture	29
3.3.1	Dependence of free energy on pressure highlights a positive extrusion pressure	29
3.3.2	Unbiased trajectories highlighting spontaneous recovery of superhydrophobicity	32
3.4	Informing the Designs of Robust Superhydrophobic Surfaces	34
3.4.1	Criteria for spontaneous recovery of superhydrophobicity	34
3.4.2	Free Energetics of Pillared Surfaces Augmented with Nanoparticles	34
3.4.3	Another augmented surfaces that features an unstable Wenzel state under ambient conditions	37
3.5	Outlook	40
CHAPTER 4 : Cooperative Effects in Dewetting can Facilitate the Spontaneous Recovery of Superhydrophobicity		
4.1	Introduction	42
4.2	Materials and Methods	45
4.3	Macroscopic theory for pillared system system consisting of n_c unit cells	47
4.4	Density-Dependent Free Energy Profiles	48

4.5	Cooperative and Barrierless Dewetting	49
4.5.1	Demonstrating region-II of 2-celled system is classical	49
4.6	Implications for the Rational Design of Robust Superhydrophobic Surfaces .	55
4.7	Effects of Geometric Parameters on Cooperative Dewetting	59
4.8	Obtaining Indicator Functions to Demarcate Distinct Dewetted Morphologies in 2-celled Systems	63
4.9	Macroscopic Theory for Predicting Cooperativity	64
4.9.1	2-celled system:	64
4.9.2	Multi-celled ($n_c \geq 4$) systems:	69
4.10	Guiding Principles for the Design of Optimal Superhydrophobic Surfaces .	71
4.11	Outlook	73
CHAPTER 5 : Influence of Length-scale of Nano-pillars on their Superhydrophobicity		75
5.1	Introduction	75
5.2	Materials and Methods	79
5.3	Comparison between Molecular Simulations and Macroscopic Theory	80
5.3.1	Macroscopic Theory	80
5.3.2	Obtaining offsets in geometric parameters	82
5.3.3	Obtaining γ , $\cos \theta$ and $\cos \theta'$	82
5.4	Procedure for obtaining the simulated values of intrusion pressure, ΔP_{int} , and extrusion pressure, ΔP_{ext}	83
5.5	Height of the pillars does not affect the performance or the robustness of superhydrophobic pillared surfaces	84
5.6	Transition from Cassie state to Wenzel state is reversible irrespective of the size of the system	86
5.6.1	Free energetics and pathways of wetting-dewetting transitions on a pillared surface with $S = 10$ nm and $W = 2$ nm	87
5.6.2	Demonstrating that dewetting is a nanoscopic phenomena	89

5.7	Separation between the pillars only affects the intrusion but not the extrusion pressure	91
5.8	Effect of pillar width on wetting-dewetting transitions	93
5.8.1	Estimating the dependence of ΔP_{ext} on W using Young's Laplace equation	95
5.9	Outlook	97
CHAPTER 6 : Spontaneous Recovery of Superhydrophobicity on Pillared Surfaces Augmented with Spherical Nanoparticles: Effects of Scaling the Feature Size		
6.1	Introduction	100
6.2	Criteria 1: Barrierless Nucleation of Vapor Bubble Underneath a Spherical Nanoparticle	103
6.2.1	Numerical optimization of the free energy	105
6.3	Criteria 2: Barrierless Formation of an Intact Vapor-liquid Interface in Pillared System Augmented with Nanoparticle	109
6.4	Criteria 3: Barrierless De-pinning of Vapor-Liquid Interface from the top of the Nanoparticle	109
6.5	Outlook & Future Work	112
CHAPTER 7 : Dewetting on Surfaces with Re-entrant Geometries: Implications for the Design of Superoleophobic Surfaces		
7.1	Introduction	115
7.2	Macroscopic Theory for Wetting-dewetting transitions	116
7.2.1	Effect of contact angle, $\cos \theta$, and separation between the particles, s , on the free energy at co-existence pressure, $\Delta f(h; p = 0)$	118
7.2.2	Effect of pressure on free energy	120
7.3	An alternate, Less Expensive Path to Dewetting on Re-entrant Surfaces	124

7.3.1	Free energetics of wetting-dewetting transition using the 2VL pathway: Demonstrating that the formation of vapor at the closest separation between the nanoparticles is most favorable	125
7.3.2	Effect of pressure on free energy, $f(h_1, h_2)$	127
7.4	Comparison of free energetics of wetting-dewetting transition using the 1VL and 2VL pathways	128
7.5	Outlook	130
APPENDIX A		133
A.1	INDirect Umbrella Sampling (INDUS) calculations	133
A.2	Estimating dependence of $\Delta F(\rho_n)$ on ΔP	134
APPENDIX B		136
B.1	Estimating Offsets in Geometric Parameters	136
APPENDIX C		138
C.1	Algorithm for Estimating Instantaneous Interfaces	138
APPENDIX D		140
D.1	Obtaining $\gamma(1 + \cos \theta)$ using interface potential calculation	140
BIBLIOGRAPHY		142

LIST OF TABLES

TABLE 3.1 : Geometric parameters for systems studied in Figure 2.5 (“Pillars”), Figure 3.4.2 (“i”, “ii”, and “iii”), Figure 3.1 (“Pillars+NP”), and Figure 3.4.3 (“Pillars _B ” and “Pillars _B +T”), are reported along with the number of waters in the fully wet state, N_{liq} , as well as the free energies of the Cassie and the barrier states relative to the Wenzel state and intrusion and extrusion pressures.	37
TABLE 4.1 : Geometric parameters for all systems studied.	46
TABLE 5.1 : Geometric parameters for all systems studied.	82

LIST OF ILLUSTRATIONS

FIGURE 1.1 : Contact angle of a liquid droplet on an ideal flat surface	2
FIGURE 1.2 : Representative snapshots of water on a textured hydrophobic surface in the Wenzel and the Cassie states	3
FIGURE 2.1 : Free energy of a system in a partially wet state using macroscopic theory	14
FIGURE 2.2 : Comparison of the simulated free energy with the corresponding macroscopic theory prediction	16
FIGURE 2.3 : Representative instantaneous interfaces and average interfaces encompassing the dewetted region for partially wet states between the Cassie and Wenzel states of the pillared system	17
FIGURE 2.4 : Simulated average height of vapor-liquid interface for the classical region agrees well with the macroscopic theory assumption of a flat interface parallel to the basal surface and varies linearly with density	18
FIGURE 2.5 : Free energetics and pathways of wetting-dewetting transitions on a pillared surface highlights a non-classical pathway preceding the formation of a vapor-liquid interface, which is facilitated by nanoscopic water density fluctuations and involves transitions between various dewetted configurations	21
FIGURE 2.6 : Effect of pressure on Cassie-Wenzel transitions reveals why wetting transition is reversible	23
FIGURE 3.1 : The free energetics of a pillared surface augmented with a spherical nanoparticle at the center of the cell, features an unstable Wenzel state under ambient conditions	30

FIGURE 3.2 : Effect of pressure on the free energy profiles and on the magnitude of the wetting and dewetting barriers for the pillared surface augmented with a nanoparticle	31
FIGURE 3.3 : Equilibrium trajectories highlighting spontaneous recovery of superhydrophobicity	33
FIGURE 3.4 : Informing the designs of robust superhydrophobic surfaces by studying dewetting on five textured surfaces augmented with nanoparticles of different shapes	36
FIGURE 3.5 : Introducing a ‘T’-element with dimensions that were judiciously chosen to satisfy the criteria that have to be satisfied for spontaneous dewetting also features no barrier to dewetting	39
FIGURE 3.6 : Average time required for “Pillars+T” system to dewet as obtained from 25 unbiased simulations initialized in the Wenzel state is 220 ps	40
FIGURE 4.1 : Free energy of a partially wet state relative to the fully wet (Wenzel) state for three systems consisting of $n_c = 1, 2$ and 4 uncoupled unit cells	48
FIGURE 4.2 : Uncovering why dewetting barrier in systems with multiple unit cells is independent of number of unit cells	50
FIGURE 4.3 : Dewetting pathway of system with $n_c = 2$ in non-classical region-0	51
FIGURE 4.4 : Free energetics of system with $n_c = 4$ as a function of ρ_n features three distinct linear regions	52
FIGURE 4.5 : For systems with $n_c = 2$, each configuration in region-II displays an intact vapor-liquid interface that is detached from, and is roughly parallel to the basal surface	53
FIGURE 4.6 : Spontaneous recovery of superhydrophobicity in optimally designed surfaces	56

FIGURE 4.7 : The free energy profile, $\beta\Delta F^{(2)}(\rho_n)$, of a $n_c = 2$ system with $S = 4$, $W = 1$ and $H = 3$ features a negative slope of region-I indicating that even after an intact vapor-liquid interface has been nucleated in one cell, an additional barrier must be overcome to dewet the second cell	58
FIGURE 4.8 : Influence of texture geometry on dewetting cooperativity	60
FIGURE 4.9 : Derivatives of the Free Energy for $n_c = 2$ Systems	61
FIGURE 4.10 :The magnitude of the dewetting barrier of a system with $n_c = 2$ relative to that of the corresponding system with $n_c = 1$ is shown for various values of S/W	62
FIGURE 4.11 :Free energetics of three 4-celled systems with increasing value of S/W highlights the effect of geometry on dewetting cooperativity	63
FIGURE 4.12 :Binary indicator functions to obtain the probability of finding a configuration with a ρ_n -value in region-II, $\langle p_{II} \rangle$ (red), region-I, $\langle p_I \rangle$ (green) and region-0, $\langle p_0 \rangle$ (blue), for five $n_c = 2$ geometries. A sharp change in an indicator function, corresponds to transition from one morphology to another, and manifests as a kink in the free energy of the system.	65
FIGURE 4.13 :Predicting cooperative dewetting criteria in 2-celled systems	66
FIGURE 4.14 :Predicting cooperative dewetting criteria in $n_c \geq 4$ systems	69
FIGURE 4.15 :Cooperative dewetting criteria in systems containing cluster of nucleating cells can increase α_c	71
FIGURE 5.1 : The dimensions that characterize the pillared nanotextured surface are the height of the pillars, H , their width, W , and the inter-pillar spacing, S	78
FIGURE 5.2 : Comparison between Molecular Simulations and Macroscopic Theory	81
FIGURE 5.3 : Procedure for obtaining the simulated values of intrusion pressure, ΔP_{int} , and extrusion pressure, ΔP_{ext}	83

FIGURE 5.4 : Effect of pillar height, H , on free energetics of wetting-dewetting transitions	85
FIGURE 5.5 : Free energetics and pathways of wetting-dewetting transitions on a pillared surface with $S = 10$ nm and $W = 2$ nm highlights that dewetting is a nanoscopic phenomena and the transition from Cassie state to Wenzel state is reversible, irrespective of the size of the system	88
FIGURE 5.6 : Showing that dewetting is a nanoscopic phenomena and why macroscopic theory over-predicts the dewetting and wetting barriers even as the system-size is scaled up	90
FIGURE 5.7 : Changing the separation between the pillars, S , only affects the intrusion and not the extrusion pressure	92
FIGURE 5.8 : Effect of pillar width, W , on wetting-dewetting transitions	94
FIGURE 5.9 : A macroscopic model to estimate the influence of W on ΔP_{ext} . .	96
FIGURE 6.1 : For spontaneous recovery of superhydrophobicity in pillared surface, augmented with spherical nanoparticle, we pictorially show the three criteria that need to be fulfilled.	101
FIGURE 6.2 : Schematic showing a spherical nanoparticle of radius, R , in contact with a plane in a wet Wenzel state and in a partially dewetted state	104
FIGURE 6.3 : For the system with spherical nanoparticle in contact with a plane, free energy as a function of the radius of vapor-pocket at the basal surface, r_o , provides the size of the largest vapor pocket, r_o^c , that can form without a barrier	106
FIGURE 6.4 : Demonstrating that simply scaling all the parameters of the system (S , W and R) for the system that spontaneously dewetted does not ensure dewetting in the scaled-up systems, maintaining $\frac{S}{\sqrt{2}} - R \lesssim 1$ nm, does.	108

FIGURE 6.5 : A partially wet state in a pillared system augmented with spherical nanoparticle can be characterized by a flat vapor-liquid interface at height, h_{vl} , rising along the pillars. plotting the free energy as a function of h , provides the criteria for barrier-less depinning of the interface at the top of the nanoparticle	110
FIGURE 6.6 : Future ideas to overcome the restrictions inherent in square-pillared system augmented with single nanoparticle	113
FIGURE 7.1 : Different liquids (with different contact angle, θ) sit at different fill-levels, characterized by the height of the vapor-liquid interface, a characteristic quality of re-entrant geometries making them extremely useful for creating oleophobic surfaces.	115
FIGURE 7.2 : The dimensions that characterize the re-entrant surface decorated with spherical nanoparticles (NPs), are the radius of the NPs, R , and the inter-particle spacing, S	117
FIGURE 7.3 : Effect of separation between the particles, s , and contact angle, $\cos \theta$, on the free energy at co-existence pressure, $\Delta f(h; p = 0)$. .	119
FIGURE 7.4 : Effect of pressure on free energy for a system with separation between the nano-particles, $s = 0.5$ and $\cos \theta = 0.5$	121
FIGURE 7.5 : Effect of pressure on free energy for a system with separation between the nano-particles, $s = 0.5$ and $\cos \theta = -0.5$; In contrast with the system with $\cos \theta > 0$ in Figure 7.4d, $h_{\max} \leq h_{\min}$ and $h_{\max}$ spans a range of positive and higher values of pressures. . . .	122
FIGURE 7.6 : Effect of contact angle and separation between the nanoparticles on the location of the extrema in free energy	123
FIGURE 7.7 : For systems with relatively lower values of contact angle, θ , and smaller value of S/R , dewetting is more likely to proceed through nucleation of vapor at the closest distance between the nanoparticles and not at the basal surface.	124

FIGURE 7.8 : A partially wet configuration following the 2VL dewetting pathway (See Figure 7.7c) is characterized by two flat vapor-liquid interfaces lying at h_1 and h_2 and the free energy plotted as a function of h_1 and h_2 highlights that the most optimal path follows the formation of nascent vapor layer at the closest distance between the nanopar- ticles at $h_1 = h_2 = 1$	126
FIGURE 7.9 : Effect of pressure on free energy, $f(h_1, h_2)$, for a system with sepa- ration between the nano-particles, $s = 0.5$ and $\cos \theta = 0.5$ following the 2VL pathway	127
FIGURE 7.10 : Comparison of free energetics of wetting-dewetting transition using the 1VL and 2VL pathways	129
FIGURE 7.11 : Comparison of free energetics of wetting-dewetting transition using the 1VL and 2VL pathways for systems with $\cos \theta < \cos \theta_c$	130
FIGURE B.1 : Obtaining offsets in geometric parameters	137
FIGURE D.1 : Obtaining $\gamma(1 + \cos \theta)$ using interface potential calculation	141
FIGURE D.2 : Obtaining $\gamma(1 + \cos \theta)$ using interface potential calculation on a substrate made of single layer of atoms	142

CHAPTER 1 : Introduction

Self-cleaning lotus leaves, legs of the water strider, and geckos feet, are remarkable examples of naturally occurring surfaces with superior wetting properties [61, 50]. Lotus leaves are considered self-cleaning because water droplets on the surface of a lotus leaf form small beads with a high contact angle in excess of 150° and roll off with the slightest nudge, while taking away any contaminant. The tiny hairs on the legs of a water strider provide it with a nanotextured surface that enhances its water repellency, as well as with a larger surface area to spread its weight over the water, enabling it to walk on water. The textures on the geckos feet equip them to adhere to most solid surfaces without requiring any external liquid medium. It is now well recognized that chemical composition and topography or texture are the two dominant factors that influence wettability of a surface and achieving the elusive combination of the two, for a given application, is an area of active research. Manipulating wetting adjacent to textured surfaces guides many industrial processes, oil recovery, lubrication, liquid coating, printing, and spray quenching [61, 50, 35]. In particular, there has been an exponentially increasing interest in the study of lotus-leaf-like “superhydrophobic” surfaces, due to their applications in, self-cleaning solar panels, micro-and-nano-fluidics devices, anti fogging wind-panes, drag reduction on ships and electrowetting [7]. Wettability studies usually involve the measurement of contact angles, which indicates the degree of wetting when a solid and liquid interact and, measurement of contact angle hysteresis, which is related to the dynamic measure of the contact angle.

1.1. Theoretical Background

1.1.1. Wetting on flat surfaces and Young’s equation

The characteristic shape of a liquid droplet on a chemically homogenous and physically flat (or smooth) surface is characterized by its contact angle and is dictated by the chemistry of the surface, the liquid and, the vapor phase. For a liquid droplet resting on a solid surface (Figure 1.1), the contact angle is defined as the angle formed by the intersection of the

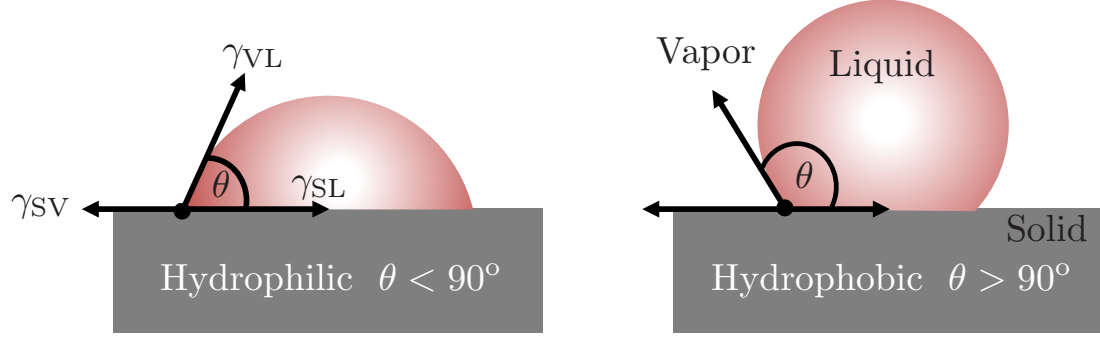


Figure 1.1: For a liquid droplet resting on a solid surface (Figure 1.1), the contact angle, θ , is defined as the angle formed by the intersection of the liquid-solid interface and the liquid-vapor interface and is given by the Young's equation, $\cos \theta = (\gamma_{SV} - \gamma_{SL})/\gamma_{VL}$. For water, if $\theta < 90^\circ$, it is an intrinsically hydrophilic surface (left). Whereas, it is an intrinsically hydrophobic surface if $\theta > 90^\circ$ as shown in right.

liquid-solid interface and the liquid-vapor interface. The liquid contact angle on the flat surface, θ can be correlated to three interfacial free energies, *i.e.*, free energies at the solid-air (γ_{SV}), solid-liquid (γ_{SL}), and liquid-vapor (γ_{VL}) interfaces, according to the Young's equation:

$$\cos \theta = \frac{(\gamma_{SV} - \gamma_{SL})}{\gamma_{VL}}, \quad (1.1)$$

For $\theta < 90^\circ$ ($\cos \theta > 0$), the solid-liquid interaction dominate and the solid surface is considered intrinsically hydrophilic. Similarly, surfaces with $\theta > 90^\circ$ ($\cos \theta < 0$) are considered hydrophobic.

1.1.2. Wetting on rough surfaces and superhydrophobicity

The effect of surface roughness on wettability was first introduced by Wenzel in his pioneering work in 1936 [84] and then extended by Cassie and Baxter in 1944 [10]. In describing wetting adjacent to a rough surface, Wenzel assumed a complete contact of the liquid with the solid surface, in a state now famously referred to as a “Wenzel state” (Figure 1.2a). In the Wenzel state, liquid will tend to spread more on a rough hydrophilic substrate to develop more solid-liquid contact, while spread less on a rough hydrophobic substrate to decrease the contact area to solid, both of which are thermodynamically more favorable. In the Wenzel state, the relationship between the apparent contact angle, θ_{Wenzel} and its

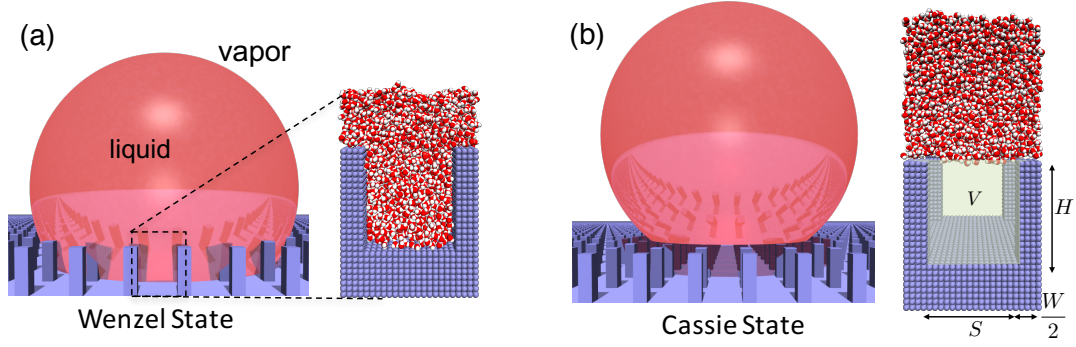


Figure 1.2: Water on textured hydrophobic surfaces can exist in either the Cassie or the Wenzel state. (a) In the Wenzel state, water wets the texture, so that there is extensive contact between water and the solid surface, leading to a large contact angle hysteresis and a smaller contact angle. (b) In the Cassie state, water is unable to penetrate the surface texture (blue) so that a water droplet (red) sits on a cushion of air, contacting only the top of the pillars. As a result, there is minimal contact between water and the solid surface, leading to a small contact angle hysteresis and a large contact angle, which are critical in conferring superhydrophobicity to the surface.

intrinsic contact angle, θ , has been described by the Wenzel's equation:

$$\cos \theta_{\text{Wenzel}} = r_f \cos \theta, \quad (1.2)$$

where r_f is the roughness factor, defined as the ratio of the actual surface area to its horizontal projection. Since r_f is always greater than 1 for a rough surface, this equation reinforces that, if $\theta < 90^\circ$, $\theta_{\text{Wenzel}} < \theta$, and if $\theta > 90^\circ$, $\theta_{\text{Wenzel}} > \theta$. Therefore, in the Wenzel state, surface roughness will make intrinsically hydrophobic surfaces more hydrophobic and intrinsically hydrophilic surfaces more hydrophilic.

However, as the surface roughness or the surface hydrophobicity increases, it may become unlikely for water to have a complete contact with the solid surface and instead air can be trapped in the surface textures. As a result, water is in contact with a composite surface of solid and air, and forms droplets also known as the fakir droplets. Such a state is referred to as a Cassie State (Figure 1.2b) and the apparent contact angle in this state is described

by the Cassie-Baxter equation:

$$\cos \theta_{\text{Cassie}} = \phi_s \cos \theta + \phi_v \cos \theta_{\text{LV}} = \phi_s \cos \theta - (1 - \phi_s), \quad (1.3)$$

where ϕ_s and ϕ_v are the fractions of solid and air making contact with the liquid droplet and satisfy $\phi_s + \phi_v = 1$. Considering the contact angle of liquid on air, $\theta_{\text{LV}} = 180^\circ$ ($\cos \theta_{\text{LV}} = -1$), air entrapment will remarkably increase the apparent surface hydrophobicity. Additionally, according to Equation 1.3, a monotonic decrease of ϕ_s results in a proportional increase of θ_{Cassie} , leading to a superhydrophobic state at $\theta_{\text{Cassie}} = 150^\circ$. For a rough hydrophobic surface in contact with water droplet, one of the two states (Wenzel state or Cassie state) may exist depending on θ and ϕ_s .

1.1.3. Contact Angle Hysteresis (CAH)

In addition to the statically measured contact angle, another parameter, contact angle hysteresis (CAH), is also important for characterizing the surface wettability. In the context of most practical applications, the phenomenon of wetting is more than just a static state and requires motion of the droplet on the solid surface. If the three-phase contact line is in motion, the contact angle is called a “dynamic” contact angle. In particular, the contact angles formed by expanding and contracting the liquid are referred to as the advancing contact angle θ_a and the receding contact angle θ_r , respectively. The contact angle hysteresis is the difference between the advancing and receding contact angles,

$$CAH = \theta_a - \theta_r \quad (1.4)$$

CAH is typically measured during expansion and contraction of the droplets induced by placing a needle in the water droplets and continuously supplying and withdrawing water through the needle. The advancing contact angle θ_a is recorded when the liquid volume reaches maximum before the liquid-solid interfacial area starts to increase; the receding contact angle θ_r is recorded when the liquid volume reaches minimum before the interfacial

area starts to decrease. Sometimes, sliding angle, which is defined as the minimum angle that the substrate needs to be tilted before a droplet starts to roll off, is also used to characterize the wettability of a surface. Due to the complexity of contact angle phenomena, its origin is not entirely understood, however, the general conclusion is that it arises from surface roughness and/or heterogeneity [24]. On ideal solid surfaces, there is no contact angle hysteresis, and the experimentally observed contact angle should be the Young’s contact angle. On rough surfaces, Cassie state offers substantially less contact between the solid surface and the liquid hence has small CAH , whereas liquid in Wenzel state experiences relatively high CAH [61, 50, 35]. $CAH < 5^\circ$ along with an apparent contact angle is typically the benchmark for a surface to be in the superhydrophobic state.

1.2. Challenges

Surface texture can transform hydrophobic surfaces into “superhydrophobic”, and endow them with properties like water-repellency, self-cleaning, interfacial slip, and fouling resistance exploited in varied applications such as self-cleaning solar panels, drag reduction on ships, anti fogging wind-panes etc [61, 50, 35]. These incredible properties, collectively referred to as superhydrophobicity, stem from the inability of water to readily penetrate the surface texture, so that a drop of water sits on top of the surface asperities and air cushion, in the Cassie state [32, 16]. Water droplets in Cassie state display higher contact angle and lower contact angle hysteresis compared to flat surface of same chemical composition. Surfaces that display an effective contact of 150° and or higher and a contact angle hysteresis of 5° or lower are commonly referred as “superhydrophobic surfaces”. However, water can readily penetrate the surface texture at elevated pressures, referred as the intrusion pressure, yielding the wet, Wenzel state [71, 52]. Such a wetting of the surface texture leads to extensive contact between the solid surface and water, and results in a loss of superhydrophobic properties; the term “superhydrophobic surface”, hence, is only meaningful for surfaces in the Cassie state. Moreover, the loss of superhydrophobicity is widely considered irreversible and a spontaneous Wenzel-to-Cassie transition has been elusive; so that once the

texture wets, it remains in the wet state, even when the pressure is subsequently lowered [7]. Insights into why achieving a Wenzel-to-Cassie transition remains challenging are provided by macroscopic interfacial thermodynamics, which suggests that the dewetting transition is impeded by a large kinetic barrier; this “classical” barrier is attributed to the work of adhesion for nucleating a vapor-liquid interface at the base of the textured surface [53]. The irreversibility of the Cassie-to-Wenzel or wetting transition has been a major impediment in the design of robust superhydrophobic surfaces, and has prompted a number of theoretical and simulation studies to focus on the thermodynamics, kinetics and mechanisms of wetting and dewetting transitions on textured surfaces [53, 12, 19, 30, 31, 73, 72]. To facilitate the recovery of superhydrophobicity and to afford reversible control over surface properties, significant efforts have focused on inducing and the reverse Wenzel-to-Cassie dewetting transition. However, most reported instances of a Wenzel-to-Cassie transition made use of trapped air or a gas film generated using an external energy source or used responsive material [29, 38, 18, 44, 83, 12] to initiate the dewetting process.

1.3. Molecular Dynamics Simulation Method

In multiple applications relying on wetting quality of a surface, textures at the nanoscale are highly desirable for their better endurance to external perturbations and transparency [7, 9]. With emergence of newer technologies focus is shifting towards creating textures at smaller and smaller lengthscales with some of the recent studies creating and employing textures at the order of 10s of nanometer [12]. Enhanced fluctuations in water density, discontinuities in solid-liquid-and-vapor interfaces, complex geometries etc. impose a limit to the usage of continuum approach in such nanoscopic systems. In particular, recent theoretical and simulation studies have shown that water density fluctuations, which are not captured in macroscopic mean-field models, are enhanced at hydrophobic surfaces [41, 11, 80, 46, 21, 56], and situate the interfacial waters at the edge of a dewetting transition [59]. A promising approach to investigate nanoscale phenomena, including wetting adjacent to textured surfaces [53, 12, 19, 30, 31, 73, 72], is Molecular Dynamics (MD) simulation. In

MD simulations, one works directly at the molecular level by solving Newton’s equation of motion of every molecule in the system of interest numerically; detailed information on the entire nanoscopic system can be obtained. Since wetting adjacent to textured surfaces involve multiple stable and metastable states (such as the Wenzel and the Cassie states) and kinetic barriers separating them, its study requires the use of enhanced sampling techniques. We make extensive use of configurational and path sampling techniques, to be able to obtain the pathways and free energetics of wetting. In particular, we employ the INDUS (INDirect Umbrella Sampling) method, for estimating the energetics of density fluctuations of water adjacent to nano-textured surfaces of various shapes and sizes [57]. We have chosen the SPC/E model of water [3] because it adequately captures the experimentally known features of water, such as surface tension, isothermal compressibility, and the vapor-liquid equation of state near ambient conditions, all of which are important in the study of dewetting on hydrophobic surfaces [11, 81, 79, 41]. We characterize wetting-dewetting transitions on nanotextured surfaces by employing the INDUS method to characterize the free energetics of the transitions, the corresponding pathways, as well as their dependence on pressure. As we get better understanding of non-classical features of wetting-dewetting tran, we also build up on existing continuum theory

1.4. Results

Our work informs both fundamental and applied aspects of superhydrophobicity, by not only uncovering non-classical Cassie–Wenzel transition pathways, but by also suggesting strategies for the rational design of robust superhydrophobic surfaces. In particular, we show that the free energetics of wetting-dewetting transitions on nanotextured surfaces, the corresponding mechanistic pathways, and their dependence on pressure, are all strongly influenced by collective water density fluctuations. In particular, we reveal non-classical dewetting pathway on pillared surfaces, which features transitions between a number of distinct dewetted morphologies that precede the formation of the classical vapor-liquid interface at the basal surface; the non-classical pathway offers a lower resistance to dewetting,

leading to reduced dewetting barriers. By uncovering the nanoscale dewetting pathways, and in particular, by finding regions of the surface texture that are hardest to dewet, our results provide strategies for augmenting the surface texture to further destabilize the Wenzel state and reduce the barriers to dewetting. We then show that these non-classical effects, *i.e.* the reduction in dewetting barrier due to morphological transitions, are prevalent even as system size increases. Finally, we extend this study to understand wetting-dewetting transitions on oleophobic (oil-repellant) surfaces on re-entrant surfaces and demonstrate that even macroscopic theory has been underutilized in describing dewetting on surfaces of larger complexity. In conjunction with recent advances in introducing texture at the nanoscale [62, 12], our results thus promise to pave the way for robust superhydrophobic surfaces with widespread applicability under the most challenging conditions. One example of such an application involves sustained underwater operation [13], which would require the surface texture to not only remain dry under hydrostatic pressure, but also be able to return to the dry state, if the texture wets in response to a perturbation. Another example pertains to condensation heat transfer [2], wherein an unstable Wenzel state would facilitate the immediate roll-off of condensing water droplets, and enable drop-wise condensation to be sustained at higher fluxes.

CHAPTER 2 : Dewetting on Superhydrophobic Surfaces: Characterizing Free Energetics, Pathways, and Pressure Dependence

The contents of this chapter were published in Proceedings of the National Academy of Sciences of the United States of America (PNAS) (2016) volume 113, issue 20, pp 5508–5513 in a modified version and are reprinted here with permission from National Academy of Sciences.

Rough or textured hydrophobic surfaces are dubbed superhydrophobic due to their numerous desirable properties, such as water repellency and interfacial slip. Superhydrophobicity stems from an aversion for water to wet the surface texture, so that a water droplet in the superhydrophobic “Cassie state”, contacts only the tips of the rough hydrophobic surface. However, superhydrophobicity is remarkably fragile, and can break down due to the wetting of the surface texture to yield the “Wenzel state” under various conditions, such as elevated pressures or droplet impact. Moreover, due to large energetic barriers that impede the reverse transition (dewetting), this breakdown in superhydrophobicity is widely believed to be irreversible. Using molecular simulations in conjunction with enhanced sampling techniques, here we show that on surfaces with nanoscale texture, water density fluctuations can lead to a reduction in the free energetic barriers to dewetting by circumventing the classical dewetting pathways. In particular, the fluctuation-mediated dewetting pathway involves a number of transitions between distinct dewetted morphologies, with each transition lowering the resistance to dewetting. Importantly, an understanding of the mechanistic pathways to dewetting and their dependence on pressure, can allow us to engineer more robust surfaces.

2.1. Introduction

Surface roughness or texture can transform hydrophobic surfaces into “superhydrophobic”, and endow them with properties like water-repellency, self-cleaning, interfacial slip, and fouling resistance [61, 50]. Each of these remarkable properties stems from the reluctance of water to penetrate the surface texture, so that a drop of water sits atop an air cushion in the so-called Cassie state, contacting only the top of the surface asperities. However, water can readily penetrate the surface texture, yielding the Wenzel state [71, 52] at elevated pressures [32, 52] or temperatures [39], upon droplet impact [27, 6], as well as due to surface vibration [33], localized defects [47], or proximity to an electric field [44]; superhydrophobicity is thus remarkably fragile and can break down due to the wetting of the surface texture under a wide variety of conditions. To facilitate the recovery of superhydrophobicity and to afford reversible control over surface properties, significant efforts have focused on inducing the reverse Wenzel-to-Cassie dewetting transition. However, a true Wenzel-to-Cassie transition has been elusive [7], with most reported instances making use of trapped air [18, 44, 83, 12] or generating a gas film using an external energy source [29, 38] to jumpstart the dewetting process. Insights into why achieving a Wenzel-to-Cassie transition remains challenging are provided by macroscopic interfacial thermodynamics [53], which suggests that the dewetting transition is impeded by a large free energetic barrier. This “classical” barrier is attributed to the work of adhesion for nucleating a vapor-liquid interface at the base of the textured surface. Consequently, the break down of superhydrophobicity upon wetting of the surface texture is widely believed to be irreversible [32, 53, 7], so that once the texture wets, it remains in the wet state, even when the pressure is subsequently lowered or the electric field is switched off.

Our work builds upon recent theoretical and simulation studies, which have shown that water density fluctuations, which are not captured in macroscopic mean-field models, are enhanced at hydrophobic surfaces [41, 11, 80, 46, 21, 56], and situate the interfacial waters at the edge of a dewetting transition [59]. Such enhanced fluctuations have also been shown

to modulate the pathways to dewetting and lead to reduced dewetting barriers in several confinement contexts [76, 43, 85, 45, 19, 69, 74, 64]. To investigate how fluctuations influence Cassie-Wenzel transitions on nanotextured surfaces, here we perform atomistic simulations of water adjacent to pillared surfaces, and employ the Indirect Umbrella Sampling (INDUS) method [57] to characterize the free energetics of the transitions, the corresponding pathways, as well as their dependence on pressure. By comparing our results to macroscopic theory, we find that while water density fluctuations do not influence the pressure at which the Cassie-to-Wenzel wetting transition occurs, they are nevertheless crucial in the Wenzel-to-Cassie dewetting transition, that is, in the process of recovering superhydrophobicity when it breaks down. In particular, fluctuations stabilize a non-classical dewetting pathway, which features crossovers between a number of distinct dewetted morphologies that precede the formation of the classical vapor-liquid interface at the basal surface; the non-classical pathway offers a lower resistance to dewetting, leading to reduced dewetting barriers.

2.2. Materials and Methods

2.2.1. Simulation Setup

Surface that we study is composed of atoms arranged on a cubic lattice with a lattice spacing of 0.25 nm; the surface atoms are constrained to remain in their initial positions throughout the simulations. The basal surface, which is situated at the bottom of the simulation box, is made of 8 layers of atoms and is 2 nm thick. On the pillared surface, square pillars of height, $H=4.5$ nm, and width, $W=2$ nm, are employed to introduce surface texture. The pillars are placed on a square lattice with inter-pillar spacing, $S=4$ nm. System is periodic in all three spatial directions and is initialized in the Wenzel state. The surface is hydrated with roughly 7,000 water molecules, so that even in the Wenzel state, a 2 nm thick water slab rests above the pillars. We also provide a buffering vapor layer at the top of the simulation box, which is roughly 6 nm thick in the Wenzel state. As waters leave the textured region, the vapor layer shrinks to roughly 2 nm in the Cassie state. The vapor layer, which is

thus present in our system at all times, ensures that water is in coexistence with its vapor, and $\Delta P = 0$ [45]. To ensure that the vapor layer remains at the top of the $6 \times 6 \times 15 \text{ nm}^3$ simulation box, we include a repulsive wall at $z=14.5 \text{ nm}$.

2.2.2. Simulation Details

The surface atoms interact with the SPC/E-water oxygens through the Lennard-Jones (LJ) potential ($\sigma=0.35 \text{ nm}$, $\epsilon=0.40 \text{ kJ/mol}$). As shown in the Subsection 2.4.3., this choice leads to a flat surface water droplet contact angle, $\theta=123.5^\circ$, in accord with contact angles observed on typical hydrophobic surfaces, such as alkyl-terminated self-assembled monolayer surfaces [21]. We use the GROMACS molecular dynamics simulation package [22], suitably modified to perform INDUS simulations in the canonical ensemble. A detailed description of the INDUS calculations [56, 57], which we use to characterize the free energetics of wetting-dewetting transitions on nanotextured surfaces, is included in the Appendix A. To maintain a constant temperature, $T=300 \text{ K}$ [8], the canonical velocity-rescaling thermostat with a time constant of 0.5 ps is employed. LJ interactions and the short-ranged part of the electrostatic interactions are truncated at 1 nm , and the Particle Mesh Ewald algorithm is employed to treat the long-ranged part of electrostatic interactions [17]. The SHAKE algorithm is used to constrain the bond lengths of the water molecules [67].

2.3. Free Energetics of Cassie-Wenzel Transitions

Figure 1.2 contrasts the behavior of water on textured surfaces in the Cassie and Wenzel states; water does not penetrate the surface texture in the Cassie state, but does so in the Wenzel state. In Figure 1.2a (right), the particular textured surface morphology that we study here is shown, and consists of square pillars of height H and width W , arranged on a square lattice, and separated by a distance S . Also highlighted is the textured volume, V , which is devoid of water molecules in the Cassie state but is filled with waters in the Wenzel state. Also shown is a simulation snapshot of the pillared surface that we study here (right), which consists of square pillars arranged on a square lattice, and is made of

atoms (blue spheres) arranged on a cubic lattice. The textured volume, V , as well as the dimensions that characterize the pillared nanotextured surface are highlighted in Figure 1.2 the width of the pillars is $W=2$ nm, their height is $H=4.5$ nm, and the inter-pillar spacing is $S=4$ nm. Details pertaining to our simulation setups, the force-field parameters and algorithms employed, are included in the Materials and Methods section. To uncover the importance of water density fluctuations on the free energetics of Cassie-Wenzel transitions, we first compare the simulated $\Delta F(\rho_n)$ with classical expectations based on macroscopic interfacial thermodynamics, which does not account for fluctuations. Here, $\rho_n \equiv N/N_{\text{liq}}$ with N and N_{liq} being the number of water molecules in V , in the partially and fully wet states respectively. The normalized water density, ρ_n in V , thus serves as a reliable order parameter to distinguish the Cassie ($\rho_n \approx 0$) and the Wenzel ($\rho_n \approx 1$) states.

2.3.1. Macroscopic Theory

Macroscopic theory envisions dewetting being initiated with the nucleation of a vapor liquid interface at the base of, and perpendicular to the pillars; dewetting then proceeds through the ascent of this interface along the pillars [53]. According to macroscopic interfacial thermodynamics [54], the free energy of a system in a partially wet state with normalized density ρ_n , relative to that in the Wenzel state is:

$$\Delta F_{\text{th}}(\rho_n) = \gamma A_{\text{vl}}(\rho_n) + \Delta\gamma A_{\text{sv}}(\rho_n) + \Delta P V(1 - \rho_n), \quad (2.1)$$

where γ is the vapor-liquid surface tension, and $\Delta\gamma$ is the difference between the solid-vapor and solid-liquid surface tensions; according to the Young's equation, $\Delta\gamma = \gamma \cos \theta$. A_{vl} and A_{sv} are the vapor-liquid and the solid-vapor interfacial areas, respectively, in the partially wet state, and ΔP is the difference between the pressures of the liquid and the vapor phases. Assuming that a partially wet state on the pillared surface is characterized by a flat vapor-liquid interface at a height h , above the base of the pillars, it follows that $h(\rho_n) = H(1 - \rho_n)$ [54, 49]. Then, $A_{\text{vl}} = S(S + 2W) \equiv A_{\text{base}}$, is independent of h , whereas $A_{\text{sv}} = A_{\text{base}} + A_{\text{side}}(h/H)$, increases linearly with h . Here, $A_{\text{side}} = 4WH$ is the area of the

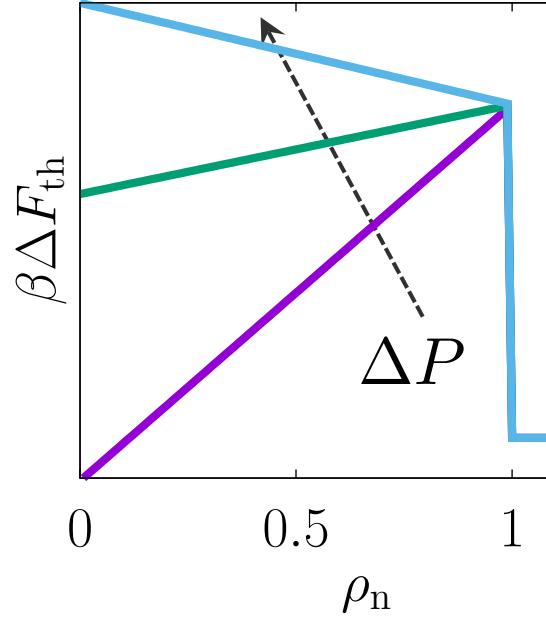


Figure 2.1: Macroscopic theory (Equation 2.2) predicts a barrier to the dewetting Wenzel-to-Cassie transition. This dewetting barrier at $\rho_n = 1$ corresponds to the work of adhesion, ΔF_{barr} , that must be performed to nucleate a vapor-liquid interface at the basal surface. The adhesion barrier is expected to be independent of pressure; ΔP only affects the slope of the linear region between the barrier and the Cassie state. As pressure is increased, the slope of this region decreases, destabilizing the partially wet states relative to the Wenzel state. For $\Delta P > \Delta P_{\text{int}}$, the Cassie state becomes unstable (blue curve).

vertical faces of the pillars. $\Delta F_{\text{th}}(\rho_n)$ is then given by:

$$\Delta F_{\text{th}}(\rho_n) = \Delta F_{\text{barr}} + [\gamma \cos \theta A_{\text{side}} + \Delta P V] \frac{h(\rho_n)}{H}, \quad (2.2)$$

where $\Delta F_{\text{barr}} \equiv \gamma A_{\text{base}}(1 + \cos \theta)$ is always unfavorable (positive), and corresponds to the work of adhesion for nucleating the vapor-liquid interface. Because $\cos \theta < 0$ for hydrophobic surfaces, the second term could be favorable (negative) if ΔP is sufficiently small, that is, if $\Delta P \leq \Delta P_{\text{int}} \equiv -\gamma \cos \theta A_{\text{side}}/V$. Thus, the two key features of $\Delta F_{\text{th}}(\rho_n)$ are: (i) a large adhesion barrier at $\rho_n \approx 1$, which must be overcome to nucleate the vapor-liquid interface, and (ii) a linear portion of $\Delta F(\rho_n)$ corresponding to the vapor-liquid interface rising along the pillars as ρ_n decreases (See Figure 2.1). As the pressure is increased, the slope of the linear portion decreases and partially wet states become less favorable compared to the Wenzel state. At sufficiently large pressures ($\Delta P > \Delta P_{\text{int}}$), the Cassie state becomes unstable, leading to the wetting of the surface texture, and the concomitant breakdown of superhydrophobicity. The presence of the adhesion barrier then precludes a recovery of the superhydrophobic Cassie state upon a subsequent lowering of pressure.

2.4. Comparison between Molecular Simulations and Macroscopic Theory

In Figure 2.2, we show the free energy, $\Delta F(\rho_n)$, of a system in the partially wet state relative to that in the Wenzel state, obtained using molecular dynamics simulations in conjunction with Indirect Umbrella Sampling (INDUS) [57]. Similar to theoretical prediction (black line), the simulated free energy profile, $\Delta F(\rho_n)$, clearly shows two basins, Cassie at $\rho_n \approx 0$ and Wenzel at $\rho_n \approx 1$, separated by a large barrier (Figure 2.2). For $0.2 < \rho_n < 0.8$, simulated $\Delta F(\rho_n)$ varies linearly with ρ_n , consistent with macroscopic theory. According to Equation 2.2, the slope of this linear region for $\Delta P = 0$, the pressure at which our simulations are performed, is expected to be $-\gamma \cos \theta A_{\text{side}}$ and the results from simulations yield the same value of slope. The partially wet configurations observed in our simulations for $0.2 < \rho_n < 0.8$ contain a vapor-liquid interface that is perpendicular to the pillars see Figure 2.3 also consistent with assumption in classical macroscopic theory. We visualize

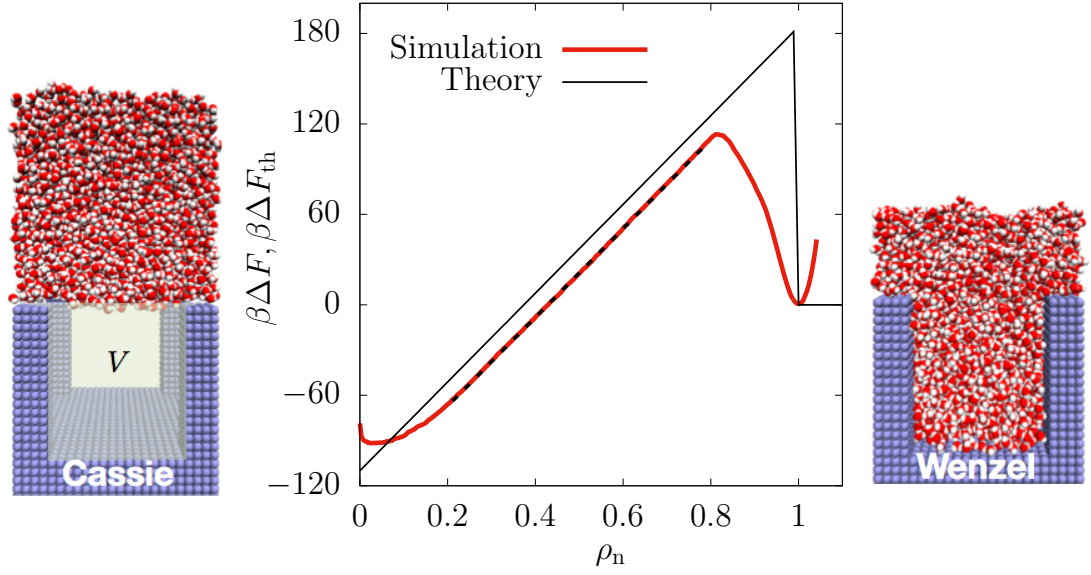


Figure 2.2: Comparison of the simulated $\Delta F(\rho_n)$ (red) with the corresponding macroscopic theory prediction, $\Delta F_{th}(\rho_n)$ (black). Similar to theoretical prediction (black line), the simulated free energy profile, $\Delta F(\rho_n)$, clearly shows two basins, Cassie at $\rho_n \approx 0$ and Wenzel at $\rho_n \approx 1$, separated by a large barrier. Macroscopic theory over-predicts the barrier for dewetting ($\approx 182 k_B T$) as compared to the simulations ($\approx 118 k_B T$) while it accurately captures the linear region ($0.2 < \rho_n < 0.8$)

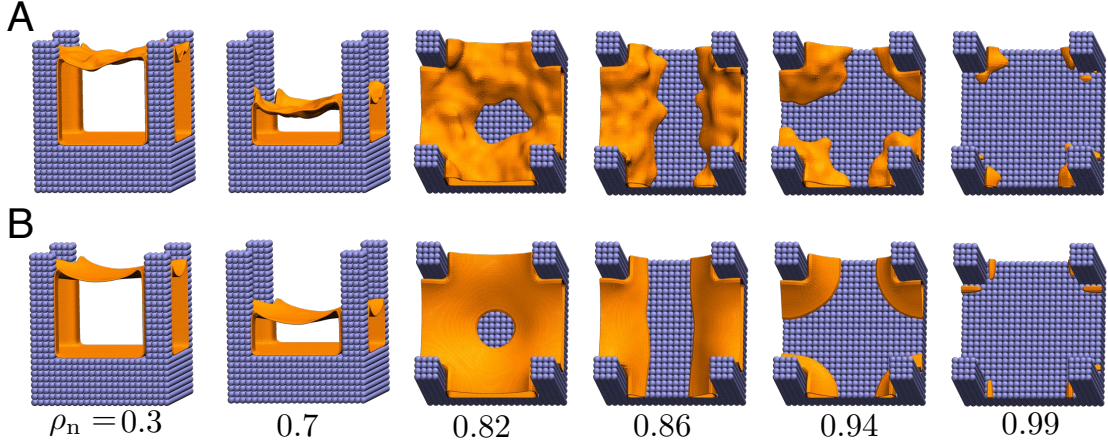


Figure 2.3: (a) Representative instantaneous interfaces and (b) average interfaces encompassing the dewetted regions are shown in orange, for partially wet states spanning the entire range of ρ_n -values between the Cassie and Wenzel states. Water molecules are not shown for the sake of clarity. The configurations for $\rho_n < 0.8$ (side view) are classical with the vapor-liquid interface ascending along the pillars as ρ_n decreases. In contrast, for $0.8 < \rho_n < 1$ (top view), the system displays non-classical configurations with at least three distinct dewetted morphologies.

our morphologies as instantaneous interfaces (See Appendix C) encompassing the dewetted regions (orange) are shown in Figure 2.3A for a range of ρ_n -values spanning the Cassie and the Wenzel states. For the same ρ_n -values, we also show the half-density iso-surfaces of the time-averaged coarse-grained density field (Figure 2.3B).

2.4.1. Average Interface Heights

For configurations with $\rho_n < 0.8$, the vapor-liquid interface is completely detached from the basal surface (Fig. 2.3). To test the macroscopic theory approximation built into Equation 2.2, that is, $h(\rho_n) = H(1 - \rho_n)$, here we obtain the average height of the vapor-liquid interface as a function of ρ_n . For each configuration, we first obtain an average interface height by averaging over the x - and y - coordinates. Before averaging over all configurations with a particular value of ρ_n , care must be exercised in assigning appropriate weights to those configurations because they were obtained using biased simulations. To ensure this, we perform this average within the framework of WHAM [75]. $\langle h \rangle$ thus obtained is plotted

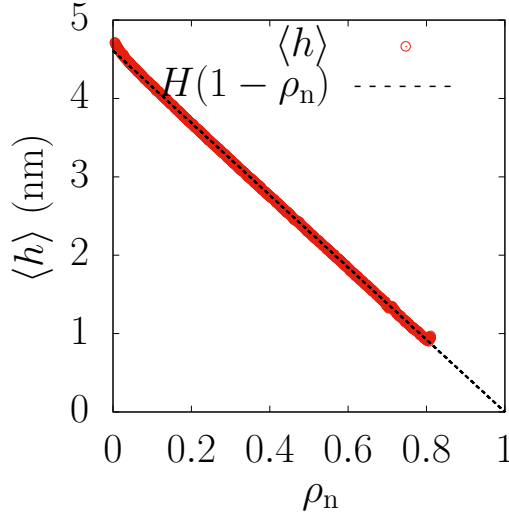


Figure 2.4: For $\rho_n < 0.8$, our simulations display an intact vapor-liquid interface that is detached from, and is roughly parallel to the basal surface. The average height of this vapor-liquid interface (symbols) plotted as a function of ρ_n , agrees well with the macroscopic theory assumption of a flat interface parallel to the basal surface (dashed line).

as a function of ρ_n in Fig. 2.4 and agrees well with the macroscopic theory approximation. The behavior of the system for $0.2 < \rho_n < 0.8$ is thus classical.

2.4.2. Obtaining offsets in geometric parameters

The values of the pillar width W , its height H and the inter-pillar separation S , reported in the Materials and Methods Section, correspond to the distances between the centers of the corresponding surface atoms. To compare our simulations with macroscopic theory, we use effective values of $W = 2.19$ nm, $S = 3.87$ nm and $H = 4.61$ nm, as described in Appendix B.

2.4.3. Obtaining γ and $\cos \theta$

For an accurate comparison with macroscopic theory, we use the procedure described in Appendix D to obtain the value of $\gamma(1 + \cos \theta) = 5.97 \pm 0.0006 k_B T / \text{nm}^2$. We then estimate $(\gamma \cos \theta)_{\text{fit}}$ by fitting the simulation data in the linear region between $0.2 < \rho_n < 0.8$ (Figure 2.2, dashed line), and comparing the fitted slope to $-(\gamma \cos \theta)_{\text{fit}} A_{\text{side}}$. Fitting a straight

line to free energy provides us with $(\gamma \cos \theta)_{\text{fit}} = -7.29 \pm 0.04 \text{ } k_{\text{B}}T/\text{nm}^2$ and combining with $\gamma(1 + \cos \theta) = 5.97 \pm 0.0006 \text{ } k_{\text{B}}T/\text{nm}^2$ we get estimated values of $\cos \theta_{\text{fit}} = -0.55$ and $\gamma_{\text{fit}} = 13.26 \pm 0.04 \text{ } k_{\text{B}}T/\text{nm}^2$.

We then obtain an accurate prediction for macroscopic theory corresponding to the simulated geometry by using Equation 2.2 as shown in Figure 2.2. From Figure 2.2 it is clear that macroscopic theory over-predicts the barrier for dewetting ($\approx 182 \text{ } k_{\text{B}}T$) as compared to the simulations ($\approx 118 \text{ } k_{\text{B}}T$) while by design it accurately captures the linear region ($0.2 < \rho_{\text{n}} < 0.8$). Thus, while the ascent of the vapor-liquid interface along the pillars is classical, the nucleation of that vapor-liquid interface and the associated dewetting barriers, which are central to the recovery of superhydrophobicity, appear to be non-classical.

2.5. Fluctuations Facilitate Non-classical Dewetting Pathways with Reduced Barriers

To understand why the dewetting barrier is smaller than the classical expectation, we take a closer look at $\Delta F(\rho_{\text{n}} > 0.8)$ (Figure 2.5) as well as the corresponding representative configurations (Figure 2c, II - IV), which are shown as instantaneous interfaces encompassing the dewetted regions (orange). Interestingly, we observe a host of non-classical partially wet configurations preceding the formation of the classical vapor-liquid interface. As ρ_{n} is decreased from 1, vapor pockets first form at the base of the pillars, then grow to round the corners around the pillars (Figure 2.5c, IV). On further reducing ρ_{n} , symmetry is broken as vapor pockets from opposite pillars merge to form stripes of vapor spanning the inter-pillar region (Figure 2.5c, III). This change in the dewetted morphology coincides with a kink in $\Delta F(\rho_{\text{n}})$, suggesting that the system adopts a lower free energy path by transitioning from the vapor pocket to the stripe morphology. Subsequent decrease in ρ_{n} results in another transition to a donut-shaped vapor layer (Figure 2.5c, II). $\Delta F(\rho_{\text{n}})$ displays a maximum in the donut morphology; the barrier thus corresponds to a configuration with water molecules sticking to the central region of the basal surface that is farthest from the pillars, rather than an intact vapor layer. Expelling the remaining water molecules to form an intact vapor layer is energetically favorable, as is the subsequent (classical) rise of the vapor-liquid inter-

face along the pillars. This novel and clearly non-classical pathway preceding the formation of a vapor-liquid interface, which is facilitated by nanoscopic water density fluctuations and involves transitions between various dewetted configurations [19, 64], results in a smaller barrier for the Wenzel-to-Cassie transition than anticipated by macroscopic theory (Equation 1). We note that the kinks in $\Delta F(\rho_n)$ are a consequence of the high-dimensional free energy landscape being projected onto the scalar order parameter, ρ_n . Consequently, while we expect ρ_n to suitably describe the transition pathway within the different regions (I – V), capturing transitions between regions with different dewetted morphologies would require consideration of additional order parameters [20].

2.6. How Pressure Influences Barriers to Wetting and Dewetting

The implications of this non-classical pathway on the pressure dependence of the dewetting transition are even more interesting. Because pressure favors configurations with higher densities in a well-defined manner, its effect on $\Delta F(\rho_n)$ can be readily estimated, as shown in Appendix A. As shown in Figure 2.6a, the most striking effect of changing pressure is seen in the slope of region I; as pressure is increased, the slope decreases and the Cassie state is destabilized. The increase in pressure also leads to a decrease in the barrier to transition from the Cassie to the Wenzel state, as shown in Figure 2.6c. The pressure at which this barrier for wetting disappears, ΔP_{int} , corresponds to the limit of stability (or spinodal) of the Cassie state; at $\Delta P = \Delta P_{\text{int}}$, a system in the Cassie state will spontaneously descend into the Wenzel state, as shown in the Cassie-to-Wenzel hysteresis curve (blue) in Figure 2.6d. The exact agreement between the theoretical and simulated ΔP_{int} -values suggests that the macroscopic theory prediction of intrusion pressure, $\Delta P_{\text{int}} = -\gamma \cos \theta A_{\text{side}}/V$ [55, 9], should be reasonably accurate even for surfaces with nanoscale texture; a finding that is in harmony with recent experiments [12]. This success of macroscopic theory in describing ΔP_{int} , the pressure at which superhydrophobicity fails, is a direct consequence of its ability to capture region I of $\Delta F(\rho_n)$ accurately.

While regions II to IV play no role in determining ΔP_{int} , their role is profoundly important

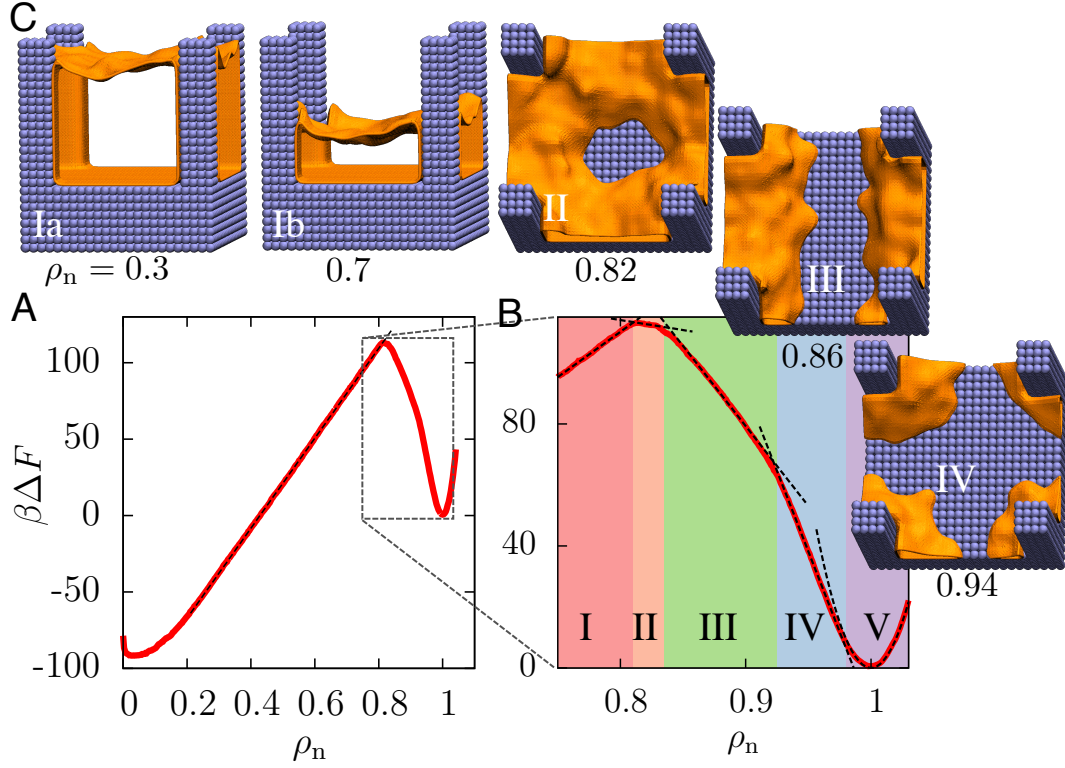


Figure 2.5: Free energetics and pathways of wetting-dewetting transitions on a pillared surface. (a) The simulated free energy, $\Delta F(\rho_n)$ (in units of the thermal energy, $k_B T \equiv \beta^{-1}$, with k_B being the Boltzmann constant and T the temperature), features two basins that are separated by a large barrier. For $0.2 < \rho_n < 0.8$, ΔF varies linearly with ρ_n , in agreement with macroscopic theory. However, the simulated barrier for dewetting is found to be smaller than the classical barrier. (b) Between the Wenzel state and the barrier ($0.82 < \rho_n < 1$), $\Delta F(\rho_n)$ is marked by several kinks, which demarcate five regions with distinct dewetted morphologies (dashed lines are a guide to the eye). (c) Representative configurations corresponding to these regions are shown as interfaces encompassing the dewetted volumes (shown in orange, waters omitted for clarity). Region V ($\rho_n \approx 1$) displays Gaussian fluctuations resulting in a parabolic basin. Region IV ($0.93 < \rho_n < 0.98$) is characterized by vapor pockets at the base of the pillars. As ρ_n is reduced, vapor pockets grow, break symmetry, and merge to form a striped vapor layer between the pillars. The stripe expands laterally in Region III ($0.83 < \rho_n < 0.93$) until a nearly intact vapor-liquid interface is formed. Region II ($0.81 < \rho_n < 0.83$) is characterized by water molecules sticking to the center of the cell, and also contains the non-classical barrier, which eventually gives way to the classical Region I at $\rho_n \approx 0.8$.

in the reverse process, that is, the Wenzel to Cassie (dewetting) transition. As pressure is decreased, not only does the slope of region I increase (Figure 2.6a), but the slopes of regions II - IV that are negative at $\Delta P = 0$, also increase, approaching zero at sufficiently negative pressures. Figure 2.6b zooms in on the liquid basin of $\Delta F(\rho_n)$, and highlights that as pressure is decreased, the location of the peak in the free energy shifts to higher ρ_n , and is accompanied by a gradual decrease in the height of the dewetting barrier (Figure 2.6c). This decrease in the dewetting barrier with decreasing pressure is in stark contrast with the classical expectation that a constant adhesion barrier must be overcome to go from the Wenzel to the Cassie state [53]. Under sufficient tension (negative pressure), the barrier goes to zero as the Wenzel basin reaches the limit of its stability. Our simulations thus suggest that superhydrophobicity can be recovered, that is, a system in the Wenzel state can spontaneously and remarkably transition back into the Cassie state below a so-called “extrusion” pressure, ΔP_{ext} (Figure 2.6d).

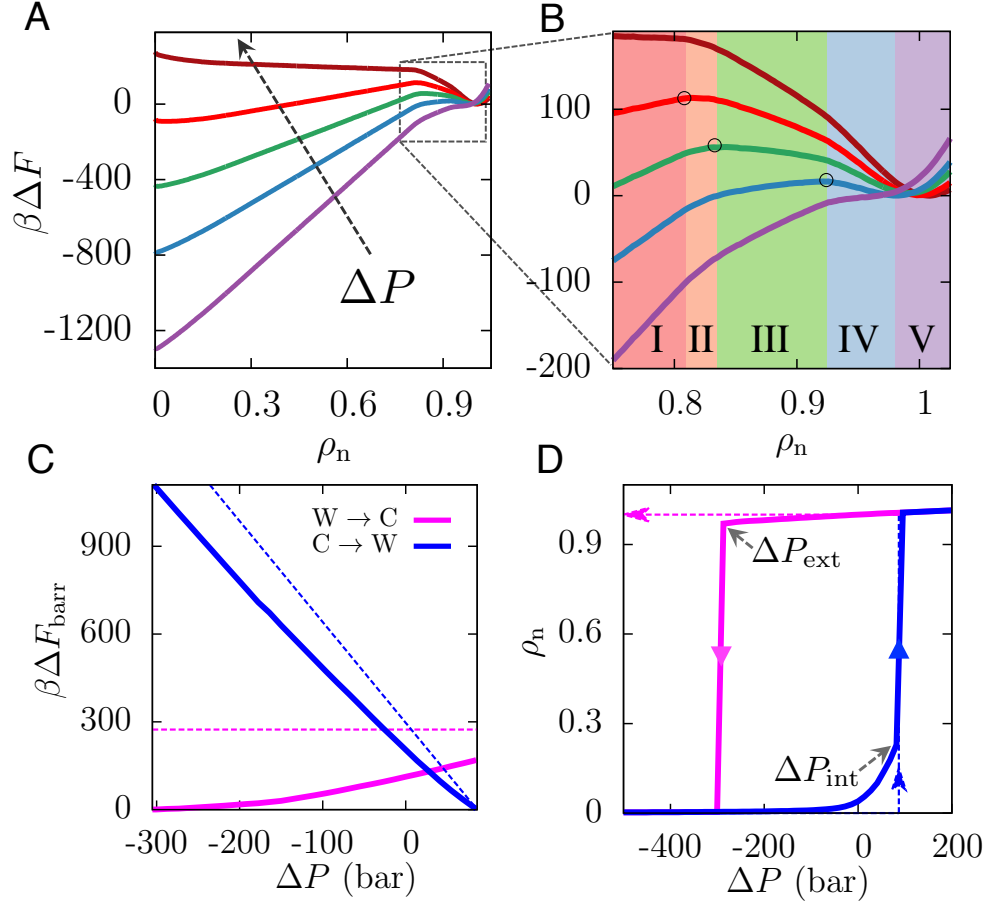


Figure 2.6: Effect of pressure on Cassie-Wenzel transitions. (a) $\Delta F(\rho_n)$ is shown for pressures ranging from -350 to 100 bar, with the arrow pointing in the direction of increasing pressure (purple: -350 bar, blue: -200 bar, green: -100 bar, red: 0 bar, brown: 100 bar). As pressure is increased, the slope of the classical region I decreases, destabilizing the Cassie state; conversely, as pressure is decreased, the Wenzel state is destabilized. (b) This destabilization of the Wenzel state is manifested not only in an increase in the slope of region I, but also in a corresponding increase in the slopes of the non-classical regions II - IV, from negative towards zero to eventually being positive. As a result, a decrease in pressure shifts the location of the barrier (black circles) to higher ρ_n and leads to a concomitant decrease in the height of the barrier. (c) The barriers for the wetting and dewetting transitions are shown here as a function of ΔP (simulation=solid lines, theory=dashed lines). Both the simulated and the classical Cassie-to-Wenzel barriers (blue) decrease on increasing pressure, eventually disappearing at the intrusion pressure, ΔP_{int} . On the other hand, while the classical Wenzel-to-Cassie barrier (magenta) is independent of pressure, simulations suggest that the barrier to dewetting disappears at a sufficiently small extrusion pressure, ΔP_{ext} . (d) Pressure dependent hysteresis curves for ρ_n , assuming the system remains in its metastable basin and is unable to surmount barriers larger than $1 k_B T$.

2.7. Outlook

Our work informs both fundamental and applied aspects of superhydrophobicity, by not only uncovering non-classical Cassie–Wenzel transition pathways, but by also revealing that a transition to Wenzel state to Cassie is possible. In particular, we show that the free energetics of wetting-dewetting transitions on nanotextured surfaces, the corresponding mechanistic pathways, and their dependence on pressure, are all strongly influenced by collective water density fluctuations. In this study we demonstrate that non-classical effects stem from the stabilization of dewetted morphologies that precede the formation of an intact vapor-liquid interface at the basal surface; once a vapor-liquid interface is nucleated, the remainder of the dewetting process is classical. While the importance of fluctuations at the nanoscale is clear, the extent to which fluctuations influence dewetting pathways at larger texture sizes has not been well understood. Because the width of this nascent vapor-liquid interface is not expected to depend on the texture size, and should always have nanoscale dimensions, fluctuations may continue to play an important role in the dewetting of surface textures with significantly larger feature sizes. We demonstrate this in Chapter 5 by characterizing free energy of wetting-dewetting transitions for a wide range of pillar sizes. Our results demonstrate that while certain aspects of dewetting on nanotextured surfaces are non-classical, other aspects can be classical. In particular, because the intrusion pressure depends on the free energetics of the (classical) ascent of the vapor-liquid interface along the pillars, it is well-described by macroscopic theory. Similarly, macroscopic models [10, 84] have also been shown to capture apparent contact angle of a liquid droplet localized in the Cassie or the Wenzel basin [31, 34, 73, 30]. However, lacking in such macroscopic models, is an understanding and even existence of a so-called “extrusion” pressure at which system can spontaneously transition from the Wenzel state into the Cassie state. Since fluctuations in water density stabilize a non-classical dewetting pathway, which features crossovers between a number of distinct dewetted morphologies that precede the formation of the classical vapor-liquid interface at the basal surface; the non-classical pathway offers a lower resistance to dewetting, leading to reduced dewetting barriers and a finite extrusion

pressure. However, it is clear that for the nano-pillared geometry shown here, the extrusion pressure is too small and barrier is still $100 k_B T$ s preventing spontaneous dewetting under ambient conditions. So the question arises, is it possible to then design geometries that can spontaneously recover their superhydrophobicity upon wetting. Chapter 3 successfully tackles this by carefully analyzing dewetting pathways on the pillared surface, and in particular, by finding regions of the surface texture that are hardest to dewet, and provides strategies for augmenting the surface texture to further destabilize the Wenzel state and reduce the barriers to dewetting. We note that the use of periodic boundary conditions in our simulations leads to the correlated dewetting of adjacent cells. We have ensured that the non-classical dewetting pathway discussed above is also observed in the absence of such correlations by additionally studying the dewetting of the first unit cell in a simulation setup containing four unit cells in Chapter 4.

CHAPTER 3 : Spontaneous Recovery of Superhydrophobicity in Nanotextured Surfaces

The contents of this chapter were published in Proceedings of the National Academy of Sciences of the United States of America (PNAS) (2016) volume 113, issue 20, pp 5508 – 5513 in a modified version and are reprinted here with permission from National Academy of Sciences.

The last decade has seen an explosion of studies pertaining to self-cleaning superhydrophobic surfaces, ranging from the development of novel techniques for their synthesis, to those aimed at understanding the properties of these surfaces and their putative applications. Superhydrophobicity stems from the presence of texture on a surface in the Cassie state in which a water droplet resides on the top of the surface asperities. One major impediment in creating superhydrophobic surfaces is the loss of superhydrophobicity upon the wetting of the surface texture in the Wenzel state. Moreover, this loss of superhydrophobicity is widely considered irreversible due to the presence of large kinetic barriers that impede the Wenzel-to-Cassie transition. To facilitate the recovery of superhydrophobicity and to afford reversible control over surface properties, significant efforts have focused on inducing the reverse Wenzel-to-Cassie dewetting transition. Using molecular simulations in conjunction with enhanced sampling techniques, here we show how an understanding of the Cassie-Wenzel transition pathway on simple pillared surfaces also facilitates the rational design of surfaces with superior superhydrophobicity. In particular, an understanding regions that are stickier than the other, allows us to augment the surface texture design, so that the barriers to dewetting are eliminated altogether and the Wenzel state becomes unstable at ambient conditions. Such robust surfaces, which defy classical expectations and can spontaneously recover their superhydrophobicity, could have widespread importance, from underwater operation to phase change heat transfer applications.

3.1. Introduction

Self-cleaning behavior, often referred to as ‘the lotus effect’, is attributed to the extreme water repellency, or superhydrophobicity, of a lotus leaf. Surfaces displaying a contact angle of 150 degrees or higher and a low contact angle hysteresis with water droplets are considered superhydrophobic and are extremely sought after due of their desirable qualities. For instance, these self-cleaning superhydrophobic surfaces can also be anti-icing, fog preventing, and anti-biofouling; hence, they are utilized in solar panels, windshields, electronics, and microfluidic devices. It is now well recognized that the superhydrophobicity of a surface is primarily influenced by its chemical composition and topography; it is the texture or topography of a surface that amplifies its hydrophobicity by trapping air within the textures in a so-called Cassie state. A water droplet in the Cassie state makes contact with only the crests of the textures, whereas the voids or the troughs are filled with air, rendering the surface superhydrophobic. However, superhydrophobicity breaks down when water penetrates these voids due to elevated pressures, temperatures, or condensation, yielding the wet Wenzel state [61, 50]. Moreover, this transition from the superhydrophobic Cassie state to the wet Wenzel state is widely considered irreversible; hence, creating surfaces that retain their superhydrophobicity for a wide range of external conditions remains an area of active research. In Chapter 2, we demonstrated that on a pillared surface water density fluctuations can lead to a reduction in the free energetic barriers to dewetting by circumventing the classical dewetting pathways. In particular, the fluctuation-mediated dewetting pathway involves a number of transitions between distinct dewetted morphologies, with each transition lowering the resistance to dewetting. This non-classical pathway also revealed that a transition from wet Wenzel state to superhydrophobic Cassie state is possible, but it’s prevented by large dewetting barriers and a very low Extrusion pressure. Importantly, by uncovering the nanoscale dewetting pathways, and in particular, by finding regions of the surface texture that are hardest to dewet, our results provide strategies for augmenting the surface texture to further destabilize the Wenzel state and reduce the barriers to dewetting. On such rationally designed surfaces, the barriers to dewetting the texture can

be eliminated altogether, so that the Wenzel state is no longer metastable, but has been rendered unstable at ambient conditions, and the superhydrophobic Cassie state can be spontaneously recovered from the wet Wenzel state.

3.2. Materials and Methods

Each of the surfaces that we study is composed of atoms arranged on a cubic lattice with a lattice spacing of 0.25 nm; the surface atoms are constrained to remain in their initial positions throughout the simulations. In this chapter we study surfaces that contain spherical or hemispherical nanoparticles, which are also made of atoms on a cubic lattice, and are placed at the center of the simulation cell of the pillared surface, touching the top of the basal surface. The pillared surface is same as the one studied in Chapter 2, *i.e.* contains square pillars of height, $H=4.5$ nm, and width, $W=2$ nm, separated by inter-pillar spacing, $S=4$ nm. Each system is periodic in all three spatial directions and is initialized in the Wenzel state. The surfaces are hydrated with roughly 7,000 water molecules, so that even in the Wenzel state, a 2 nm thick water slab rests above the pillars. We also provide a buffering vapor layer at the top of the simulation box, which is roughly 6 nm thick in the Wenzel state. As waters leave the textured region, the vapor layer shrinks to roughly 2 nm in the Cassie state. The vapor layer, which is thus present in our system at all times, ensures that water is in coexistence with its vapor, and $\Delta P = 0$ [45]. To ensure that the vapor layer remains at the top of the $6 \times 6 \times 15$ nm³ simulation box, we include a repulsive wall at $z=14.5$ nm. We additionally study a pillared surface of dimension $W = 2$ nm, $H = 3$ nm, and $S = 3$ nm (“Pillars_B”). This surface was augmented with a ‘T’ shaped nanoparticle; the vertical element of the ‘T’ is 1 nm in height and has a square cross-section with a width of 0.5 nm, whereas the horizontal element is composed of one layer of atoms and has a square cross-section with a width of 2 nm. The dimensions of each of the surfaces studied in this chapter along with the number of water molecules in the textured volume, V , are provided in Table 3.1. The simulation details are identical to that provided in Chapter 2 (section 2.2.2).

3.3. Spontaneously Recovering Superhydrophobicity on a Novel Surface Texture

For the pillared surface studied in Chapter 2, Figure 2.4 and 2.5, the extrusion pressure, $\Delta P_{\text{ext}} = -300$ bar, is quite small. While water can sustain significant tension, and experiments have been able to access $\Delta P \lesssim -1200$ bar before cavitation occurs [51], from a practical standpoint, robust superhydrophobic surfaces with significantly larger ΔP_{ext} values that exceed atmospheric pressure are desirable. Clues for designing such surfaces are contained within the dewetting pathway of pillared surfaces (Figure 2.4), which suggests that it is hardest to remove water molecules from the center of the simulation cell. To destabilize those waters and facilitate the formation of the vapor-liquid interface, we modify the pillared surface by adding a spherical nanoparticle at the center of the cell; see inset of Figure 3.1a. A comparison of the free energy profile, $\Delta F(\rho_n)$, of this novel surface with that of the pillared surface (Figure 3.1) highlights that the introduction of the nanoparticle has a dramatic influence on $\Delta F(\rho_n)$; the Wenzel state is destabilized to such an extent that it is no longer metastable, but has been rendered unstable at $\Delta P = 0$. The dewetting trajectory as well as characteristic configurations along the dewetting pathway (Figure 3.1c), highlight that the strongly confined region between the nanoparticle and the basal surface nucleates a vapor bubble ($\rho_n \approx 1$), which then grows to facilitate the spontaneous formation of an intact vapor-liquid interface ($\rho_n = 0.83$). Once formed, the vapor-liquid interface begins to rise, and although it adheres to the top of the nanoparticle, the interface continues to rise along the pillars; the unfavorable density gradient between the center and the edges of the cell then facilitates the barrierless de-pinning of the interface.

3.3.1. Dependence of free energy on pressure highlights a positive extrusion pressure

In Figure 3.2, we plot the pressure dependence of $\Delta F(\rho_n)$ for this surface using the procedure outlined in Appendix A. The Cassie-to-Wenzel barrier (blue) decreases on increasing the pressure, eventually disappearing at the intrusion pressure, $\Delta P_{\text{int}} = 369$ bar (Figure 3.2b). Similarly, the Wenzel-to-Cassie barrier (magenta) barrier decreases upon decreasing pressure, and disappears at a positive extrusion pressure, $\Delta P_{\text{ext}} = +68$ bar. In Figure 3.2c, the

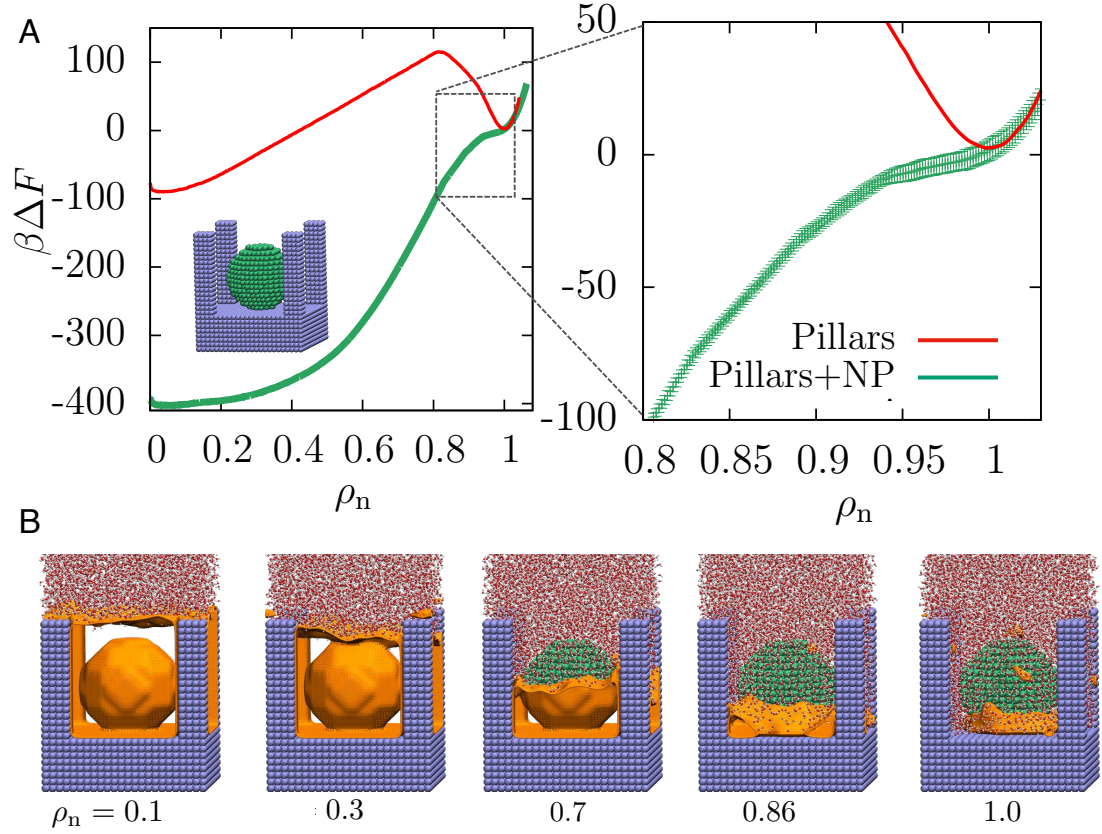


Figure 3.1: The free energetics of a pillared surface augmented with a spherical nanoparticle at the center of the cell, features an unstable Wenzel state under ambient conditions. (a) The free energetics of a surface with a 3.5 nm diameter spherical nanoparticle at the center of the cell (inset) are compared to the corresponding pillared surface; the surface modification stabilizes the superhydrophobic Cassie state and renders the Wenzel state unstable. (b) Representative instantaneous interface configurations highlight that dewetting commences at the center of the cell and spreads outwards, facilitating the spontaneous formation of the vapor-liquid interface, which then rises along the pillars. While waters stick to the top surface of the nanoparticle, the unfavorable gradient in water density between the edges and the center of the cell facilitates the depinning of the vapor-liquid interface.

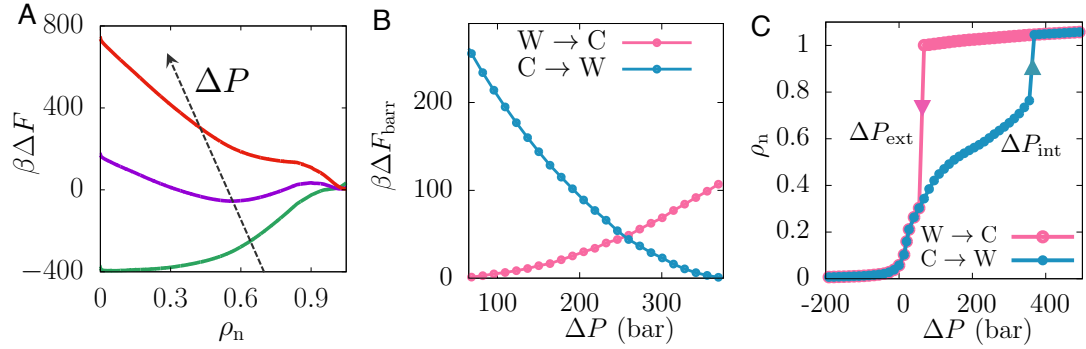


Figure 3.2: Effect of pressure on the free energy profiles and on the magnitude of the wetting and dewetting barriers for the pillared surface with a 3.5 nm nanoparticle. (a) $\Delta F(\rho_n)$ is shown for three different pressures. At $\Delta P = 0$ (green), the Wenzel state has been rendered unstable. Higher pressures favors states with higher densities; as pressure is increased to $\Delta P = 200$ bar (purple), the Wenzel and the Cassie states co-exist. At higher pressures, such as $\Delta P = 400$ bar (red), the Wenzel state becomes the stable state. (b) The barriers for the wetting (Cassie-to-Wenzel) and dewetting (Wenzel-to-Cassie) transitions are shown. The Cassie-to-Wenzel barrier (blue) disappears at the intrusion pressure, $\Delta P_{\text{int}} = 369$ bar. Similarly, the Wenzel-to-Cassie barrier (magenta) barrier disappears at a positive extrusion pressure, $\Delta P_{\text{ext}} = +68$ bar. (c) Pressure dependent hysteresis curves for ρ_n also highlights spontaneous recovery of superhydrophobicity at ambient conditions, *i.e.* at any pressure below 68 bar.

pressure dependent hysteresis curves assuming the system remains in its metastable basin and is unable to surmount barriers larger than 1 kBT highlights that system in Wenzel state should spontaneously dewet on decreasing the pressure below 68 bar, and lead to a recovery of the superhydrophobic Cassie state.

3.3.2. Unbiased trajectories highlighting spontaneous recovery of superhydrophobicity

The absence of a dewetting barrier in Figure 3.1a for the pillared surface containing a 3.5 nm nanoparticle at the center of the basal surface, suggests that a system initially in the Wenzel state should undergo spontaneous dewetting. However, because ρ_n serves to project the high-dimensional vector of molecular configurations (positions of all waters) onto a single (scalar) co-ordinate, the absence of a barrier in $\Delta F(\rho_n)$ does not guarantee that the system will spontaneously dewet. Dewetting can be impeded if barriers exist in any of remaining degrees of freedom that the system possesses once the ρ_n co-ordinate is projected out; in such an instance, a system initialized in the wet state would remain in the wet state. To examine this possibility and investigate whether barriers exist in co-ordinates orthogonal to ρ_n , we performed 26 unbiased simulations at $\Delta P = 0$, starting from the fully wet state. The 26 different initial configurations were randomly picked from a biased simulation run at a pressure higher than the intrusion pressure of the system ($\Delta P = 400$ bar) to ensure that system was in fully wet state before running the unbiased simulations. In each case, the system spontaneously transitions to the Cassie state within 700 ps, suggesting a barrierless transition from the Wenzel to the Cassie state. ρ_n as a function of time is shown for one such trajectory in Figure 3.3a and the distribution of times required to reach $\rho_n = 0.2$ across the 26 simulations is shown in Figure 3.3b. In Figure 3.1c, we show that a typical trajectory of the system dewetting from Wenzel to Cassie state follows the same path that was obtained from free energy calculations in Figure 3.1b.

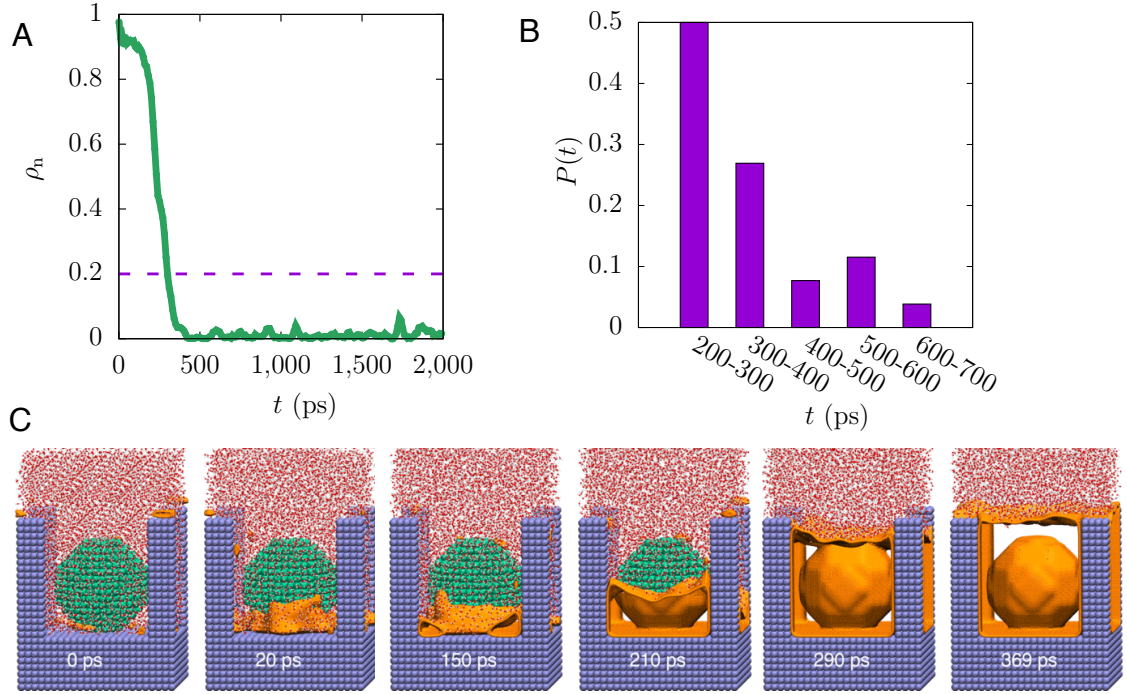


Figure 3.3: Equilibrium trajectories highlighting spontaneous and barrierless recovery of superhydrophobicity on the pillared surface with a 3.5 nm nanoparticle. (a) ρ_n as a function of time for a typical unbiased simulation initialized in the Wenzel state for the system described in Figure 3.1. (b) The distribution of times for the system to reach a configuration with $\rho_n = 0.2$ was obtained from 26 trajectories initialized in the Wenzel state. The average time to reach $\rho_n = 0.2$ is 375 ps. (c) Instantaneous interface configurations corresponding to unbiased trajectory shown in (a) highlight that dewetting commences at the center of the cell and spreads outwards, facilitating the spontaneous formation of the vapor-liquid interface in accordance with the pathway suggested by the free energy calculations shown in Figure 3.1b.

3.4. Informing the Designs of Robust Superhydrophobic Surfaces

The dewetting trajectory as well as characteristic configurations along the dewetting pathway (Figure 3.1b), highlight that the strongly confined region between the nanoparticle and the basal surface nucleates a vapor bubble ($\rho_n \approx 1$), which then grows to facilitate the spontaneous formation of an intact vapor-liquid interface ($\rho_n = 0.83$). Once formed, the vapor-liquid interface begins to rise, and although it adheres to the top of the nanoparticle, the interface continues to rise along the pillars; the unfavorable density gradient between the center and the edges of the cell then facilitates the barrierless depinning of the interface.

3.4.1. Criteria for spontaneous recovery of superhydrophobicity

This dewetting pathway suggests that the spontaneous recovery of superhydrophobicity requires: (i) a confined (negative curvature) region of nanoscopic dimensions to nucleate a vapor bubble, which (ii) must grow to a large enough size to facilitate the formation of an intact vapor-liquid interface, which in turn (iii) must not be pinned by surface features as it rises along the pillars.

To test the validity of these criteria, we study three additional surfaces that each destabilize the central waters, but violate exactly one of the above criteria (Figure 3.4.2a). By running unbiased simulations initialized in the Wenzel state, we show that none of the three surfaces are able to spontaneously transition to the Cassie state (Figure 3.4.2b).

3.4.2. Free Energetics of Pillared Surfaces Augmented with Nanoparticles

In Figure 3.4.2c,d, we compare the free energetics of each of these augmented surfaces with that of the pillared system (red curve), and the pillared system with 3.5 nm spherical nanoparticle (green curve). The addition of a 3.5 nm hemispherical particle to the pillared surface (blue curve), destabilizes the waters in the central region and significantly reduces the dewetting barrier (from $118 k_B T$ to $11.5 k_B T$); however, due to its inability to nucleate and grow a sufficiently large vapor bubble, it presents a barrier to dewetting. Similarly, the

pillared surface containing a 3 nm spherical nanoparticle (orange curve), which nucleates a vapor bubble but not one that is large enough to form an intact vapor-liquid interface, also has a small dewetting barrier ($8 k_B T$). In contrast, the pillared surface augmented with an inverted 3.5 nm hemispherical particle (purple curve), is able to successfully nucleate an intact vapor-liquid interface and features an unstable Wenzel state; however, water molecules eventually get pinned to the top of the hemisphere leading to the formation of a partially wet metastable state. This metastable state at $\rho_n \approx 0.7$ presents a barrier of $14 k_B T$ that must be overcome to recover the superhydrophobic Cassie state. In Table 3.1, we report the number of waters in the Wenzel state, N_{liq} , as well as the free energy of the Cassie state, ΔF_{Cassie} , and barrier state, ΔF_{barr} , relative to the Wenzel state, for each of these surfaces. In each case, the destabilization of the central waters by the nanoparticle leads to a substantial reduction in the dewetting barrier; however, this destabilization alone is insufficient to lead to the spontaneous recovery of the superhydrophobic Cassie state. Because augmenting the surface texture alters the stability of the barrier and the Wenzel states in different ways, and can also change the partially dewetted morphologies observed along the dewetting pathway, the relationship between the surface texture geometry and the height of the dewetting barrier is non-trivial. In particular, the extent to which a change in surface texture influences the dewetting barrier does not depend on its ability to (de)stabilize the barrier state or the Wenzel state alone; rather, how the surface texture modification influences the entire dewetting pathway is important.

Even more non-trivial is the effect of geometry of the augmentation on the intrusion and extrusion pressures; See Table 3.1. Since system-i fails to nucleate a vapor bubble due to lack of negative curvature, it has a relatively lower resistance to intrusion with $P_{\text{int}} = 130$ bar, and a small value of extrusion pressure, $P_{\text{ext}} = -93$ bar; both of which are better than the corresponding bare pillared system ($P_{\text{int}} = 96$ bar and $P_{\text{ext}} = -300$ bar). System-ii is more robust with higher intrusion pressure of 286 bar and $P_{\text{ext}} = -53$ bar. Since, system-iii with inverted hemispherical nanoparticle forms an intact vapor layer that sits on top of the nanoparticle, it features a very high intrusion pressure of $P_{\text{ext}} = 369$ bar identical to that

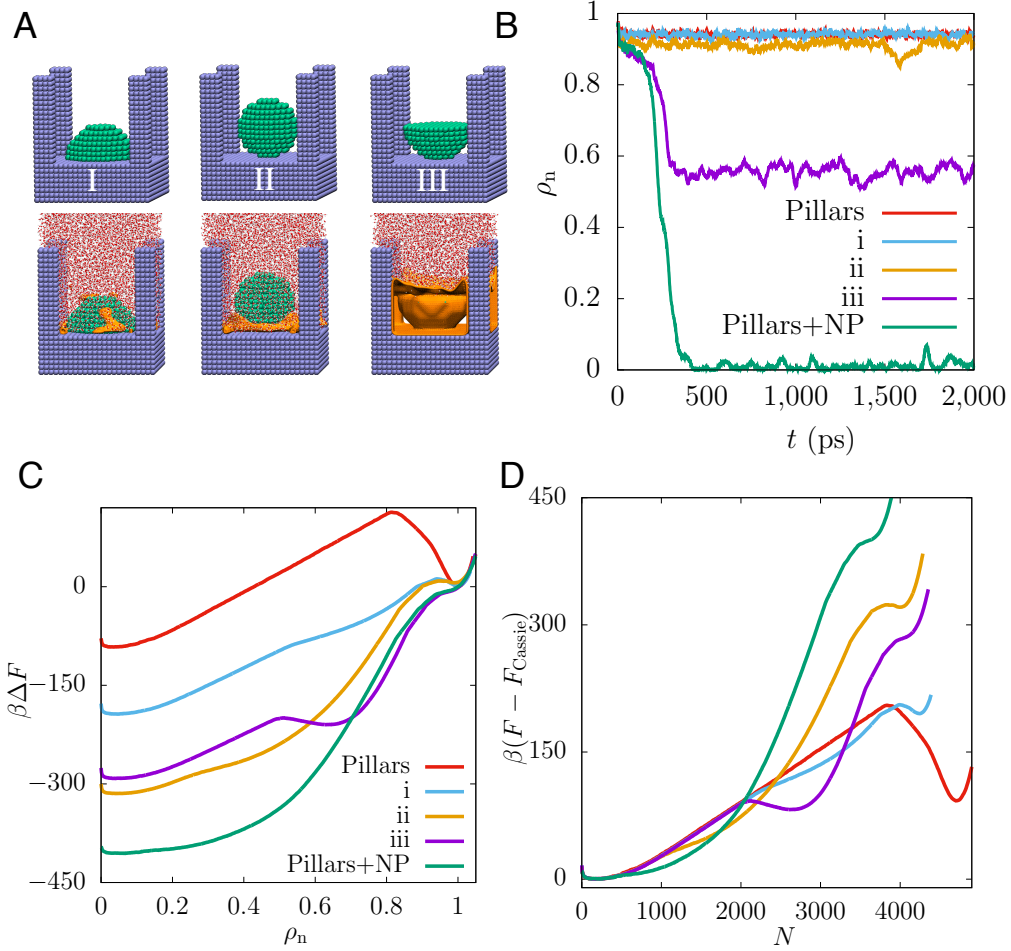


Figure 3.4: Free energy profiles of five textured surfaces augmented with nanoparticles of different shapes. (a) The three additional variants of the pillared surface containing (i) a 3.5 nm hemispherical particle, (ii) a 3 nm spherical nanoparticle, and (iii) an inverted 3.5 nm hemispherical particle (top row) each violate one of the three criteria for spontaneous dewetting outlined in the text. When initialized in the Wenzel state, these surfaces are unable to undergo complete dewetting, as evidenced by the final configurations of 2 ns long unbiased simulations (bottom row). (b) The time dependence of ρ_n for such unbiased simulations highlights that the Wenzel state is unstable only for the pillared system with a 3.5 nm spherical nanoparticle. (c) The free energy profile, $\Delta F(\rho_n)$, of the bare pillared surface shown in Figure 2.4 (“Pillars”), is compared with the free energy profiles of the three pillared surfaces shown in part a. While the surface modifications reduce the barrier to dewetting significantly in each case, none of the three surfaces display barrierless dewetting. In contrast, no dewetting barrier is observed in $\Delta F(\rho_n)$ for the pillared surface with a 3.5 nm spherical particle (“Pillars+NP”) shown in Figure 3.1. (d) The free energy profiles shown in panel c, are replotted here as a function of the number of waters, N in V (as opposed to ρ_n), and with the Cassie (as opposed to Wenzel) state serving as the reference.

Table 3.1: Geometric parameters for systems studied in Figure 2.5 (“Pillars”), Figure 3.4.2 (“i”, “ii”, and “iii”), Figure 3.1 (“Pillars+NP”), and Figure 3.4.3 (“Pillars_B” and “Pillars_B+T”), are reported along with the number of waters in the fully wet state, N_{liq} , as well as the free energies of the Cassie and the barrier states relative to the Wenzel state and intrusion and extrusion pressures.

System	H	W	S	N_{liq}	ΔF_{Cassie}	ΔF_{barr}	ΔP_{int}	ΔP_{ext}
System	(nm)	(nm)	(nm)	#	($k_{\text{B}}T$)	($k_{\text{B}}T$)	bar	bar
Pillars	4.5	2	4	4710	-92	118	96	-300
i	4.5	2	4	4240	-194	11.5	130	-93
ii	4.5	2	4	4040	-320	8	286	-53
iii	4.5	2	4	4150	-292	14*	369	-34
Pillars+NP	4.5	2	4	3710	-406	0	369	+68
Pillars _B	3	2	3	2040	-83	42	136	-232
Pillars _B +T	3	2	3	1830	-149	0	220	+55

^{1*} – The reported barrier to dewetting in “iii” is not relative to the unstable Wenzel state, but relative to the metastable partially wet state; see Figure. 3.4.2.

of the pillars+NP system shown in figure 3.2 and a relatively moderate extrusion pressure of -34 bar. The results summarized in Table 3.1, hence suggest that there is non-trivial effects of geometry on the robustness of the surface and there is no correlation between number of water molecules in the liquid basin and the intrusion and extrusion pressures of a system.

3.4.3. Another augmented surfaces that features an unstable Wenzel state under ambient conditions

By following the three design criteria outlined above we were able to design a second surface texture, which displays an unstable Wenzel state at ambient conditions; see (Figure 3.4.3). To ensure that there are no barriers in any coordinate orthogonal to N , we performed 25 unbiased simulations at $\Delta P = 0$, starting from the fully wet state for this system described in Figure 3.4.3. The initial positions of the waters were the same for each simulation, but their initial velocities were randomized. In each case, the system spontaneously transitions to the Cassie state within 300 ps, suggesting a barrierless transition from the Wenzel to the

Cassie state. Thus, the pillared surface with a 3.5 nm spherical nanoparticle in Figure 3.1 is not unique; introducing a ‘T’-element with dimensions that were judiciously chosen to satisfy the criteria described in the main text, enables us to similarly destabilize the Wenzel state. The free energetics are reported as a function of the number of waters, N , in V , and using the Cassie (as opposed to Wenzel) state as reference. Free energy profiles, $\beta\Delta F(\rho_n)$, at three different pressures for the pillared surface with the ‘T’-element, highlights that a partially filled state ($N \approx 1400$) can become the stable state at intermediate pressures (Figure 3.4.3b, purple). Pressure dependent hysteresis curves, in Figure 3.4.3c also highlight the presence of an intermediate state corresponding to partially wet state wherein the basal surface is fully dewetted, but water molecules adhere to the top of the ‘T’-element. This surface also features a positive extrusion pressure of +55 bar and an intrusion pressure of 100 bar. In Figure 3.4.3d, the dewetting pathway for the pillared surface with the ‘T’-element is shown using instantaneous interfaces encompassing the dewetted regions (in orange, water molecules are omitted for clarity). A vapor bubble initially forms at the bottom of the ‘T’-element ($\rho_n \equiv N/N_{\text{liq}} \approx 1$). The bubble then grows in size as ρ_n decreases, and forms a partially wet state wherein the basal surface is fully dewetted, but water molecules adhere to the top of the ‘T’-element ($\rho_n = 0.62$). With a further decrease in ρ_n , the vapor-liquid interface continues to rise along the sides of pillars, whereas the top of the ‘T’-element remains wet, creating an unfavorable density gradient ($\rho_n = 0.5$). This density gradient eventually facilitating a barrierless transition to the Cassie state ($\rho_n = 0.1$) under ambient conditions. The fact that each of these complex criteria have to be satisfied for spontaneous dewetting, could help explain why nanotextured surfaces that spontaneously recover superhydrophobicity have not been discovered serendipitously, despite the use of both nanoparticles and nanoscale pillars to texture surfaces [88, 12].

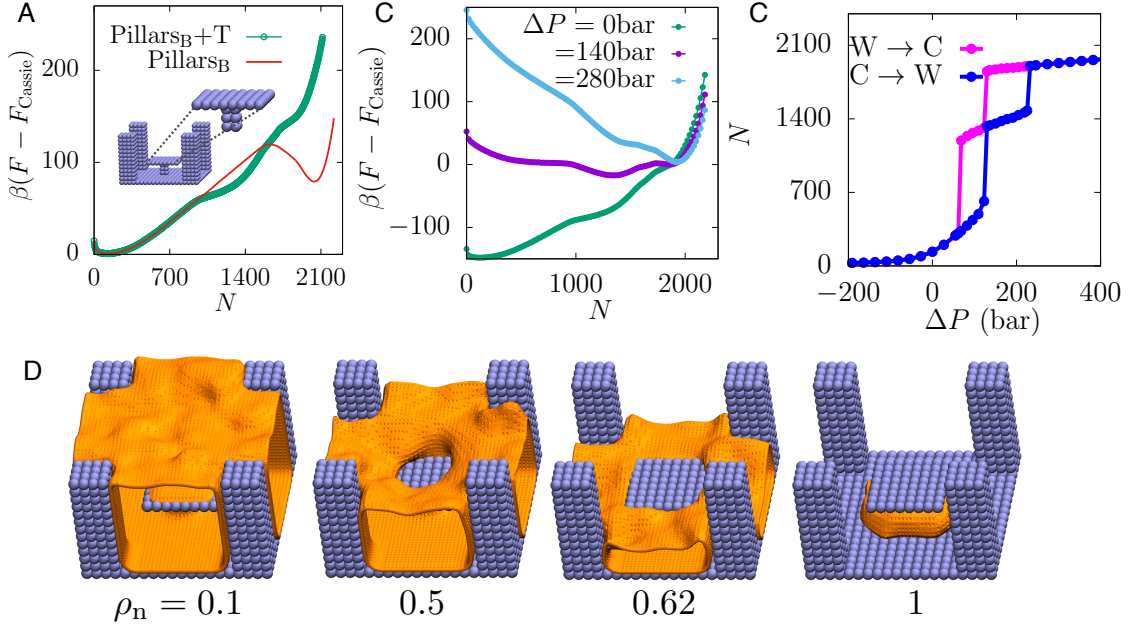


Figure 3.5: Another modified surface that displays no barrier to dewetting. (a) Inset: Unit cell of a pillared surface with a ‘T’-element at the center of the cell. The free energetics of this surface with $W = 2$ nm, $H = 3$ nm, and $S = 3$ nm (“Pillars_B+T”), are compared to the corresponding pillared surface (“Pillars_B”); the surface modification destabilizes the Wenzel state and renders it unstable. (b) Free energy profiles, at three different pressures for the pillared surface with the ‘T’-element, highlights that a partially filled state ($N \approx 1400$) can become the stable state at intermediate pressures. (c) Pressure dependent hysteresis curves highlight a positive extrusion pressure, $\Delta P_{\text{ext}} = +55$ bar. (d) The dewetting pathway for the pillared surface with the ‘T’-element is shown using instantaneous interfaces encompassing the dewetted regions (in orange, water molecules are omitted for clarity). A vapor bubble initially forms at the bottom of the ‘T’-element which then grows in size as ρ_n decreases, and forms a partially wet state wherein the basal surface is fully dewetted, but water molecules adhere to the top of the ‘T’-element ($\rho_n = 0.62$). With a further decrease in ρ_n , the vapor-liquid interface continues to rise along the sides of pillars, whereas the top of the ‘T’-element remains wet, creating an unfavorable density facilitating a barrierless transition to the Cassie state under ambient conditions.

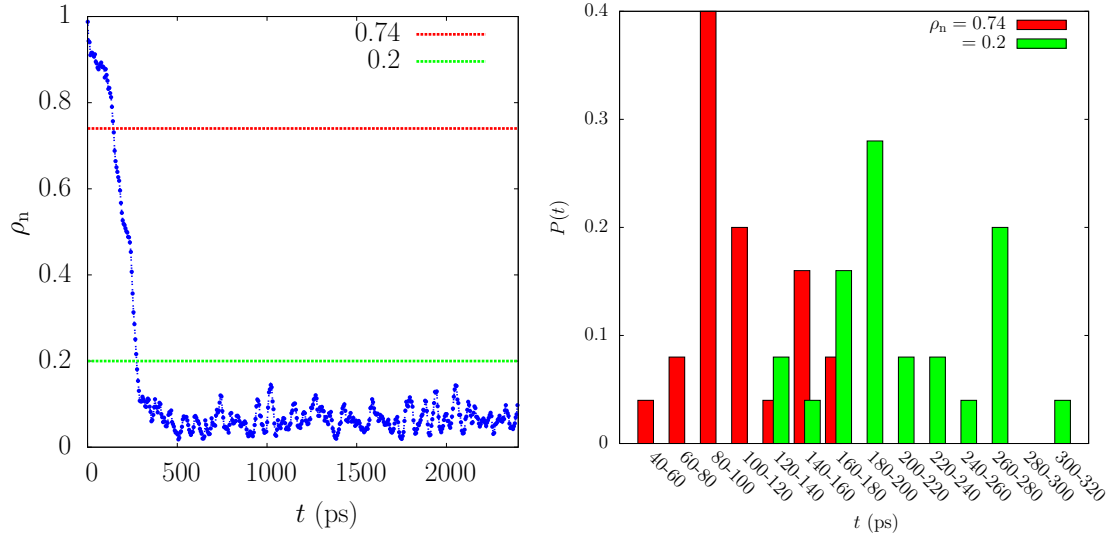


Figure 3.6: (a) ρ_n as a function of time for a typical unbiased simulation initialized in the Wenzel state for the “Pillars_B+T” system described in Figure 3.4.3. (b) The distribution of times for the system to reach a configuration with $\rho_n = 0.2$, indicating a transition to Cassie state and $\rho_n = 0.74$, indicating a transition to a metastable state obtained from 25 trajectories initialized in the Wenzel state. The average time to reach $\rho_n = 0.2$ is 220 ps.

3.5. Outlook

Although numerous methods have been suggested for texturing hydrophobic surfaces, from top-down fabrication to bottom-up self-assembly techniques [36, 77, 26], a key bottleneck in their widespread adoption has been the fragility of the superhydrophobic Cassie state and the associated irreversible breakdown of superhydrophobicity upon wetting [7]. Our findings represent a major step in addressing this challenge, highlighting the importance of water density fluctuations in stabilizing non-classical pathways on nanotextured surfaces, which reduce dewetting barriers and enable the spontaneous recovery of superhydrophobicity. Our results also suggest a general strategy for augmenting the design of existing nanotextured surfaces. By identifying the pathways to dewetting, and in particular, the regions that are hardest to dewet, we were able to inform the location of sites, where the introduction of additional texture would be optimal. The rational design of nanotextured surfaces with superior superhydrophobicity could be further bolstered by investigating the extent to which

the dewetting of a unit cell is influenced by whether an adjacent cell is wet or dry. In particular, if a dry cell could facilitate the dewetting of adjacent cells, then not all cells would have to possess a nanoparticle for the spontaneous recovery of superhydrophobicity; once a nanoparticle-containing cell dewetted spontaneously, it could facilitate the dewetting of cells adjacent to it. Such co-operative effects would also have interesting implications on whether dewetting is nucleated at the edges or the center of a water droplet, and on the pinning of the three phase contact line and the associated contact angle hysteresis [15, 5]. The underpinnings of such co-operative dewetting phenomena have been explored Chapter 4.

CHAPTER 4 : Cooperative Effects in Dewetting can Facilitate the Spontaneous Recovery of Superhydrophobicity

A water droplet in the Cassie state sits on the peaks of a textured surface, has almost spherical shape, and rolls off effortlessly, conferring the surface superhydrophobic. However, water on textured surfaces can readily impale into a wet Wenzel state under a variety of perturbations such as elevated pressure, temperature or due to condensation resulting in a loss of superhydrophobicity. Upon removing the perturbation, spontaneous dewetting from the Wenzel state to the Cassie state is required for the recovery of superhydrophobicity. It's recently shown that one strategy to create spontaneously dewetting surfaces, is to identify the dewetting pathway of a surface, and provide optimally designed nucleating sites such as spherical nanoparticles at the places where water molecules are hardest to dewet. Using molecular dynamics, here we simulate uncoupled nanopillared cells to explore whether such nucleating sites have to be present in each and every cell of a periodic system to create spontaneously dewetting surfaces. We reveal that dewetting on periodic pillared surfaces follows an extremely cooperative pathway and dewetting in one of the cells can facilitate barrierless dewetting in neighboring cells; in such systems, placing a spherical nano-particle in only one cell leads to spontaneous dewetting of entire surface under ambient conditions. Additionally, this cooperative dewetting effect is dictated by the ratio of inter-pillars spacing to the pillar width and the contact angle of the surface.

4.1. Introduction

Water droplets display large contact angles (above 150°) and small contact angle hysteresis on superhydrophobic surfaces, making them versatile materials with self-cleaning, anti-fogging, anti-icing, and other desirable qualities [89, 14, 35, 90]. Superhydrophobicity derives from a texturing of hydrophobic surfaces; the aversion of water for the hydrophobic surface impedes wetting of the surface texture, and stabilizes a “Cassie” state, in which the water droplet sits on the tips of the surface asperities [32, 16]. However, water can penetrate the surface texture to yield the so-called “Wenzel” state under a variety of conditions, such as elevated hydrostatic or dynamic pressure, surface vibration or defects, or due to condensation [71, 47, 52, 27, 6, 68, 37, 33]. Such a wetting of the surface texture leads to extensive contact between the solid surface and water, and results in a breakdown of superhydrophobicity. In fact, by employing periodic surface textures, recent studies have shown that the wetting of a single unit cell or a cluster of adjoining cells can bring about the wetting of the entire surface texture [47, 44, 65, 91, 42]. Moreover, due to large energetic barriers that impede the reverse (dewetting) transition, this breakdown in superhydrophobicity is widely believed to be irreversible [53, 61, 7, 50]. The irreversibility of the Cassie-to-Wenzel or wetting transition has been a major impediment in the design of robust superhydrophobic surfaces, and has prompted a number of theoretical and simulation studies to focus on the thermodynamics, kinetics and mechanisms of wetting and dewetting transitions on textured surfaces [53, 12, 19, 30, 31, 73, 72, 60]. Classical theoretical treatments, based on macroscopic interfacial thermodynamics, attribute the Wenzel-to-Cassie dewetting barrier to the work of adhesion for nucleating a vapor-liquid interface. Recent molecular simulation studies of wetting-dewetting transitions on nanotextured surfaces, have additionally shown that fluctuations can play an important role in dewetting at the nanoscale, and stabilize non-classical transition pathways [19, 69, 70, 74, 60]. In particular, in Chapter 2 we have shown that dewetting on nanotextured surfaces is indeed non-classical, involving transitions between a number of distinct dewetted morphologies, and resulting in a reversible Cassie to Wenzel transition [60]. An understanding of the non-classical pathways further

enabled us to propose surface texture modifications, which defied conventional expectations, and featured an unstable Wenzel state at ambient conditions (Chapter 3). On such rationally designed surfaces, we demonstrated that the superhydrophobic Cassie state could be spontaneously recovered from the Wenzel state through a barrierless dewetting transition; augmenting pillared surfaces with spherical nanoparticles facilitated a spontaneous recovery of the Cassie state under ambient conditions [60]. However, because this simulation study employed periodic boundary conditions, the system was equivalent to infinite system made of indistinguishable periodic cells with identical wetting/dewetting pathway. Here we investigate whether dewetting transitions can display cooperativity akin to the previously observed cooperative wetting transitions, that is, can the dewetting of single unit cell or a cluster of cells on a periodic surface stimulate to the dewetting of the entire surface. The answer to this question has important implications for the design of superhydrophobic surfaces that can spontaneously recover their superhydrophobicity. For instance, in the absence of cooperative dewetting, such proposed modifications to the surface texture would have to be extensive, that is, such modifications would have to be made in every unit cell. In contrast, if a dry cell could facilitate the dewetting of adjacent cells, then not all cells would have to possess modifications such as nanoparticles for the spontaneous recovery of superhydrophobicity; once a nanoparticle-containing cell dewetted spontaneously, it could facilitate the dewetting of cells adjacent to it.

To understand the dewetting pathways in realistic and distinguishable cells, we study systems in which one, two, or four unit cells of a pillared geometry are explicitly simulated. We show that the dewetting in such systems is indeed a cooperative process; one dewetted cell leads to a barrierless dewetting of the neighboring cells. For instance, placing an optimally designed nanoparticle in one of the cells in a four celled system was enough to spontaneous dewet all four cells without any barrier. We additionally show that such cooperative dewetting effects are significantly affected by the contact angle and the geometry of the system, particularly, on the ratio of inter-pillar separation, S to the pillar-width, W . Interestingly, for surfaces with $\alpha \equiv S/W$ less than a critical value α_c , dewetting in one cell facilitates

dewetting of the entire surface without any additional energy barrier. Conversely, systems with $\alpha > \alpha_c$ demonstrate cooperative wetting *i.e.* complete collapse of superhydrophobic Cassie state if one of the cells becomes wet. We then provide a simple macroscopic framework to predict $\alpha_c = 1.09$, such that an infinitely large system with one nucleating cell would spontaneously dewet. However, a small value of α_c limits the apparent contact angle that can be achieved as $\cos \theta_{\text{app}} = -1 + (1 + \cos \theta)/(1 + \alpha)^2$. To address this, we provide a simple solution of using a cluster of cells containing nucleating sites as opposed to only one, which then increases the value of α_c .

4.2. Materials and Methods

To characterize the free energetics of wetting-dewetting transitions on nano-textured surfaces, we use molecular dynamics simulations in conjunction with the Indirect Umbrella Sampling (INDUS) method [57, 56] and Appendix A. The surfaces are composed of atoms that are arranged on a cubic lattice with a spacing of 0.25 nm and are constrained to remain in their positions throughout the simulations. Each surface consists of a flat basal surface made of a single layer of atoms which is textured using pillars of height, H , and a square cross-section with width, W . The pillars are arranged on a square lattice with inter-pillar spacing, S . To understand whether wetting and dewetting transitions on such surfaces are cooperative, we study surfaces wherein one, two, or four unit cells of this square lattice are explicitly represented, and replicated using periodic boundary conditions. Table 4.1 lists the geometric parameters of all the pillared systems studied here by accounting for offsets in geometric parameters as described in Appendix B. We also study surfaces that additionally contain a spherical nanoparticle; like the pillars, the nanoparticle is made of atoms on a cubic lattice with a spacing of 0.25 nm, and it is placed at the center of a unit cell, touching the top of the basal surface. Enough water molecules are included in the simulation box to wet the surface texture in the Wenzel state, and a 2 nm thick water slab is added above the pillars. A wall of purely repulsive particles is included at the top of the simulation box to maintain a buffering vapor layer above the water slab. We ensure that this buffering vapor

Table 4.1: Geometric parameters for all systems studied.

S/W	W (nm)	S (nm)	H (nm)
0.81	2.19	1.77	3.11
1.26	2.19	2.77	3.11
1.48	1.19	1.77	3.11
1.72	2.19	3.77	3.11
2.33	1.19	2.77	3.11
3.17	1.19	3.77	3.11
4.85	1.19	5.77	3.11

layer is at least 2 nm thick, even in the Cassie state, wherein water molecules leave the textured region and cause the buffering vapor layer to shrink. Thus, the buffering vapor layer is present in our system at all times and ensures that water remains in coexistence with its vapor throughout and, correspondingly, that the system pressure is equal to the water-vapor coexistence pressure at the system temperature [45]. The surface atoms interact with the oxygen atoms of the SPC/E model of water [3] through the Lennard-Jones (LJ) potential ($\sigma = 0.35$ nm, $\epsilon = 0.40$ kJ/mol) truncated at 1 nm leading to a flat surface water droplet contact angle of $\theta = 123^\circ$ on the basal surface (see Section 2.4.3). We use the GROMACS (version 4.5.3) molecular dynamics (MD) simulation package [22], suitably modified to perform INDUS simulations in the canonical (NVT) ensemble. The INDUS method allows us obtain free energy, $F(N)$, of observing N waters in textured volume, V [57]. The parameters and implementation pertaining to the INDUS method are the same as those used in Chapter 2 and is described in Appendix A. To compare partially wet states across different surfaces, we define a normalized water density, $\rho_n \equiv N/N_{\text{liq}}$, with N being the number of water molecules in V in the partially wet state and N_{liq} being the corresponding value in the fully wet (Wenzel) state. The simulated free energies that we report, $\Delta F(\rho_n)$, correspond to the free energy of a system in a partially wet state relative to that in the Wenzel state, that is, $\Delta F(\rho_n) = F(N) - F(N_{\text{liq}})$.

4.3. Macroscopic theory for pillared system system consisting of n_c unit cells

According to macroscopic interfacial thermodynamics [53], the free energy of a system in a partially wet state with normalized density ρ_n , relative to that in the Wenzel state, can be written as:

$$\overline{\Delta F}(\rho_n) = \gamma A_{vl}(\rho_n) + \Delta\gamma A_{sv}(\rho_n) + \Delta PV(1 - \rho_n), \quad (4.1)$$

where the over-bar in $\overline{\Delta F}$ signifies a theoretical (as opposed to simulation) estimate, γ is the vapor-liquid surface tension, and $\Delta\gamma$ is the difference between the solid-vapor and solid-liquid surface tensions; according to the Young's equation, $\Delta\gamma = \gamma \cos \theta$, where θ is the water droplet contact angle on a flat surface. A_{vl} and A_{sv} are the vapor-liquid and the solid-vapor interfacial areas, respectively, in the partially wet state, and ΔP is the difference between the system pressure and the co-existence pressure at the system temperature, T . Because our simulations are conducted at the co-existence pressure, $\Delta P = 0$, the pressure-volume contribution is not included in subsequent equations. Assuming that a partially wet state, on the pillared surfaces described in the previous section, is characterized by a flat vapor-liquid interface at a height h , above the base of the pillars, it follows that $h(\rho_n) = H(1 - \rho_n)$ [53, 48]. Then, for a unit cell, $A_{vl} = S(S + 2W) \equiv A_{\text{base}}$, is independent of h , whereas $A_{sv} = A_{\text{base}} + A_{\text{side}}(h/H)$, increases linearly with h . Here, $A_{\text{side}} = 4WH$ is the area of the vertical faces of the pillars. The free energy profile, $\overline{\Delta F}^{(n_c)}(\rho_n)$, of a system consisting of n_c unit cells, at $\Delta P = 0$ is then given by:

$$\overline{\Delta F}^{(n_c)}(0 \leq \rho_n < 1) = \gamma(1 + \cos \theta)A_{\text{base}}n_c + \gamma \cos \theta A_{\text{side}}n_c(1 - \rho_n), \quad (4.2)$$

where $\gamma A_{\text{base}}n_c(1 + \cos \theta)$ is the dewetting barrier, which corresponds to the work of adhesion for nucleating the vapor-liquid interface, and is always positive (unfavorable). Because $\cos \theta < 0$ for hydrophobic surfaces, the second term is favorable, so that the system is expected to spontaneously dewet (to reach the Cassie state), once an intact vapor-liquid

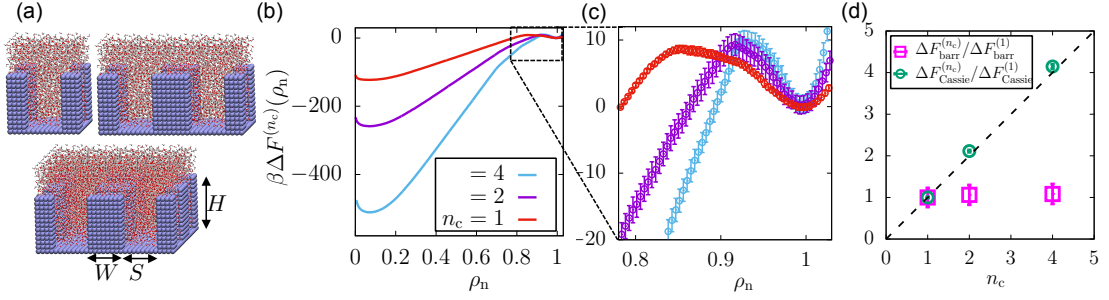


Figure 4.1: Free energetics of wetting-dewetting transitions on pillared surfaces. (a) The surfaces are textured using square pillars of width, $W = 2$ nm, and height, $H = 3$ nm, placed on a square lattice with inter-pillar separation, $S = 2$ nm. Simulation snapshots from systems consisting of $n_c = 1, 2$ and 4 uncoupled unit cells, are shown in the Wenzel state. Because our simulations employ periodic boundary conditions, the unit cells in our simulation box are coupled to their periodic images; n_c represents the number of uncoupled unit cells that are explicitly simulated. (b) The simulated free energy, $\beta \Delta F(\rho_n)$, of a partially wet state relative to the fully wet (Wenzel) state, is shown as a function of the normalized water density, ρ_n , in the textured region, for three systems with $n_c = 1, 2$ and 4 ; here, $\beta \equiv 1/k_B T$ with k_B being the Boltzmann constant and T the temperature. In each case, $\Delta F(\rho_n)$ features characteristic Cassie ($\rho_n \approx 0$) and Wenzel ($\rho_n \approx 1$) states that are separated by a barrier. (c) Focusing on $\Delta F(\rho_n)$ between the Wenzel basin and the barrier highlights that the barriers to dewetting (ΔF_{barr}) in each of the three systems are comparable. (d) Although the free energy difference between the Cassie and the Wenzel state, ΔF_{Cassie} , is proportional to the number of simulated unit cells, n_c , as expected, the barrier to dewetting, ΔF_{barr} , is observed to be independent of n_c .

interface is nucleated. Importantly, Equation 4.2 predicts that both the height of the barrier at $\rho_n \rightarrow 1^-$, and the free energy difference between the Cassie and Wenzel states ($\rho_n \rightarrow 0$) should scale linearly with the the number of unit cells, n_c .

4.4. Density-Dependent Free Energy Profiles

To investigate the role of cooperativity in dewetting, we explicitly simulate systems with $n_c = 1, 2$, and 4 uncoupled unit cells, as shown in shown in Figure 4.1a. Our simulations employ periodic boundary conditions, so that each of the above surfaces are identical; however, the water molecules in the $n_c = 1$ are intricately coupled to their periodic images, and simulating systems with $n_c = 2$ and 4 allows us to study uncoupled cells, and thereby investigate inter-cell interactions. The simulated density dependent free energy profiles, $\Delta F^{(n_c)}(\rho_n)$,

are shown in Figure 4.1b, and highlight the presence of Cassie ($\rho_n \approx 0$) and Wenzel ($\rho_n \approx 1$) states, separated by an energy barrier. Interestingly, as shown in Figure 4.1c, which zooms in on the region of $\beta\Delta F^{(n_c)}(\rho_n)$ between the barrier and the Wenzel state, the barriers to dewetting are comparable in all three cases; that is, the free energetic barrier for emptying a system with 4 cells is the same as that for emptying a unit cell. Furthermore, while this invariance of the dewetting barrier, $\Delta F_{\text{barr}}^{(n_c)}$, with n_c is in contrast with the prediction of macroscopic theory, the free energy difference between the Cassie and Wenzel states, $\Delta F_{\text{Cassie}}^{(n_c)}$, is proportional to n_c , as anticipated by Equation 4.2; see Figure 4.1d.

4.5. Cooperative and Barrierless Dewetting

To investigate why systems with $n_c = 1, 2$ and 4 cells displayed comparable barriers, we analyze the underlying configurations spanning a range of ρ_n -values for each system. In particular, by employing the algorithm described in Appendix C, we visualize the regions in our simulation box that are dewetted, that is, devoid of water. For the 2-celled system shown in Figure 4.1, such snapshots shown in Figure 4.2 suggest the presence of three distinct regions, which can be demarcated based on their respective dewetted morphologies. The configurations in region-II ($0.2 < \rho_n < 0.71$) are characterized by a vapor-liquid interface that is perpendicular to the pillars and spans both cells (Figure 4.2, red).

4.5.1. Demonstrating region-II of 2-celled system is classical

For 2-celled systems ($n_c = 2$), the configurations in region-II are characterized by a vapor-liquid interface that is perpendicular to the pillars and spans both cells (See Figure 4.2 and Figure 4.7). Therefore the height, h , of such a vapor-liquid interface should follow the relation, $h = H(1 - \rho_n)$. Figure 4.5a shows an excellent agreement between the simulated, $\langle h \rangle$ and theoretical expectations of h for all five geometries listed in Table 4.1, suggesting that region-II is indeed classical. Additionally, from the macroscopic theory described in Equation 4.2 the free energy of an $n_c = 2$ system relative to the free energy of the Cassie

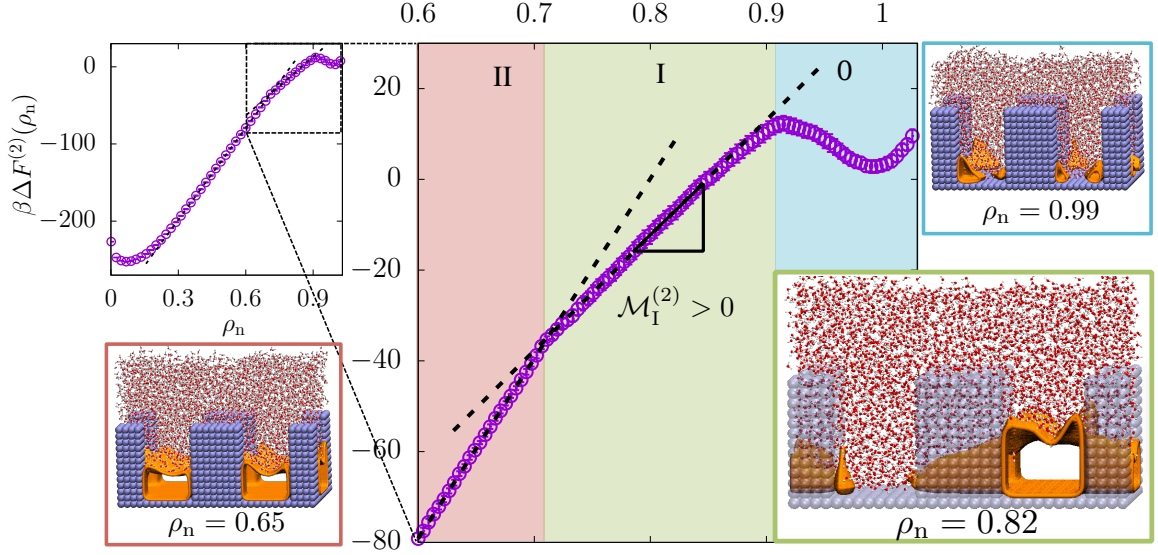


Figure 4.2: Uncovering why ΔF_{barr} is independent of n_c Based on the corresponding dewetted configurations, we demarcate the free energy profile, $\beta\Delta F^{(2)}(\rho_n)$ for the $n_c = 2$ system, into three distinct regions shaded in red, green and blue. Representative simulation snapshots from these regions are shown along with instantaneous interfaces encompassing the dewetted volumes (orange). In region-0 ($\rho_n > 0.91$), partial dewetting is observed in one or both the unit cells, but neither cell features an intact vapor-liquid interface. In region-I ($0.71 > \rho_n > 0.91$), an intact vapor-liquid interface is observed in one cell, but not the other. As ρ_n decreases, the intact vapor-liquid interface rises along the pillars in region-I. $\Delta F^{(2)}(\rho_n)$ is roughly linear in region-I, and because the slope, $\mathcal{M}_I^{(2)} \equiv d\Delta F^{(2)}/d\rho_n$ is positive, the intact vapor-liquid interface is expected to ascend spontaneously along the pillars. If the pillars are sufficiently tall, the unfavorable inter-cell water density gradient eventually facilitates the formation of an intact vapor-liquid interface spanning both cells, giving way to region-II ($0.2 > \rho_n > 0.71$). No additional barriers are thus associated with the dewetting of the second cell.

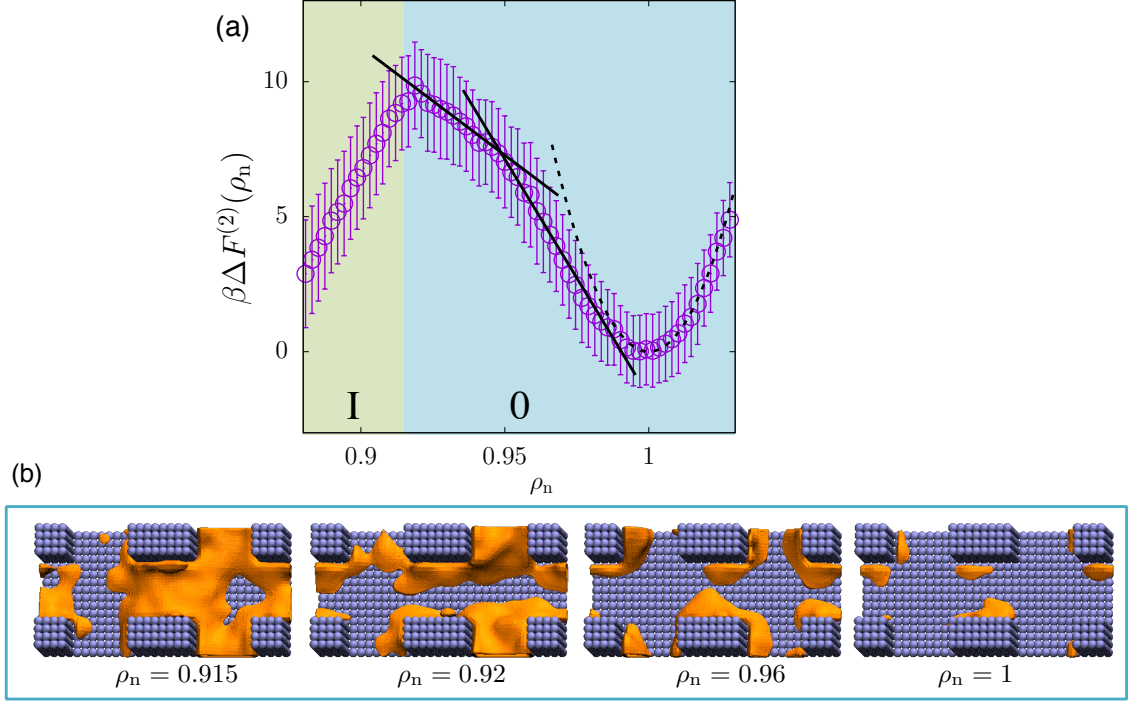


Figure 4.3: (a) Free energy of the system ($n_c = 2$, $H = 3$ nm, $W = 2$ nm, $S = 2$ nm) zoomed-in for $\rho_n > 0.88$. Region-0 has a complex landscape consisting of multiple functional forms each separated by kinks indicating crossovers in dewetted morphologies; $\Delta F^{(2)}(\rho_n \approx 1)$ features a harmonic basin (dashed curve), followed by two almost linear regions (solid lines) as ρ_n is reduced, eventually transitioning into region-I at $\rho_n = 0.91$. (b) Instantaneous interfaces encompassing the dewetted regions are shown in orange (water molecules not shown for clarity) and pillar atoms are shown in blue. For $\rho_n > 0.91$ (region-0, top view), the system displays non-classical configurations with at least three distinct dewetted morphologies; vapor bubbles first form at the base of the pillars at $\rho_n \approx 1$ and grow in size as ρ_n is reduced, opposite vapor bubbles then merge to form “striped” morphologies (see snapshot at $\rho_n = 0.92$), eventually leading to an enclosed “donut” of vapor in the right cell close to the barrier in free energy (see snapshot at $\rho_n = 0.915$), finally transitioning into region-I with intact vapor-liquid interface in the right cell.

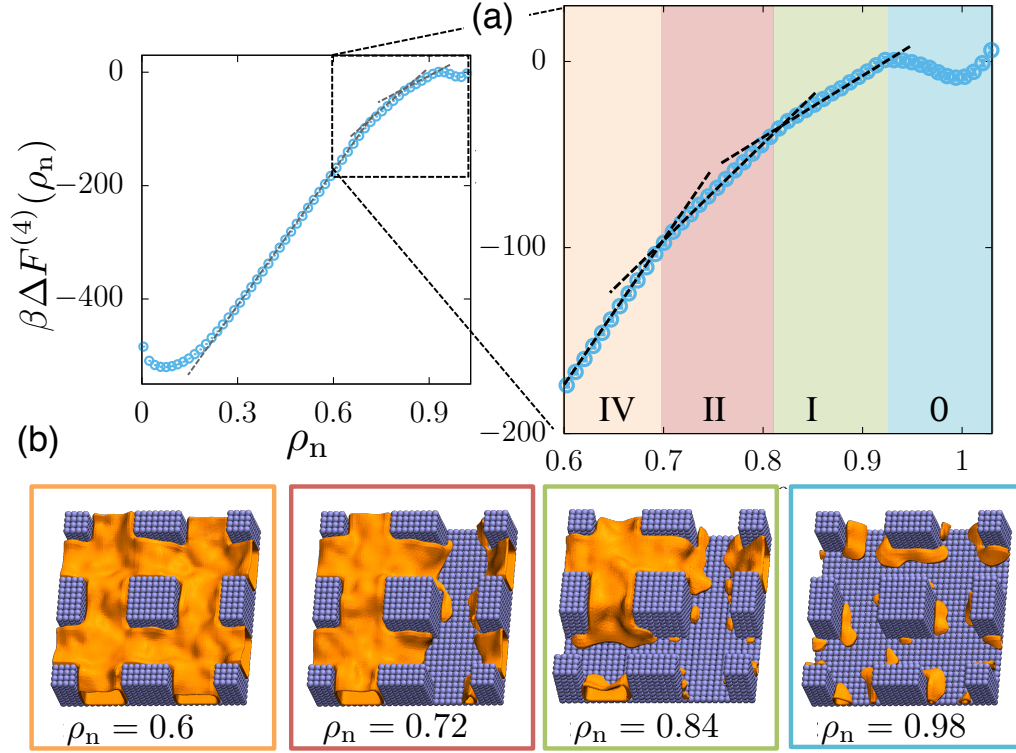


Figure 4.4: Free energetics of system with $n_c = 4$. (a) $\beta \Delta F^{(4)}(\rho_n > 0.6)$ shows the presence of three distinct linear regions. Region-0 ($\rho_n > 0.92$) corresponds to all cells wet leading to the formation of vapor-liquid interface in a single cell and region-I ($0.92 > \rho_n > 0.81$) corresponds to the rise of the vapor-liquid interface in that single dewetted cell as ρ_n decreases. Configurations lying in region-II ($0.81 > \rho_n > 0.7$) contain intact vapor liquid interface spanning two neighboring cells while the other two cells remain largely wet giving way to the classical region-IV with vapor liquid interface spanning all four cells. Region-III, which belongs to configurations having three partially dewetted cells with intact vapor-liquid interface and one cell with wet basal surface, is restricted to very small range of ρ_n -values at the kink connecting regions-II and-IV (b) Representative simulation snapshots corresponding to ρ_n -values falling in the different regions.

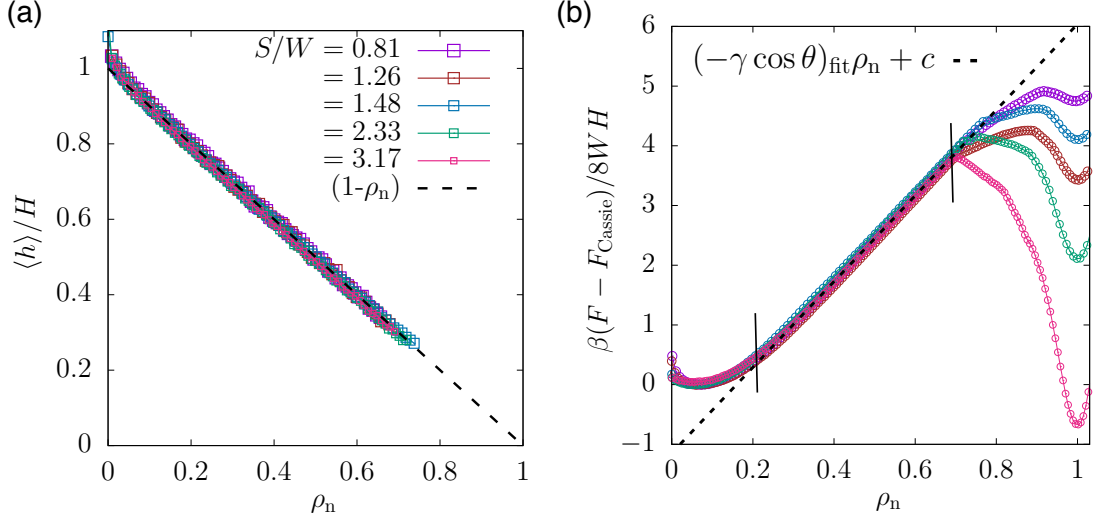


Figure 4.5: For systems with $n_c = 2$, each configuration in region-II displays an intact vapor-liquid interface that is detached from, and is roughly parallel to the basal surface. (a) The average height of this vapor-liquid interface, $\langle h \rangle$ normalized with height of the pillars, H plotted as a function of ρ_n (symbols) for 5 geometries, agrees well with the macroscopic theory assumption of a flat interface parallel to the basal surface (dashed-line) given by $h/H = (1 - \rho_n)$. For each geometry, we first obtain an average coarse grained density, $\tilde{\rho}_{\text{total}}(x, y, z)$ described in Appendix C for all $(x, y, z) \in V$; where V is the textured volume between the pillars and z is the direction perpendicular to the basal surface. Then for each $(x, y \in V)$, we find z_c such that $\tilde{\rho}_{\text{total}}(x, y, z_c) = 0.5$. We obtain average interface height by averaging z_c over the x- and y- coordinates for configurations containing intact vapor-liquid interface in both the cells. Because the configurations are generated from simulations with a biasing potential we perform this average within the framework of WHAM [75, 57] and obtain $\langle h \rangle$. (b) Since region-II follows classical macroscopic theory outlined in Equation 4.2 of the main text, the slope resulting from fitting the simulated values of $(F^{(2)}(\rho_n \in \text{II}) - F_{\text{Cassie}}^{(2)}) / 8WH$ to a straight line to provides $(-\gamma \cos \theta)_{\text{fit}}$. The range of ρ_n used in the fit, is shown through the black solid lines. The non-zero value of intercept $c = -1.1$, arises from the fact that density in the Cassie basin in the simulated free energy, is not exactly zero.

state, in region-II, is given by:

$$\overline{F}^{(2)}(\rho_n \in \text{II}) - \overline{F}_{\text{Cassie}}^{(2)} = (\gamma \cos \theta) 8WH(1 - \rho_n), \quad (4.3)$$

Therefore, fitting the simulated values of $(F^{(2)} - F_{\text{Cassie}}^{(2)})/8WH$ as a function of $\rho_n (\in \text{II})$ to a straight line allows us to extract the value of $\gamma \cos \theta$ (see Figure 4.5b). We obtain an average value of $(-\gamma \cos \theta)_{\text{fit}} = 7.186 \pm 0.03 \text{ } k_B T / \text{nm}^2$ from the free energy of five geometries shown in Figure 4.5; the reported error is the standard error. Consequently, we expect the slope of region-II, $\mathcal{M}_{\text{II}}^{(2)} \equiv d\Delta F^{(2)} / d\rho_n (0.2 < \rho_n < 0.71)$, obtained from our simulations, to agree well with the macroscopic prediction,

$$\overline{\mathcal{M}}_{\text{II}}^{(2)} = (-\gamma \cos \theta) 2A_{\text{side}} = (-\gamma \cos \theta) 8WH. \quad (4.4)$$

Such an agreement between $\mathcal{M}_{\text{II}}^{(2)}$ and $\overline{\mathcal{M}}_{\text{II}}^{(2)}$, is indeed observed, as the value of $(-\gamma \cos \theta)_{\text{fit}} = -0.72 \pm 0.03 \text{ } k_B T / \text{nm}^2$ agrees well with its independently obtained estimate in section 2.4.3 from the slope of single celled pillar system. The reported error is obtained as the standard error in value of $(-\gamma \cos \theta)_{\text{fit}}$ obtained from the 5 geometries and can be attributed to the finite-size effect in surface tension and contact angle across the geometries. We use the value of $\gamma(1 + \cos \theta) = 5.97 \pm 0.0006 \text{ } k_B T / \text{nm}^2$ described in Appendix D to extract $\gamma_{\text{fit}} = 13.16 \pm 0.03 \text{ } k_B T / \text{nm}^2$ and $\cos \theta_{\text{fit}} = -0.546 \pm 0.0026 \equiv \theta = 123 \pm 0.2^\circ$.

While configurations in region-II ($0.2 < \rho_n < 0.71$) are classical, those at higher- ρ_n values are not. In particular, the configurations in region-I ($0.71 < \rho_n < 0.91$) feature an intact vapor-liquid interface in one of the cells, the other cell is largely wet (Figure 4.2, green). Similarly, no intact vapor-liquid interface perpendicular to the pillars is observed in region-0 ($\rho_n > 0.91$), which corresponds to the region between the Wenzel state and the barrier state. In Chapter 2, we have demonstrated that region-0, which precedes the formation of an intact vapor-liquid interface, is indeed highly non-classical, and features transitions between a number of distinct dewetted morphologies, which results in a significantly lower barrier for nucleating the vapor-liquid interface than suggested by the macroscopic theory,

Equation 4.2. A detailed description of the various dewetted morphologies observed in region-0 are included in Figure 4.3. Because the classical behavior of region-II, as well as the non-classical behavior in region-0 are well understood, here we focus on region-I, and the reason for the lack of barrier in transition from region-I to region-II. Free energy in both region-I and region-II is linear and the two regions are separated by a kink (sharp change in slope) at $\rho_n = 0.71$ (See Figure 4.9a for the derivative of free energy). In Figure 4.12a we have also included calculations of binary indicator functions corresponding to the probability of finding region-0, region-I and region-II for a given ρ_n values; such calculations allow us to accurately locate the kinks separating one region from another. Such kinks in free energy profiles are typically associated with a crossover in the dewetted morphology [64, 60]; the functional dependence of the free energy profile on ρ_n is expected to depend on the particular dewetted morphology, and as the system switches from one dewetted morphology to another, the kink in the free energy profile represents the inability of the one-dimensional order parameter, ρ_n , to capture the crossover. For the surface geometry considered in Figure 4.2, the slope of region-I, $\mathcal{M}_I^{(2)}$, is positive, suggesting that once an intact vapor liquid interface has formed in one cell, it is favorable for the vapor-liquid interface to spontaneously rise along the pillars. As the vapor-liquid interface rises in one cell, with the other cell remaining wet, the corresponding inter-cell density gradient unfavorably increases eventually facilitating the barrierless formation of vapor-liquid interface in the second cell. Hence, the overall dewetting barrier of the $n_c = 2$ system is the same as that of the $n_c = 1$ system. Similarly, for the $n_c = 4$ system, the formation of an intact vapor-liquid interface facilitates the barrierless dewetting of an adjacent cell, further enabling the barrierless dewetting of the remaining two cells; see Figure 4.4. Thus, the invariance of the dewetting barriers with respect of n_c , seen in Figure 4.1d, is a result of the inter-cell cooperativity in dewetting.

4.6. Implications for the Rational Design of Robust Superhydrophobic Surfaces

In this section we show cooperative effects in dewetting can have important implications for the design of robust superhydrophobic surfaces. In Chapter 3, we showed that a general

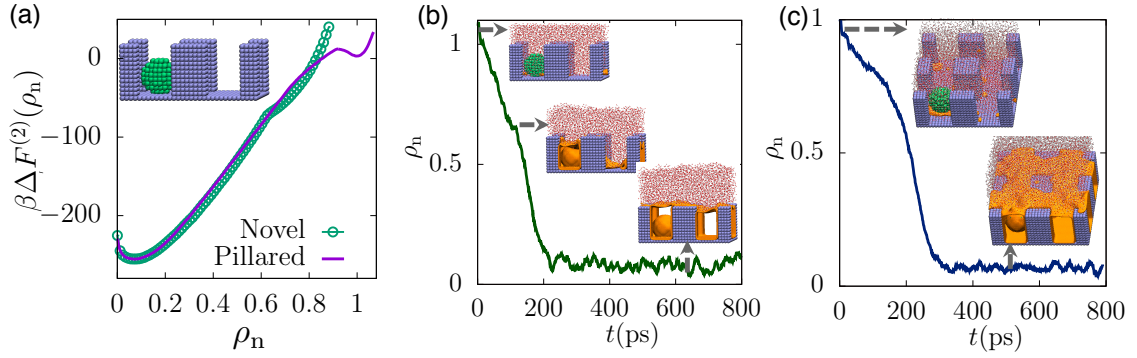


Figure 4.6: Spontaneous recovery of superhydrophobicity in optimally designed surfaces. (a) Free energy of a 2-celled system containing a nanoparticle (dia. 2nm) at the center of one of the cells (green curve) compared with the free energy of corresponding pillared system (purple curve) - the presence of the nanoparticle results in the complete destabilization of the Wenzel state. (b) ρ_n versus time is shown for an unbiased simulation trajectory initiated in the Wenzel state of the $n_c = 2$ system containing a 2 nm spherical nanoparticle in one of the cells. The corresponding simulation snapshots (inset) highlight that the cell containing the nanoparticle dewets first, and its dewetting facilitates the barrierless dewetting of the adjacent cell, which does not contain the nanoparticle. (c) Similarly, the system with $n_c = 4$, also containing a 2 nm spherical nanoparticle in one of the cells, spontaneously dewets from the Wenzel state to the Cassie state.

strategy for augmenting the design of existing nano-textured surfaces is to destabilize the water molecules that are hardest to remove by introduction of confined surface textures at the locations of such water molecules. For instance, the pillared system that was augmented using a spherical nano-particle at the center of the cell featured an unstable Wenzel state under ambient conditions. Here we use one such surface augmentation strategy by placing a spherical nanoparticle in only one cell in the 2-celled and 4-celled systems described in Figure 4.1 and demonstrate that cooperative dewetting effects lead to spontaneous and barrierless dewetting of the neighboring cells. In Figure 4.6a, we compare the free energy of the 2-celled system containing a spherical NP(dia. 2nm) with the corresponding pillared system; the presence of the nanoparticle results in the complete destabilization of the Wenzel state. Additionally, we plot ρ_n as a function of simulated time, t , of unbiased simulation trajectories initiated from the Wenzel state for $n_c = 2$ system (Figure 4.6b) and $n_c = 4$ system (Figure 4.6c), each containing a nanoparticle in one of the cells. Both the systems undergo complete dewetting within 400 ps, highlighting the crucial role of inter-cell cooperativity in dewetting in such systems.

In order to better understand how such cooperative dewetting effects depend on surface geometry, we take a closer look at the free energetics and the morphologies of region-I (Figure 4.2a). The energy term favorable for the rise of the vapor-liquid interface in the partially dewetted cell (say at height h_I) is the vapor-solid interfacial area term scaling as $Wh_I \cos \theta$ for $\cos \theta < 0$. Whereas, the unfavorable energy term opposing the previous term scales as the vapor-liquid interfacial area between the two cells, Sh_I . In order to achieve cooperative dewetting of the wet cell, the favorable term ($\propto W \cos \theta h_I$) must be larger than the unfavorable term ($\propto Sh_I$) indicating that small S/W and large $\cos \theta$ is favorable. Hence, in next section we look at system with various S/W values to understand its precise role on cooperative dewetting.

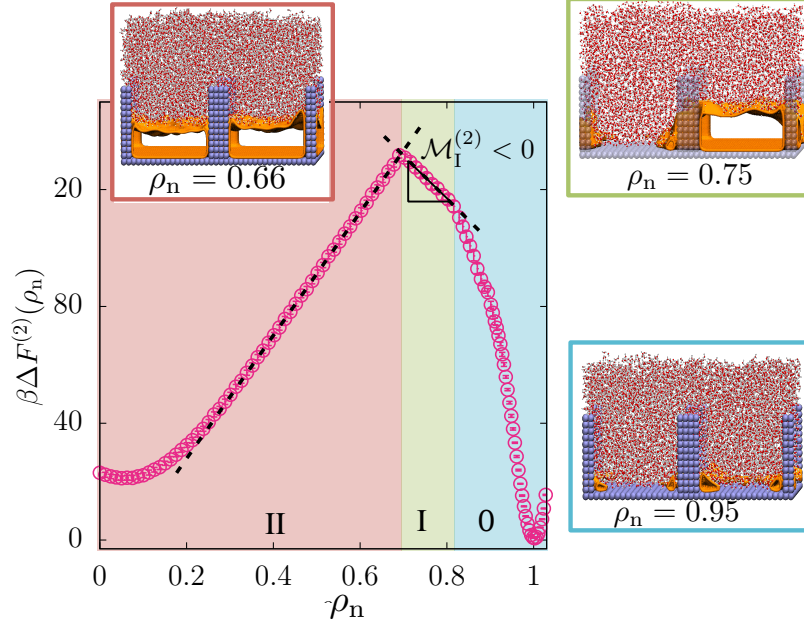


Figure 4.7: The free energy profile, $\beta\Delta F^{(2)}(\rho_n)$, of a $n_c = 2$ system with $S = 4$, $W = 1$ and $H = 3$ is shown; the relevant geometric parameter, $\alpha \equiv S/W$, as shown in Table 4.1, is 3.17 for this system. Once again, based on the observed dewetted configurations, three ρ_n -regions are identified. A sharp kink separates the linear regions, region-II ($0.2 > \rho_n > 0.69$) and region-I ($0.69 > \rho_n > 0.82$). For this geometry, the slope of region-I, $\mathcal{M}_I^{(2)}$, is negative, indicating that even after an intact vapor-liquid interface has been nucleated in one cell, an additional barrier must be overcome to dewet the second cell. Conversely, starting from the Cassie state, if one cell wets, it will facilitate the barrierless wetting of the adjacent cell.

4.7. Effects of Geometric Parameters on Cooperative Dewetting

In Figure 4.7, we plot the free energy, $\Delta F^{(2)}(\rho_n)$, of a $n_c = 2$ system with $\alpha \equiv S/W = 3.17$, and also show characteristic dewetted morphologies. The dewetted morphologies are very similar to those in the system with a smaller $\alpha = 0.81$ (Figure 4.2a), and the free energy profiles are once again linear in regions I and II, and are separated by a kink at $\rho_n = 0.69$. However, as opposed to the system with $\alpha = 0.81$ (Figure 4.2), the slope of region-I is negative for this larger α system, indicating that once a vapor-liquid interface has been nucleated in one cell, an additional barrier must be overcome for nucleating the interface in the second cell. Conversely, Figure 4.7 highlights that a system initially in the Cassie state will wet spontaneously if one of the cells wets; that is, starting from a configuration in region-I, wetting (as opposed to dewetting) is barrierless and cooperative.

To further understand the effect of α on dewetting cooperativity, in Figure 4.8 we plot the free energy profiles corresponding to 6 different geometries listed in Table 4.1, for both $n_c = 1$ and $n_c = 2$. In Figure 4.10, the magnitude of the dewetting barrier of a system with $n_c = 2$ relative to that of the corresponding system with $n_c = 1$ is shown for 6 values of α ; systems with $\mathcal{M}_I^{(2)} > 0$ are represented with green symbols, whereas those with $\mathcal{M}_I^{(2)} < 0$ are represented in red. The dewetting of the second cell is cooperative and barrierless for systems with $\mathcal{M}_I^{(2)} > 0$, so that $\Delta F_{\text{barr}}^{(2)}/\Delta F_{\text{barr}}^{(1)} \approx 1$. Interestingly, $\Delta F_{\text{barr}}^{(2)}/\Delta F_{\text{barr}}^{(1)} < 2$ for systems with $\mathcal{M}_I^{(2)} < 0$, suggesting that while an additional barrier must be overcome to dewet the second cell, that barrier is smaller than the one required to dewet the first cell. We additionally calculate smoothed derivatives of $\Delta F^{(2)}(\rho_n)$, by first computing derivative using finite difference method, and then by smoothing the resultant, $\mathcal{M}^{(2)}(\rho_n) = \partial \Delta F(\rho_n)^{(2)}/\partial \rho_n$, by averaging over 20 data points. The error in $\mathcal{M}^{(2)}(\rho_n)$ was estimated using block averaging. The simulation trajectories were divided into five blocks of 400 ps each, and $\mathcal{M}^{(2)}(\rho_n)$ was obtained for each of the five blocks; the errorbars shown in 4.9 correspond to the standard error of the block averaging. In Figure 4.9, we plot the slope of free energy, normalized by corresponding slope of free energy in region-

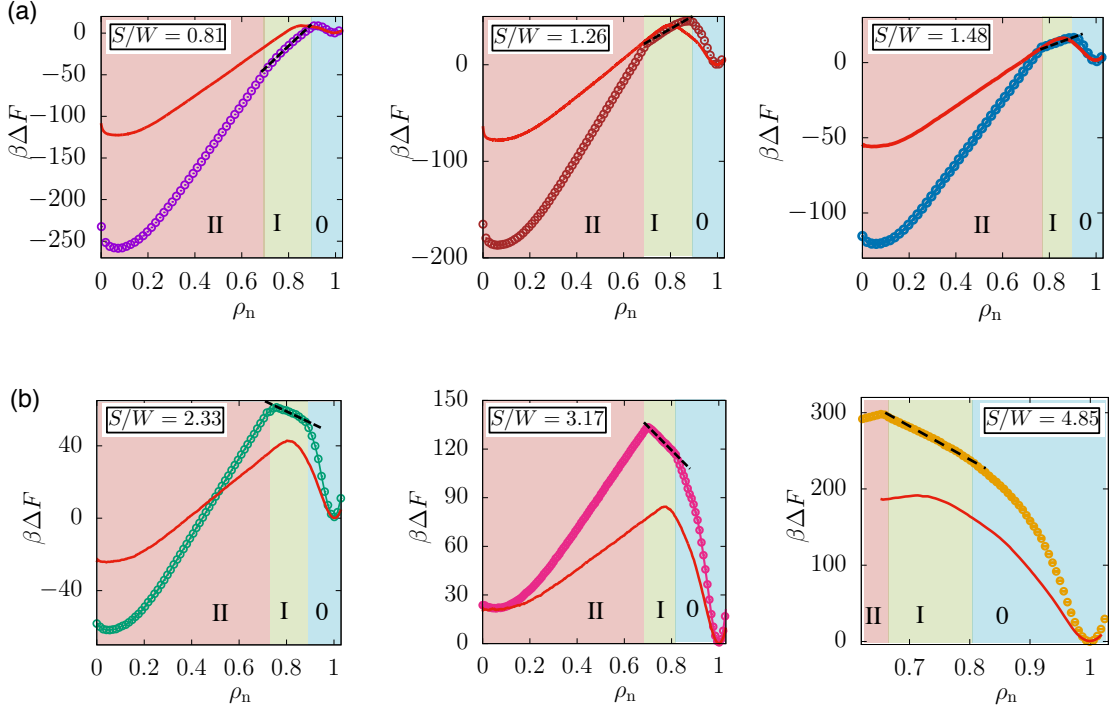


Figure 4.8: $\Delta F^{(2)}(\rho_n)$ (symbols) and corresponding $\Delta F^{(1)}(\rho_n)$ (red line), for the $n_c = 2$ systems for 6 different geometries (See Table 4.1). Regions-0 through II are demarcated for each of these geometries according to the corresponding dewetted morphologies; region-0 (blue), region-I (green) and region-II (red) respectively correspond to exactly 0, 1 and 2 cells featuring an intact vapor-liquid interface. (a) For the geometries with smaller values of S/W , the dewetting barrier for systems with $n_c = 2$, $\Delta F_{\text{barr}}^{(2)}$, and the dewetting barrier for corresponding systems with $n_c = 1$, $\Delta F_{\text{barr}}^{(1)}$, are comparable. $\Delta F^{(2)}(\rho_n)$ for each of these systems also features a positive slope in region-I ($\mathcal{M}_I^{(2)} > 0$) explaining the absence of additional barrier required for dewetting of the second cell. (b) Whereas, for systems with larger S/W -values, $\Delta F_{\text{barr}}^{(2)}/\Delta F_{\text{barr}}^{(1)} < 2$ and $\mathcal{M}_I^{(2)} < 0$, suggesting that while an additional barrier must be overcome to dewet the second cell, that barrier is smaller than that required to dewet the first cell.

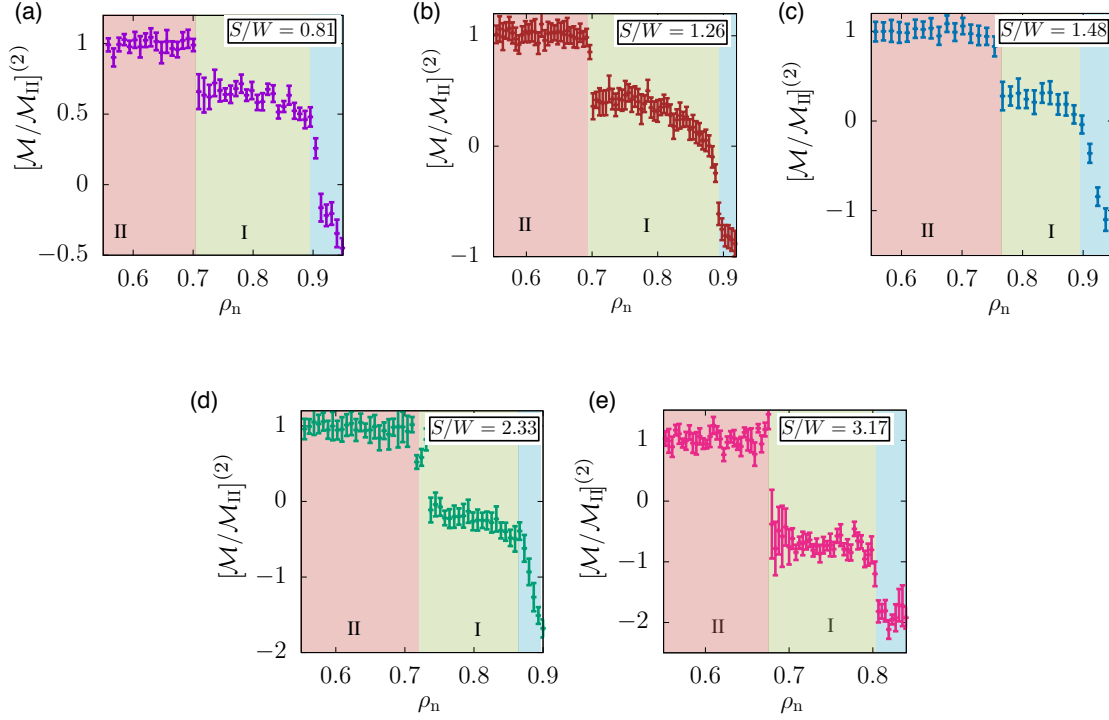


Figure 4.9: Derivatives of free energy, $\mathcal{M}^{(2)}(\rho_n) = \partial \Delta F(\rho_n)^{(2)} / \partial \rho_n$, normalized by slope of region-II, $\mathcal{M}_{\text{II}}^{(2)}$, for 2-celled geometries with (a) $S/W = 0.81$, (b) $S/W = 1.26$, (c) $S/W = 1.48$, (d) $S/W = 2.33$, (e) $S/W = 3.17$ and (f) $S/W = 4.85$. Regions-I and II are demarcated for each of the $n_c = 2$ geometries according to the corresponding dewetted morphologies (obtained through indicator function calculations in Figure 4.12). Slope of region-I, in each of the five geometries, is roughly constant for the range of ρ_n in which the binary indicator function of region-I, $\langle p_I \rangle = 1$ (Figure 4.12).

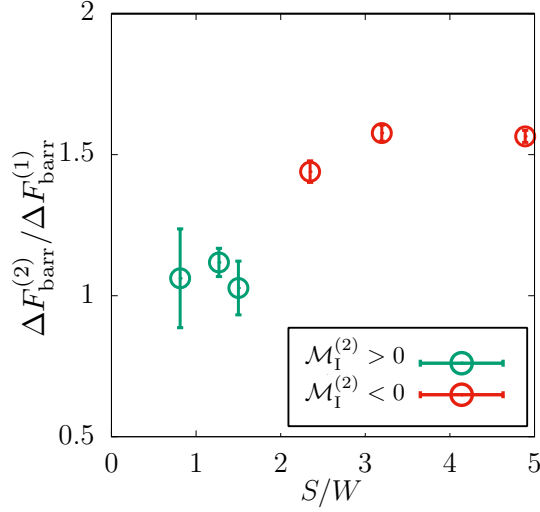


Figure 4.10: The magnitude of the dewetting barrier of a system with $n_c = 2$ relative to that of the corresponding system with $n_c = 1$ is shown for various values of S/W . The $n_c = 2$ systems, which displayed $\mathcal{M}_I^{(2)} > 0$ are represented with green symbols, whereas those that displayed $\mathcal{M}_I^{(2)} < 0$ are represented in red. The dewetting of the second cell is cooperative and barrierless for systems with $\mathcal{M}_I^{(2)} > 0$, so that $\Delta F_{\text{barr}}^{(2)} / \Delta F_{\text{barr}}^{(1)} \approx 1$. Interestingly, $\Delta F_{\text{barr}}^{(2)} / \Delta F_{\text{barr}}^{(1)} < 2$ for systems with $\mathcal{M}_I^{(2)} < 0$, suggesting that while an additional barrier must be overcome to dewet the second cell, that barrier is smaller than the one required to dewet the first cell.

II, for the 5 geometries listed in Table 4.1. Figure 4.9 highlights the existence of kinks in $\Delta F^{(2)}(\rho_n)$ reflected in sharp changes in $\mathcal{M}^{(2)}(\rho_n)$, corresponding to the morphological transitions between region-II to region-I and region-I to region-0; the various regions are demarcated according to the indicator function calculations (See Figure 4.12). The slope of the region-I, $\mathcal{M}_I^{(2)}$, is thus an important quantity, and determines whether a geometry with given α will display cooperative dewetting or cooperative wetting. We see a very similar behavior in the free energetics of 4-celled systems with three different values of α in Figure 4.11. To generalize our findings to a wide range of α -values, as well as for systems with an arbitrarily large number of cells, n_c , here we propose a revised macroscopic theory that attempts to incorporate the role of inter-cell cooperativity in the free energetics of wetting-dewetting transitions.

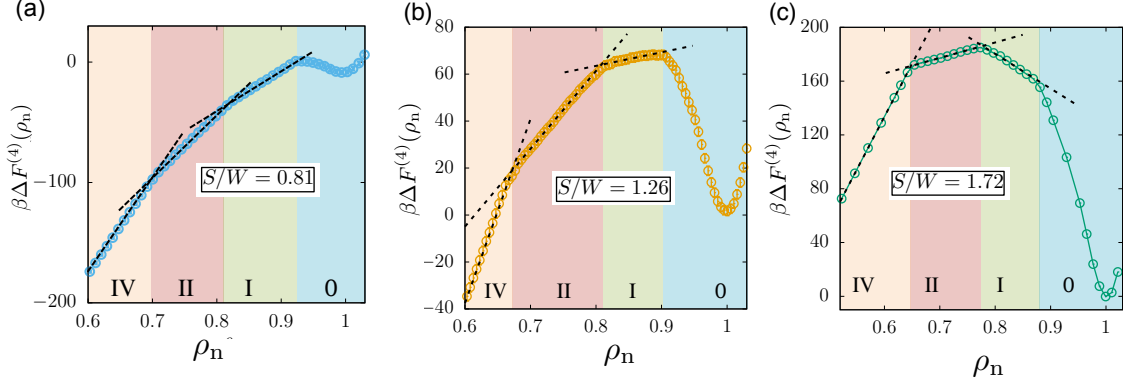


Figure 4.11: Free energetics of two additional 4-celled systems. The geometry with (a) $S/W = 0.81$ (also shown in Figure 4.4), and (b) $S/W = 1.26$, both feature a positive slope of region-I, $\mathcal{M}_I > 0$, suggesting that once one of the cells has been dewetted, the entire system would spontaneously dewet. $\mathcal{M}_I$ decreases with increasing value of S/W , consistent with 2-celled systems. (c) For geometry with $S/W = 1.72$, $\mathcal{M}_I < 0$, implying that even after an intact vapor liquid interface has been nucleated in one of the cells, additional barrier must be overcome to dewet the neighboring cells.

4.8. Obtaining Indicator Functions to Demarcate Distinct Dewetted Morphologies in 2-celled Systems

To accurately determine whether a configuration of a 2-celled geometry, with a particular value of ρ_n , lies in region-II, region-I, or region-0, we perform indicator function calculations. The indicator functions, p_{II} , p_I and p_0 are determined by examining the coarse-grained density, $\tilde{\rho}_{\text{total}}(x, y, z)$, described in equation C.1. We define the z-coordinate to be perpendicular to the basal surface, y-coordinate to be into the plane and x-coordinate to be the horizontal direction for the 2-celled systems. To determine whether or not a cell features an intact vapor-liquid interface, we then define a coarse grained density corresponding to the nascent region adjacent to the basal surface, $\tilde{\rho}_{\text{nascent}}(x, y)$, in the textured region, V , as:

$$\begin{aligned} \tilde{\rho}_{\text{nascent}}(x, y) &= \tilde{\rho}_{\text{total}}(x, y, z) \\ \forall (x, y \in V) \\ \forall (z_{\text{basal}} + \sigma_s < z < z_{\text{basal}} + \sigma_s + \sigma_w), \end{aligned} \tag{4.5}$$

where z_{basal} is the z-value of the centers of the atoms of the basal surface and σ_s and σ_w are the coarse graining parameters pertaining to the calculation of the coarse-grained density, $\tilde{\rho}_{\text{total}}(x, y, z)$ described in the previous section. If $\tilde{\rho}_{\text{nascent}}(x, y) < 0.5$ at all $(x < S + W, y)$, we have an intact vapor layer in the left cell and correspondingly we assign $p_L = 1$; in any other case fractions of left cell is wet, and we assign $p_L = 0$. Similarly, we assign $p_R = 1$ if $\tilde{\rho}_{\text{nascent}}(x, y) < 0.5$ for all $(x > S + W, y)$ corresponding to the presence of an intact vapor layer in the right cell and $p_R = 0$ otherwise. Hence, p_L and p_R correspond to the probability of finding an intact vapor-liquid interface in the left and the right cells respectively. For configurations lying in classical region-II, both the cells must feature intact vapor-liquid interface, *i.e.* $(p_{\text{II}} \equiv (p_L \text{ AND } p_R) = 1)$. Whereas, for configurations lying in region-I, exactly one cell must contain an intact vapor-liquid interface, corresponding to $(p_{\text{I}} \equiv (p_L \text{ XOR } p_R) = 1)$. Finally for configurations lying in region-0, $(p_0 \equiv (p_L \text{ NOR } p_R) = 1)$ corresponding to morphologies with an intact vapor-liquid interface in neither cell. To calculate unbiased ensemble average of the three indicator functions, we perform this average within the framework of WHAM [75, 57] and obtain $\langle p_{\text{II}} \rangle$, $\langle p_{\text{I}} \rangle$ and $\langle p_0 \rangle$. In Figure 4.12, all five geometries display a sharp transition in $\langle p_{\text{II}} \rangle$ from 1 to 0, and a corresponding transition of $\langle p_{\text{I}} \rangle$ from 0 to 1, as ρ_n is decreased; the value of ρ_n corresponding to $\langle p_{\text{II}} \rangle = 0.5$ is used to demarcate region-I from region-II in Figures 4.2, Figure 4.3, 4.8 and 4.9. Similarly, transition between region-I and region-0 is captured by a sharp drop in $\langle p_{\text{I}} \rangle$ from 1 to 0, and corresponding increase in $\langle p_0 \rangle$ from 0 to 1 as ρ_n is further reduced, allowing us to extract the value of ρ_n separating region-I and region-0.

4.9. Macroscopic Theory for Predicting Cooperativity

4.9.1. 2-celled system:

The competition between the favorable solid-vapor interfacial (adhesion) energy and the unfavorable vapor-liquid interfacial energy, as caused by the gradient in the density of water between the wet and the dewetted cells, dictates whether a system in region-I will spontaneously dewet or wet. This competition is reflected in the sign of the slope of free

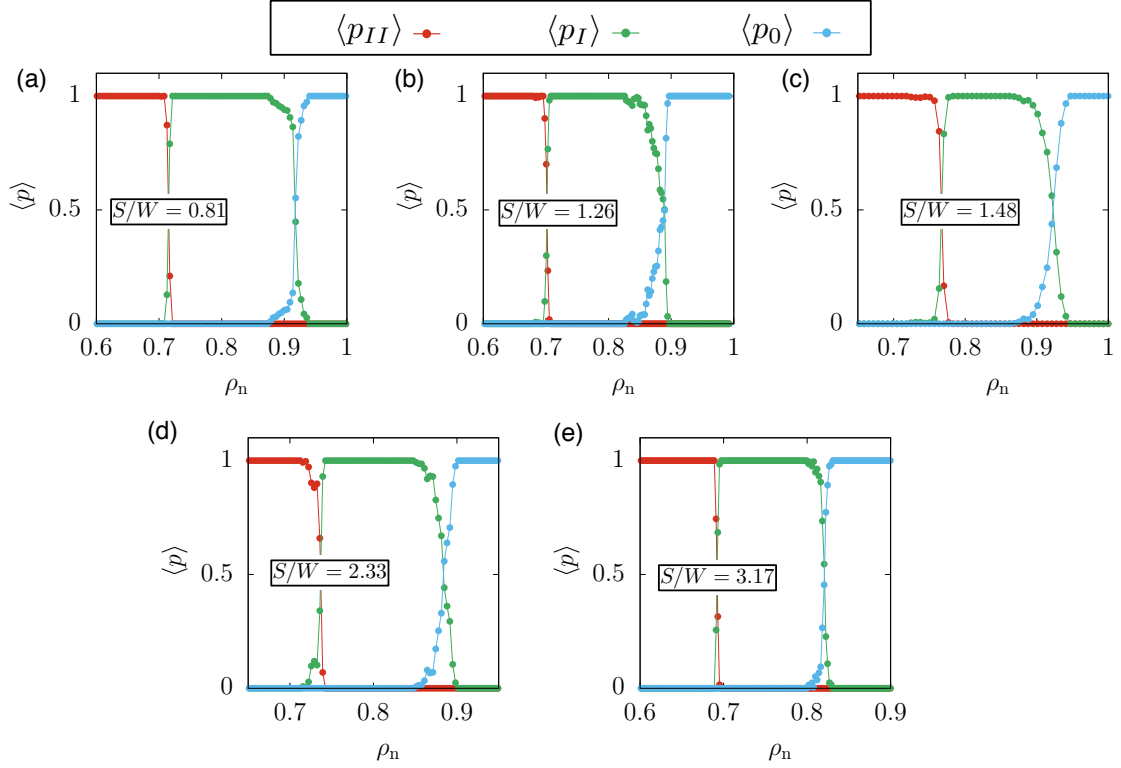


Figure 4.12: Binary indicator functions to obtain the probability of finding a configuration with a ρ_n -value in region-II, $\langle p_{II} \rangle$ (red), region-I, $\langle p_I \rangle$ (green) and region-0, $\langle p_0 \rangle$ (blue), for five $n_c = 2$ geometries. A sharp change in an indicator function, corresponds to transition from one morphology to another, and manifests as a kink in the free energy of the system.

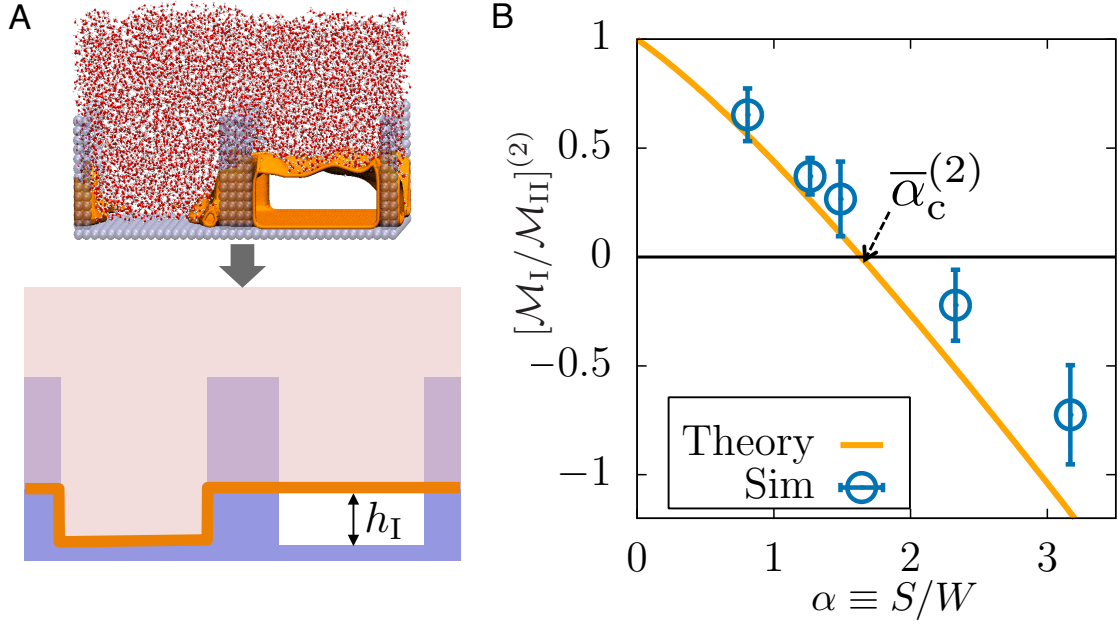


Figure 4.13: Predicting cooperative dewetting criteria in 2-celled systems. (a) To estimate the slope of $n_c = 2$ systems in region-I, we replace the ensemble of configurations constituting region-I by those containing an intact vapor-liquid interface in one of the cells at a height h_I above the basal surface, and a wet second cell. (b) We compare the ratio of the slope of free energy in region-I and the slope of free energy in region-II, $[\frac{\mathcal{M}_I}{\mathcal{M}_{II}}]^{(2)}$ as a function of α for 5 simulated geometries to that obtained from macroscopic theory. We find a reasonable agreement between the prediction of $\alpha_c^{(2)} = 1.88 \pm 0.11$ from simulation and $\bar{\alpha}_c^{(2)} = 1.64$ from theory.

energy in region-I; if the favorable solid-vapor interfacial energy dominates, $\mathcal{M}_I^{(2)} > 0$ and if the unfavorable vapor-liquid interfacial energy dominates, $\mathcal{M}_I^{(2)} < 0$. So in order to predict the cooperative behavior of a given geometry, we need to predict $\mathcal{M}_I^{(2)}$. Here, we propose a simple macroscopic model corresponding to the morphology shown in Figure 4.13a; this model assumes that the horizontal vapor-liquid interface remains parallel to the basal surface at a height h_I , while the vertical vapor-liquid interfaces are perpendicular to the basal surface. We also assume that the region between the opposite pillars, separating the wet and partially dewetted cells, are also partially dewetted such that:

$$\begin{aligned} h(x, y) &= 0 \quad \forall \quad W/2 < x < W/2 + S \\ &= h_I \quad \text{otherwise} \end{aligned} \tag{4.6}$$

assuming x is the horizontal direction and y is the direction into the plane and $h(x, y)$ is the height of the vapor-liquid interface parallel to the basal surface (See Figure 4.13a). Also in equation 4.6, h_I , is the height of the vapor-liquid interface in the partially empty cell, directly related to ρ_n such that, $dh_I/d\rho_n = -2H(\alpha + 2)/(\alpha + 3)$. With the above approximations, the slope of free energetics of the $n_c = 2$ system in region-I can then be expressed as:

$$\overline{\mathcal{M}}_I^{(2)} \equiv \frac{d\overline{\Delta F}^{(2)}}{d\rho_n}(\rho_n \in \text{I}) = \gamma(2S + 6W \cos \theta) \frac{dh_I}{d\rho_n}, \tag{4.7}$$

where, the term $\gamma(2S) \frac{dh_I}{d\rho_n}$ accounts for the two unfavorable vapor-liquid interfacial areas between the two pillars, whereas the term $\gamma 6W \cos \theta \frac{dh_I}{d\rho_n}$ accounts for the favorable solid-vapor interfacial areas on the vertical faces of the pillars. The ratio of the slopes of free energy in region-I (Equation 4.7) and region-II (Equation 4.4) is then given by:

$$\left[\frac{\overline{\mathcal{M}}_I}{\overline{\mathcal{M}}_{II}} \right]^{(2)} = \frac{(\alpha + 2)(\alpha + 3 \cos \theta)}{2 \cos \theta (\alpha + 3)}. \tag{4.8}$$

In Figure 4.13b, we find reasonable agreement between $\left[\frac{\overline{\mathcal{M}_I}}{\overline{\mathcal{M}_{II}}}\right]^{(2)}$ and the corresponding values obtained from 5 simulated geometries. Where $\mathcal{M}_{II}^{(2)} = -\gamma_{\text{fit}} \cos \theta 8WH$ as described in Equation 4.4 and Figure 4.5. To obtain $\mathcal{M}_I^{(2)}$ of a $n_c = 2$ geometry, first we identify the range of ρ_n values with configurations containing intact vapor-liquid in exactly one cell *i.e.* configurations with $\langle p_I \rangle = 1$ (See Figure 4.12). The value of $\mathcal{M}_I^{(2)}$ for a geometry is then extracted as the slope resulting from fitting a straight line to the free energy, $\Delta F^{(2)}(\rho_n)$, for the range of ρ_n in which $\langle p_I \rangle = 1$. The errorbars were obtained using block averaging of the data by dividing each simulated trajectory in 5 block of 400ps data each and then calculating the standard error of the mean value of $[\mathcal{M}_I/\mathcal{M}_{II}]^{(2)}$.

For the 2-celled systems, $\alpha_c^{(2)}$ is the critical value of α at which $\mathcal{M}_I^{(2)}$ changes sign; for geometries with $\alpha < \alpha_c^{(2)}$, dewetting in one cell can lead to spontaneous dewetting. The prediction of $\alpha_c^{(2)}$ from equation 4.8, $\overline{\alpha_c^{(2)}} = 3(-\cos \theta) = 1.64$ is reasonably good estimate of $\alpha_c^{(2)} = 1.88 \pm 0.11$ obtained from simulations. The simulated value of $\alpha_c^{(2)}$ was obtained by linear interpolation $\mathcal{M}_I^{(2)}$ versus α data shown in Figure 4.13b. Aside from providing a good estimate of $\alpha_c^{(2)}$, this model also closely captures the free energetics of the region-I ; Equation 4.7 predicts $\frac{d\Delta F^{(2)}}{d\rho_n}$ to be constant for all $\rho_n \in \text{I}$ and as seen in Figure 4.9 this is true for all cases within the error-bars. We note that, our prediction of $\alpha_c^{(2)}$ involves the prediction of the slope of the free energy in region-I, $\mathcal{M}_I^{(2)}$, of the system containing one partially dewetted cell containing an intact vapor-liquid interface at height, h_I . However, an effective nucleating geometry, such as the nanoparticle in system shown in Figure 4.6a, increases $\mathcal{M}_I^{(2)}$ pertaining to the rise of the vapor-liquid interface, in non-trivial ways, and can result in a larger value of $\alpha_c^{(2)}$. Hence, Equation 4.8, provides a conservative estimate of $\alpha_c^{(2)}$ and presence of any optimal nucleating site in one of the cells for systems with $\alpha < \alpha_c^{(2)}$, would certainly lead to the spontaneous dewetting of the second cell.

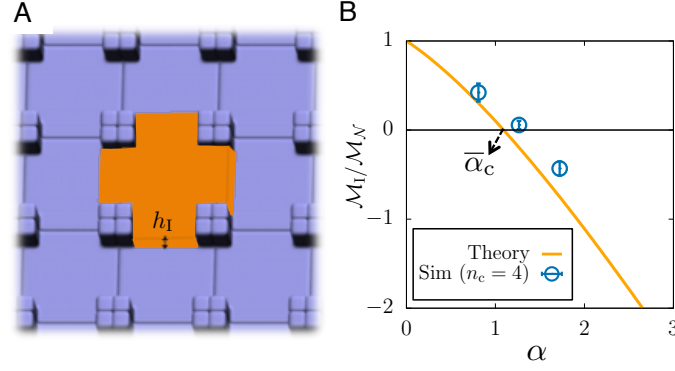


Figure 4.14: Predicting cooperative dewetting criteria in $n_c \geq 4$ systems. (a) To estimate the slope of $n_c \geq 4$ systems in region-I, we replace the ensemble of configurations constituting region-I by those containing an intact vapor-liquid interface in one of the cells (including the region between the pillars) at a height h_I above the basal surface, and a wet second cell. (b) Ratio of slope of free energy in region-I to slope of free energy in classical region- $\mathcal{N}$, $\mathcal{M}_I/\mathcal{M}_\mathcal{N}$ is plotted as function of α .

4.9.2. Multi-celled ($n_c \geq 4$) systems:

Finally, we generalize the macroscopic model shown in Figure 4.13, for systems with $n_c \geq 4$ to find out the criteria for cooperative dewetting. Region-0 in system with n_c identical cells corresponds to all wet cells (Wenzel) leading up to the nucleation of vapor-liquid interface in one cell leading to region-I which corresponds to a single partially dewetted cell with an intact vapor-liquid interface. Similarly, Region- $\mathcal{N}$ corresponds to the classical region with all n_c partially dewetted cells with intact vapor-liquid interface at height h . For instance, in a system with $n_c = 4$, we show the morphologies corresponding to regions-0, I, II and IV (Figure 4.4) containing 0, 1, 2 and 4 intact vapor-liquid interfaces respectively. Extending the theoretical model to describe the free energetics of region-I in 2-celled system (Figure 4.13a), morphologies lying in region-I of $n_c \geq 4$ can also be replaced by those containing a single partially dewetted cell with an intact vapor-liquid interface at height h_I . The key difference for systems with $n_c \geq 4$ is that now this partially dewetted cell in region-I is surrounded by wet cells on all sides, *i.e.* 4 wet cells (Figure 4.14a) as opposed to 2 in the $n_c = 2$ system (Figure 4.13a). The slope of region-I for systems with $n_c \geq 4$ for the

theoretical model shown in Figure 4.14a is then given by:

$$\overline{\mathcal{M}}_I = \gamma(4S + (8W) \cos \theta) \frac{dh_I}{d\rho_n}, \quad (4.9)$$

where $dh_I/d\rho_n = -n_c H(\alpha + 2)/(\alpha + 4)$. We can then estimate the maximum value of $\alpha = S/W$ allowed to achieve the dewetting of the entire system ($n_c \geq 4$) if one of the cells is dewetted, as,

$$\overline{\alpha}_c = 2(-\cos \theta) = 1.09. \quad (4.10)$$

Additionally, the ratio of slope of region-I to the slope of classical Region- $\mathcal{N}$, is independent of n_c , and is given by:

$$\frac{\overline{\mathcal{M}}_I}{\overline{\mathcal{M}}_{\mathcal{N}}} = \frac{(\alpha + 2 \cos \theta)(\alpha + 2)}{(\cos \theta)(\alpha + 4)}. \quad (4.11)$$

We compare the simulated ratio, $\mathcal{M}_I/\mathcal{M}_{IV}$, for three $n_c = 4$ geometries (Figure 4.11) with the predicted, $\frac{\overline{\mathcal{M}}_I}{\overline{\mathcal{M}}_{\mathcal{N}}}$, from Equation 4.11 in Figure 4.14b. However, for systems with $n_c \geq 4$, we also need to make sure the slopes of subsequent regions, region-II, region-IIIregion- $\mathcal{N}$ to be positive for geometries with $\alpha < \alpha_c$ to achieve complete dewetting of the system if we manage to dewet one cell. The slope of region-II, in $n_c \geq 4$ system where two neighboring cells have intact vapor-liquid interface at height h_{II} , is given by:

$$\overline{\mathcal{M}}_{II} = \gamma(6S + 14W \cos \theta) \frac{dh_{II}}{d\rho_n}. \quad (4.12)$$

Where, $\frac{1}{H} \frac{dh_{II}}{d\rho_n} = -n_c(\alpha + 2)/(2\alpha + 7)$. Equation 4.12 suggests that for $\mathcal{M}_{II} > 0$, an $\alpha > (-7/3) \cos \theta$ is required which is larger than the value of α_c obtained in Equation 4.10; hence for $\alpha > \alpha_c$, $\mathcal{M}_{II}$ is always positive. Similarly, the expressions of the slope of free energy of subsequent regions to confirm that all the subsequent slopes are also positive for $\alpha < \alpha_c$. For instance, Figure 4.11, suggests that the slopes of subsequent regions, region-II and region-IV are not only positive they progressively increase in going from region-I to

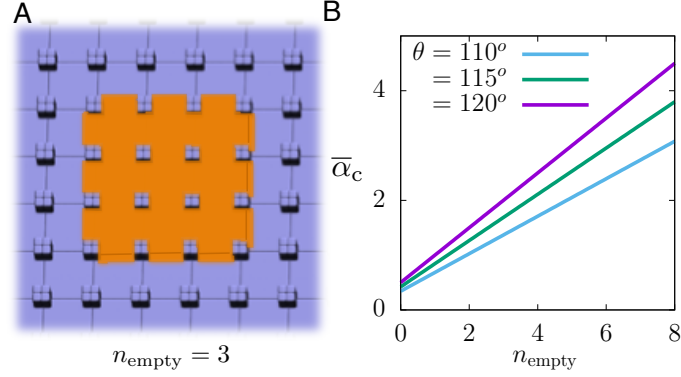


Figure 4.15: Cooperative dewetting criteria in systems containing cluster of nucleating cells can increase α_c (a) Representative sketch of a system with $n_{\text{empty}} = 3$ empty cells. (b) α_c is plotted as function of n_{empty} for various values of $\cos \theta$. For any geometry with $\alpha < \alpha_c$, n_{empty}^2 dewetted cells can cause spontaneous dewetting of entire system.

region-IV. As more cells start to dewet and form a cluster, say a cluster of n_{empty}^2 cells, the favorable solid-vapor interfacial area corresponding to the vertical faces of pillars in partially dewetted cells roughly scales as n_{empty}^2 , as opposed to the unfavorable vapor-liquid interfacial areas (separating wet and dry cells) roughly scaling with the perimeter, n_{empty} . In fact, in the next section we demonstrate that the value of α_c can be systematically increased if instead of providing a single with a nucleating site, a cluster of cells are provided with such sites.

4.10. Guiding Principles for the Design of Optimal Superhydrophobic Surfaces

Cooperativity in dewetting is highly desirable, because then vapor-liquid interfaces could be nucleated in isolated cells containing nano-particle (see Figure 4.6), and this would lead to spontaneous dewetting of the whole surface, and recovery of superhydrophobicity, leading to robust surfaces. On the other hand, performance of superhydrophobic surfaces depends on fractional solid contact area, $\phi = W^2/(S + W)^2 = (1 + \alpha)^{-2}$ and the the Young's contact angle, $\cos \theta$ which influence apparent water droplet contact angle in Cassie state as $\cos \theta_{\text{app}} = -1 + (1 + \cos \theta)\phi$. However, to ensure dewetting cooperativity in systems with one nucleating site, we need $\alpha < \alpha_c = 1.06$ (see equation 4.10), which requires $\phi < 0.25$ limiting the value of $\cos \theta_{\text{app}}$ that can be achieved. To remove this limitation, we consider

vapor-liquid interface nucleating sites spanning n_{empty}^2 cells, possibly by having NPs in a $n_{\text{empty}} \times n_{\text{empty}}$ square array of cells. We estimate using macroscopic theory whether a system with $n_c \rightarrow \infty$ in a state where it has n_{empty}^2 partially dewetted cluster of cells, will spontaneously wet those cells or dewet the rest of the system. In Figure 4.15a, we show a representative sketch of such a system with $n_{\text{empty}} = 3$, while a $n_{\text{empty}} = 1$ system is identical to Figure 4.14a. the slope of free energy with such a square arrangement of $n_{\text{empty}} \times n_{\text{empty}}$ partially dewetted cells at a height, h_e , from the basal surface, is then given by:

$$\overline{\mathcal{M}} = \gamma(4n_{\text{empty}}S)\frac{dh_e}{d\rho_n} + \gamma \cos \theta [4n_{\text{empty}}(n_{\text{empty}} + 1)]W\frac{dh_e}{d\rho_n}. \quad (4.13)$$

Where, the first term corresponds to the unfavorable interfacial energy resulting due vapor-liquid interface between the n_{empty}^2 partially dewetted cells and the surrounding wet cells. The second term in equation 4.13 is favorable for $\cos \theta < 0$ and corresponds to the solid-vapor interfacial energy proportional to the area of the vertical faces of the pillars; this energy has 2 parts, first part arises from the pillars with all side faces partially dewetted until height, h_e while the second part is contributed by the pillars at the boundary between wet and partially dewetted cells. For the system to spontaneously dewet from a configuration with n_{empty}^2 partially empty cells, we need the vapor-liquid interface to favorably rise along the pillars *i.e.* $\overline{\mathcal{M}} < 0$ resulting in:

$$\alpha > \overline{\alpha_c}(n_{\text{empty}}) = (n_{\text{empty}} + 1)(-\cos \theta) \quad (4.14)$$

This gives us an estimate of critical $\overline{\alpha_c}(n_{\text{empty}})$ needed for complete dewetting of system with n_{empty} empty cluster of cells. We recover Equations 4.9 and 4.10 by using $n_{\text{empty}} = 1$ in Equations 4.13 and 4.14 respectively. We finally plot $\overline{\alpha_c}(n_{\text{empty}})$ for various values of $\cos \theta$ in Figure 4.15b to identify the respective regimes of cooperative dewetting. Here we have made a simplistic choice of arrangement of n_{empty} empty cells to demonstrate the calculations, however this framework can be very easily extended to more complicated cluster arrangements or pillar packing. Our prediction of α_c involves the prediction of free

energetics of the system containing a cluster of partially dewetted cells, each containing an intact vapor-liquid interface at certain height, h_e ; this allows us to find the criteria for this vapor-liquid interface to favorably rise. We also note that, an effective nucleating geometry increases the slope of the free energy pertaining to the rise of the vapor-liquid interface and can result in a larger value of α_c ; the exact dependence of the slope as a function of h_e non-trivially depends on size and the shape of the nucleating site and will be explored in future publications. Nevertheless, our theoretical model provides a conservative estimate of α_c and systems with $\alpha < \alpha_c$ for any optimal nucleating site should lead to the dewetting of the entire system.

4.11. Outlook

Both theory and simulations have shown that water density fluctuations, and fluctuations leading to low densities in particular, are enhanced in the vicinity of hydrophobic surfaces [41, 11, 46, 21, 56]. This finding has enabled the use of water density fluctuations as molecular measures of surface hydrophobicity [1, 58, 66, 25], and also clarified that water molecules in the vicinity of hydrophobic surfaces are situated at the edge of a dewetting transition and are sensitive to perturbations [59, 82]. Confining waters between hydrophobic surfaces can provide such an unfavorable perturbation, and such enhanced fluctuations have been shown to play a crucial role in modulating the pathways to dewetting and facilitate the onset of dewetting by leading to reduced dewetting barriers in several confinement contexts [76, 43, 86, 45, 64]. Chapter 2 highlighted one such context in which the pathway of dewetting transition on nano-textured systems offered a lower dewetting barrier as compared to its macroscopic expectation, owing to transitions between various dewetted morphologies stabilized by fluctuations. Not only did we uncover that the transition from the wet Wenzel state to superhydrophobic Cassie state is possible for nano-pillared system at low “extrusion” pressure, we also identified ways to augment the pillared system to create novel textures that spontaneously dewet under ambient conditions; pillared system that was augmented with a hydrophobic nanoparticle at the center had an unstable Wenzel

state and an extrusion pressure over 50 bar (Chapter 3). However, this study led us to ask a very important question of whether such surface augmentation have to be intensive *i.e.*, do we need a nucleating site such as a hydrophobic nanoparticle in each cell for the system to spontaneously dewet or having nucleating sites in one or a cluster of cells sufficient. In fact, most theoretical and simulation studies employ a unit cell replicated periodically and hence lack in information on inter-cell cooperativity; an understanding of such cooperative effects could have crucial implications for the design of robust superhydrophobic surfaces and would be required to answer whether one or a cluster of cell containing nucleating sites can lead to the dewetting of entire system. Here, we obtain the free energetics and dewetting pathways of systems containing multiple uncoupled cells to identify inter-cell cooperative effects in dewetting. Our study highlights the existence of a cooperative dewetting effect mediated by inter-cell gradient in water density resulting in the barrierless dewetting of neighboring cells following a single cell that has been dewetted using a nucleating site. As a result of cooperative dewetting, the overall dewetting barrier in the system is significantly reduced and does not scale linearly with the total number of cells in the system contrary to theoretical predictions. Our results also show that these cooperative effects as caused by the inter-cell density gradient are significantly affected by the ratio, $\alpha \equiv S/W$ of the inter-pillar spacing (S) to pillar width (W) and the hydrophobicity of the surface.

CHAPTER 5 : Influence of Length-scale of Nano-pillars on their Superhydrophobicity

A water droplet placed on a rough hydrophobic surface sits atop a cushion of air, making contacts with only the tips of the surface asperities. In this “Cassie state”, the surface is deemed superhydrophobic, due to its numerous beneficial properties such as self-cleaning and interfacial slip [50, 32, 16]. However, water can readily penetrate the surface texture above a modest pressure, resulting in a “Wenzel state”, which is no longer superhydrophobic [32, 71, 61, 52]. Furthermore, due to large energetic barriers, which prevent the reverse Wenzel-to-Cassie dewetting transition, this breakdown in superhydrophobicity is believed to be irreversible [32, 53, 7]. Superhydrophobicity is thus fragile, and strategies for stabilizing the superhydrophobic Cassie state and facilitating its recovery from the Wenzel state are needed to realize its full technological potential [50]. In previous chapters we showed that on surfaces with nanoscale pillared texture, water density fluctuations can lead to a reduction in the free energetic barriers to dewetting by circumventing the classical dewetting pathways [76, 19, 64]. Our work also highlighted the presence of a finite extrusion pressure; a system in the Wenzel state can spontaneously transition to the Cassie state at a pressure below its extrusion pressure. In this chapter, we extend our study by simulating a wide array of pillared system and understand how the non classical pathways to dewetting, the barriers and intrusion and extrusion pressures scale as we systematically increase the size of the system. In particular, we systematically vary the heights and the width of the square pillars and the inter-pillar spacing and obtain the free energy of wetting dewetting transitions.

5.1. Introduction

Superhydrophobicity can break down due to the intrusion of water into the surface texture at elevated pressures [32, 52] or temperatures [39], upon droplet impact [27, 6], as well as due to surface vibration [33], localized defects [47], or proximity to an electric field [44].

The superhydrophobic Cassie state is thus remarkably fragile, readily giving way to the wet, Wenzel state [32, 71, 47, 39, 27, 44, 6, 52, 33]. To facilitate the recovery of superhydrophobicity and to afford reversible control over surface properties, significant efforts have focused on inducing the reverse Wenzel-to-Cassie drying transition. Insights into why achieving a Wenzel-to-Cassie transition remains challenging are provided by macroscopic interfacial thermodynamics [53], which suggests that the dewetting transition is impeded by a large free energetic barrier. This “classical” barrier is attributed to the work of adhesion for nucleating a vapor-liquid interface at the base of the textured surface. While large kinetic barriers typically separate the dry Cassie state and the wet Wenzel states at ambient conditions, water can readily descend into the surface texture at modest intrusion (Laplace or hydrostatic) pressures, ΔP_{int} . In Chapter 2, we showed that the wetting transition is actually reversible and system can analogously transition back to the Cassie state at so called “Extrusion pressure, ΔP_{ext} due to the collective and cooperative nature of dewetting transitions. Dewetting in textured surfaces proceeds through a complex pathway involving transitions between multiple partially dewetted morphologies with each transition lowering the resistance to dewetting; such a collective dewetting path is facilitated by fluctuation in density of the water. Whether or not such effects persist as the size of the texture is increased, then, becomes a crucial question to address. For a pillared geometry shown in Figure 5.1a it is important to assess the effect of each of the parameters, height of the pillars, H , the width of the pillars, W , and separation between the pillars, S , on the pathways to dewetting, the dewetting barrier, intrusion pressure and more importantly the elusive extrusion pressure. Understanding how each of these quantities scales with geometry will help establish connection between the simulation results and the experimental systems.

Importantly, the apparent contact angle of the system in the Cassie state, depends on the fraction of solid making contact with the liquid, ϕ_s , and is given by:

$$\cos \theta_{\text{Cassie}} = \phi_s \cos \theta - (1 - \phi_s) \quad ; \quad \phi_s = \frac{W^2}{(S + W)^2} = \frac{1}{(S/W + 1)^2}. \quad (5.1)$$

Therefore, an increase in S/W results in an increase of θ_{Cassie} , leading to a superhydrophobic state at $\theta_{\text{Cassie}} = 150^\circ$ (See Figure 5.1b). Aside from understanding the effects of each, H , W and S , it is important to study geometries with larger values of S/W as those are highly sought after for their high apparent contact angles.

To systematically study the effect of scaling H , W and S , we characterize the free energy, the pathways to dewetting, the wetting and dewetting barriers, and their response to pressure for 10 different systems. We also characterize the intrusion pressure, ΔP_{int} , pressure at which the barrier to wetting vanishes and the extrusion pressure, ΔP_{ext} , pressure at which the barrier to dewetting vanishes for each of the systems. We demonstrate that the height of the pillars, H , plays no role in the determining the superhydrophobicity (θ_{Cassie}) or on the robustness (ΔP_{int} and ΔP_{ext}) of the square nano-pillars. An increase in S/W , increases the superhydrophobicity of the surfaces; apparent contact angle in Cassie state increases and contact angle hysteresis decreases. However, the intrusion pressure and hence robustness of the superhydrophobic surfaces decreases as S/W increases; the dependence of ΔP_{int} on S and W is known through macroscopic theory and is in excellent agreement with simulated values. So judicious choice of S/W would be required for specific applications pertaining to the tradeoff between the performance and the robustness of a superhydrophobic surface. While classical macroscopic theory does an excellent job at describing the wetting transition, and specifically, the intrusion pressure, it fails at predicting the dewetting transition and the extrusion pressure, ΔP_{ext} . In chapters 2, we showed that not only do the pillared geometry have a finite extrusion pressure, we can design geometries with positive values of extrusion pressure. However, due to extremely non classical nature of the extrusion pressure, little-to-nothing is known about the dependence of ΔP_{ext} on geometry. In this study, we reveal that the separation between the pillars S does not change ΔP_{ext} as it depends on the morphologies of vapor pockets at the bottom of the pillars and as the pillars are separated by larger and larger distances, the energetics of the vapor pockets remain the same. We also show that the extrusion pressure increases as W is increased, also suggesting that the surfaces with larger W -values would be more robust.

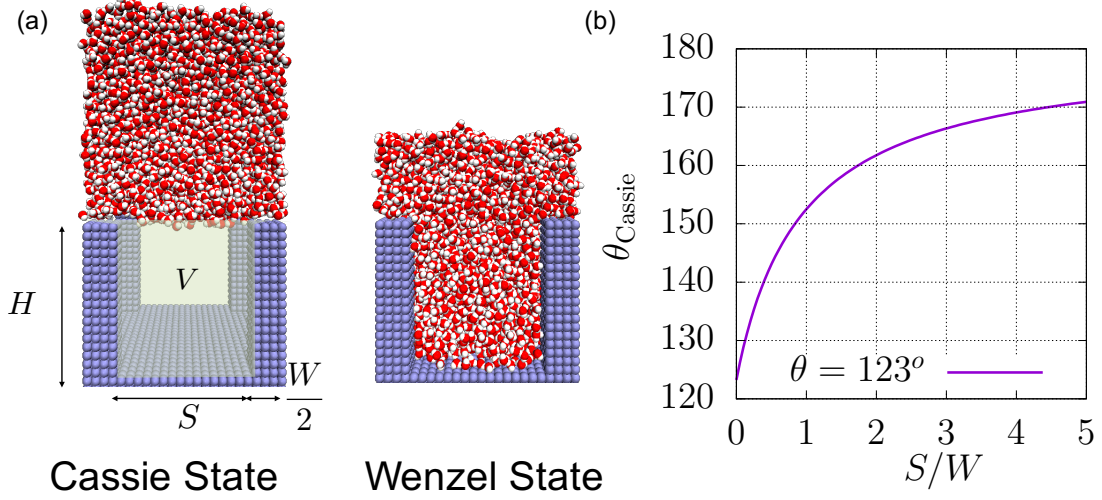


Figure 5.1: The dimensions that characterize the pillared nanotextured surface are the height of the pillars, H , their width, W , and the inter-pillar spacing, S . (a) In the Cassie state (left), water is unable to penetrate the surface texture so that a water molecules sit on a cushion of air, leading to a small contact angle hysteresis and a large contact angle, which are critical in conferring superhydrophobicity to the surface. Also shown is a simulation snapshot of the pillared surface that we study here, which consists of square pillars arranged on a square lattice. The textured volume, V , as well as the dimensions that characterize the pillared nanotextured surface are highlighted; the width of the pillars, W , their height, H , and the inter-pillar spacing, S . In the Wenzel state(right), water wets the texture, so that there is extensive contact between water and the solid surface, leading to a large contact angle hysteresis and a smaller contact angle; in this state, the surface is no longer superhydrophobic. (b) We plot apparent contact angle in the Cassie state, θ_{Cassie} for our system which has a flat contact angle, $\theta = 123^\circ$ as a function of S/W (See Equation 5.1). Larger values of S/W are desirable to create superhydrophobic surfaces with larger apparent contact angles.

5.2. Materials and Methods

The pillared surfaces that we study here are composed of atoms that are arranged on a cubic lattice with a spacing of 0.25 nm and are constrained to remain in their positions throughout the simulations. Each surface consists of a flat basal surface made of a single layer of atoms which is textured using pillars of height, H , and a square cross-section with width, W and the pillars are arranged on a square lattice with inter-pillar spacing, S . We then, systematically vary H , W and S to understand their effects on wetting transitions from the Cassie to the Wenzel state as shown in Figure 5.1. Enough water molecules are included in the simulation box to wet the surface texture in the Wenzel state, and a 2 nm thick water slab is added above the pillars. A wall of purely repulsive particles is included at the top of the simulation box to maintain a buffering vapor layer above the water slab and we ensure that this buffering vapor layer is at least 2 nm thick, even in the Cassie state. Thus, the buffering vapor layer is present in our system at all times and ensures that water remains in coexistence with its vapor throughout and, correspondingly, that the system pressure is equal to the water-vapor coexistence pressure at the system temperature [45]. The surface atoms interact with the oxygen atoms of the SPC/E model of water [3] through the Lennard-Jones (LJ) potential ($\sigma = 0.35$ nm, $\epsilon = 0.40$ kJ/mol) truncated at 1 nm, leading to a contact angle of 123° . Since the basal surface has a single layer of atoms, its interaction strength with water is slightly different from that of the pillars which are at least 2 nm thick in each of the systems studied (See Section 5.3.3).

We use the GROMACS (version 4.5.3) molecular dynamics (MD) simulation package [22], suitably modified to perform INDUS simulations in the canonical (NVT) ensemble. The INDUS method allows us obtain free energy, $F(N)$, of observing N waters in textured volume, V [57]. The parameters and implementation pertaining to the INDUS method are the same as those used in Chapter 2 and is described in Appendix A. To compare partially wet states across different surfaces, we also define a normalized water density, $\rho_n \equiv N/N_{\text{liq}}$, with N being the number of water molecules in V in the partially wet state and N_{liq} being

the corresponding value in the fully wet (Wenzel) state. The simulated free energies that we report, $\Delta F(\rho_n)$, correspond to the free energy of a system in a partially wet state relative to that in the Wenzel state, that is, $\Delta F(\rho_n) = F(N) - F(N_{\text{liq}})$.

5.3. Comparison between Molecular Simulations and Macroscopic Theory

5.3.1. Macroscopic Theory

As described in Chapter 2, assuming that a partially wet state on the pillared surface is characterized by a flat vapor-liquid interface at a height h , above the base of the pillars, it follows that $h(\rho_n) = H(1 - \rho_n)$ (See figure 2.4). The theoretical estimate of free energy of any partially wet state relative to the Wenzel state, $\overline{\Delta F}(\rho_n)$, is then given by:

$$\overline{\Delta F}(\rho_n; \Delta P) = \gamma(1 + \cos \theta')A_{\text{base}} + (\gamma \cos \theta)A_{\text{side}}(1 - \rho_n) + \Delta PV(1 - \rho_n), \quad (5.2)$$

where ΔP is the difference between the pressures of the liquid and the vapor phases, $A_{\text{base}} = S(S + 2W)$ is the basal area, $A_{\text{side}} = 4WH$ and $V = A_{\text{base}}H$. Since each of the pillared system that we study, have a basal surface made of single layer of atoms while the pillars are at least 2 nm thick, we have slightly different values of contact angles; $\cos \theta'$ for the basal surface and $\cos \theta$ for the slope (see section below). Equation 5.2 allows us to obtain the value of the wetting or Cassie-to-Wenzel barrier as:

$$\overline{\Delta F}_{\text{C} \rightarrow \text{W}}(\Delta P) = -(\gamma \cos \theta)A_{\text{side}} - \Delta PV = -(\gamma \cos \theta)4WH - (\Delta P)S(S + 2W)H \quad (5.3)$$

It is clear from Equation 5.3 that the wetting barrier depends on ΔP , the higher the external pressure, the lower the wetting barrier is. The pressure at which the wetting barrier vanishes is given by the intrusion pressure, ΔP_{int} , given by,

$$\overline{\Delta P}_{\text{int}} = -(\gamma \cos \theta) \frac{4W}{S(S + 2W)} \quad (5.4)$$

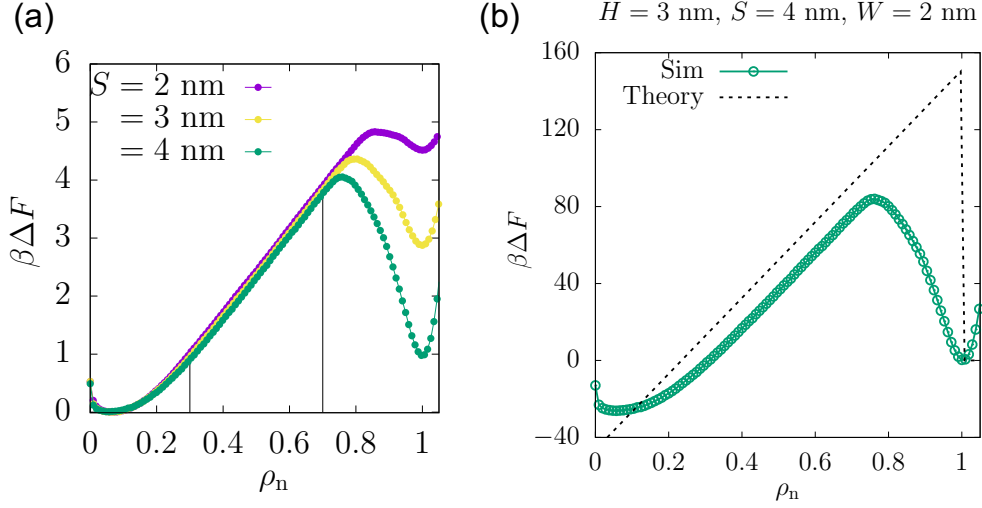


Figure 5.2: (a) The simulated free energy, $F(\rho_n) - F_{\text{Cassie}}$ (in units of the thermal energy, $k_B T \equiv \beta^{-1}$, with k_B being the Boltzmann constant and T the temperature) is shown for three systems (each with $H = 3$ nm and $W = 2$ nm and S values as shown). For ρ_n -values lying between the barrier and the Cassie state, our simulations display an intact vapor-liquid interface that is detached from, and is roughly parallel to the basal surface consistent with the assumption in macroscopic theory. Therefore, the slope resulting from fitting the simulated values of $(F(0.3 < \rho_n < 0.7) - F_{\text{Cassie}})/4WH$ to a straight line provides $(-\gamma \cos \theta)_{\text{fit}}$. We use the free energy of three different systems to extract the average value of $(\gamma \cos \theta)_{\text{fit}} = -7.24 \pm 0.03 k_B T/\text{nm}^2$. (b) The simulated free energy for a pillared system with $H = 3$ nm, $W = 2$ nm and $S = 4$ nm is compared with its macroscopic theory prediction shown with the black dashed line. We use Equation 5.2, the values of $(\gamma \cos \theta)_{\text{fit}}$ as obtained from (a), as well as the value of $\gamma(1 + \cos \theta')$ as obtained in the Appendix D to obtain an accurate prediction for the macroscopic theory

Analogously, the dewetting barrier, also referred to as the work of adhesion is given by:

$$\overline{\Delta F}_{W \rightarrow C} = \gamma(1 + \cos \theta') A_{\text{base}} = \gamma(1 + \cos \theta') S(S + 2W) \quad (5.5)$$

One of the limitations of this classic macroscopic model is that the macroscopic estimate of dewetting barrier is independent of the pressure of the system, whereas in chapter 2 highlighted that the simulated dewetting barrier changes with pressure, eventually vanishing at ΔP_{ext} .

Table 5.1: Geometric parameters for all systems studied.

System	H (nm)	W (nm)	S (nm)	N_{liq}
H3W2S3	3.11	2.19	2.77	2040
H3W2S4	3.11	2.19	3.77	3150
H3W2S5	3.11	2.19	4.77	4480
H3W2S6	3.11	2.19	5.77	6020
H3W2S7	3.11	2.19	6.77	7750
H3W2S8	3.11	2.19	7.77	9650
H3W2S10	3.11	2.19	9.77	14170
H4W2S4	4.11	2.19	3.77	4180
H5W2S4	5.11	2.19	3.77	5200

5.3.2. Obtaining offsets in geometric parameters

The values of the pillar width W , its height H and the inter-pillar separation S , reported in the Materials and Methods Section, correspond to the distances between the centers of the corresponding surface atoms. To compare our simulations with macroscopic theory, we use effective values of $W + 19$ nm, $S - 0.23$ nm and $H + 0.11$ nm by accounting for offsets in geometric parameters as described in Appendix B. Table 5.1 lists the geometric parameters of all the pillared systems studied in this chapter.

5.3.3. Obtaining γ , $\cos \theta$ and $\cos \theta'$

The procedure to obtain $\cos \theta$ and γ for their use in comparison with macroscopic theory closely follows the procedure described in section 2.4.2. We first obtain $\gamma(1 + \cos \theta) = 5.97 \pm 0.0006$ $k_{\text{B}}T/\text{nm}^2$ as independently calculated in Appendix D, Figure D.1. We then estimate $(\gamma \cos \theta)_{\text{fit}}$ by fitting the simulation data in the linear region between $0.3 < \rho_{\text{n}} < 0.7$ (Figure 2.2, dashed line), and comparing the fitted slope to $-(\gamma \cos \theta)_{\text{fit}} A_{\text{side}}$. We follow this procedure for three different systems and get the similar values of $(\gamma \cos \theta)_{\text{fit}} = -7.24 \pm 0.03$ $k_{\text{B}}T/\text{nm}^2$ within error-bars and consistent with its value obtained in Section 2.4.2.

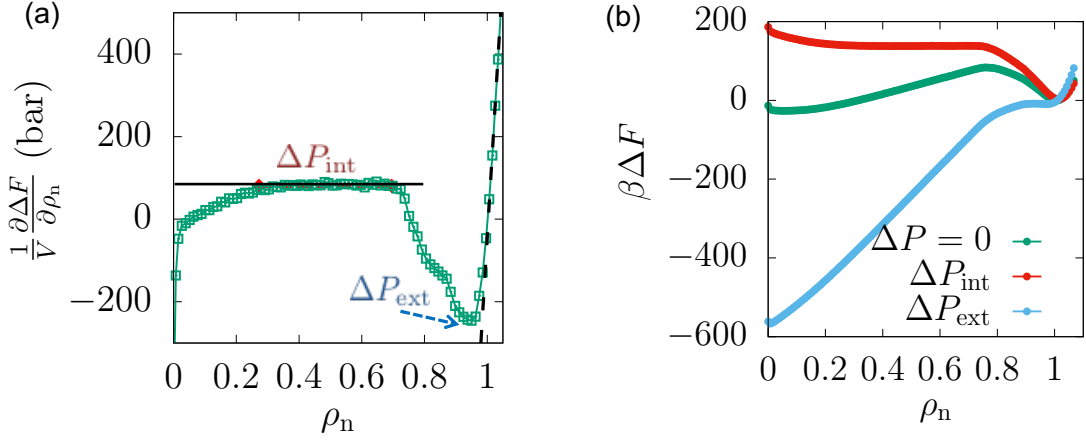


Figure 5.3: Procedure for obtaining the simulated values of intrusion pressure, ΔP_{int} , and extrusion pressure, ΔP_{ext} . (a) The derivative of simulated free energy normalized by the textured volume, $\frac{1}{V} \frac{d\Delta F(\rho_n)}{d\rho_n}$, in units of bar is shown for system with $H = 3$ nm and $W = 2$ nm and $S = 4$ nm. The region for which system displays intact vapor-liquid interface ($\rho_n < 0.7$), consistent with macroscopic theory, ΔF varies linearly with ρ_n , hence the values of $\frac{d\Delta F(\rho_n)}{d\rho_n}$ is constant and its value normalized by V provides an estimate of ΔP_{int} . We fit the data for the $0.3 < \rho_n < 0.7$ to obtain ΔP_{int} (we exclude $\rho_n < 0.3$ as it contains effect of Gaussian fluctuations in the Cassie basin). The pressure corresponding to the minimum slope of the system provides us an estimate of the the extrusion pressure, as it is the value at which the barrier between the Wenzel state to Cassie state vanishes. (b) The free energy of the system at the estimated values of intrusion pressure (red), extrusion pressure (blue) as well as at the simulated value of $\Delta P = 0$.

The error-bars are obtained using dividing the data in 5 different blocks and using standard error of the mean value as the reported error. This allows us to obtain the value of $\gamma_{\text{fit}} = 13.21 \pm 0.03 \text{ k}_B T/\text{nm}^2$ and $\cos \theta = -0.548$ ($\theta = 123.3^\circ$). To obtain the value of $\cos \theta'$, we use the value of $\gamma(1 + \cos \theta') = 4.91 \pm 0.001 \text{ k}_B T/\text{nm}^2$ and extract $\theta' = 128^\circ$.

5.4. Procedure for obtaining the simulated values of intrusion pressure, ΔP_{int} , and extrusion pressure, ΔP_{ext}

We first calculate smoothed derivatives of ΔF , by first computing derivative using finite difference method, and then by smoothing the resultant, $d\Delta F(\rho_n)/d\rho_n$, by averaging over 20 data points. The error in $d\Delta F(\rho_n)/d\rho_n$ was estimated using standard block averaging

procedure. We plot the derivative of the free energy of system with $H = 3$ nm, $W = 2$ nm and $S = 4$ nm in Figure 5.3a. The region for which system displays intact vapor-liquid interface ($\rho_n < 0.7$), consistent with macroscopic theory, ΔF varies linearly with ρ_n , hence the values of $\frac{d\Delta F(\rho_n)}{d\rho_n}$ is constant and its value normalized by V provides an estimate of ΔP_{int} . We fit the data for the $0.3 < \rho_n < 0.7$ to obtain ΔP_{int} (we exclude $\rho_n < 0.3$ as it contains effect of Gaussian fluctuations in the Cassie basin). The error in the value of ΔP_{int} is obtained as the standard error obtained from fitting the range of data. The pressure corresponding to the minimum slope of the free energy provides an estimate of the the extrusion pressure, as it is the value at which the barrier between the Wenzel state to Cassie state vanishes. In Figure 5.3b, we plot the free energy of the system at the estimated values of intrusion pressure (red), extrusion pressure (blue) as well as at the simulated value of $\Delta P = 0$.

5.5. Height of the pillars does not affect the performance or the robustness of superhydrophobic pillared surfaces

It is important to note that heights of the pillars play no role in determining the apparent contact angle of the system in the superhydrophobic Cassie state (Equation 5.1). The effect of pillar height on free energetics of wetting-dewetting transitions using macroscopic theory can be obtained from Equation 5.2 through Equation 5.5. In Figure 5.4, we study the effect of height on free energetics of wetting-dewetting transitions as obtained from the simulations and compare them with their macroscopic expectations. We first plot the simulated free energy, $\Delta F(\rho_n)$ three systems with different pillar heights, H while keeping the pillar width, W , and the separation between the pillars S the same; $\rho_n \equiv N/N_{\text{liq}}$ is the normalized density in textured region V (See Figure 5.1). Each of the three free energy curves features a Cassie state at $\rho_n \approx 0$ and a Wenzel basin at $\rho_n \approx 1$ separated by a barrier (Figure 5.4a). In Figure 5.4b, we plot the two barriers as a function of H ; consistent with macroscopic theory (Equation 5.3), the wetting barrier, $\Delta F_{\text{C} \rightarrow \text{W}}$ scales linearly with H . The Wenzel-to-Cassie dewetting barrier, $\Delta F_{\text{W} \rightarrow \text{C}}$, remains constant with

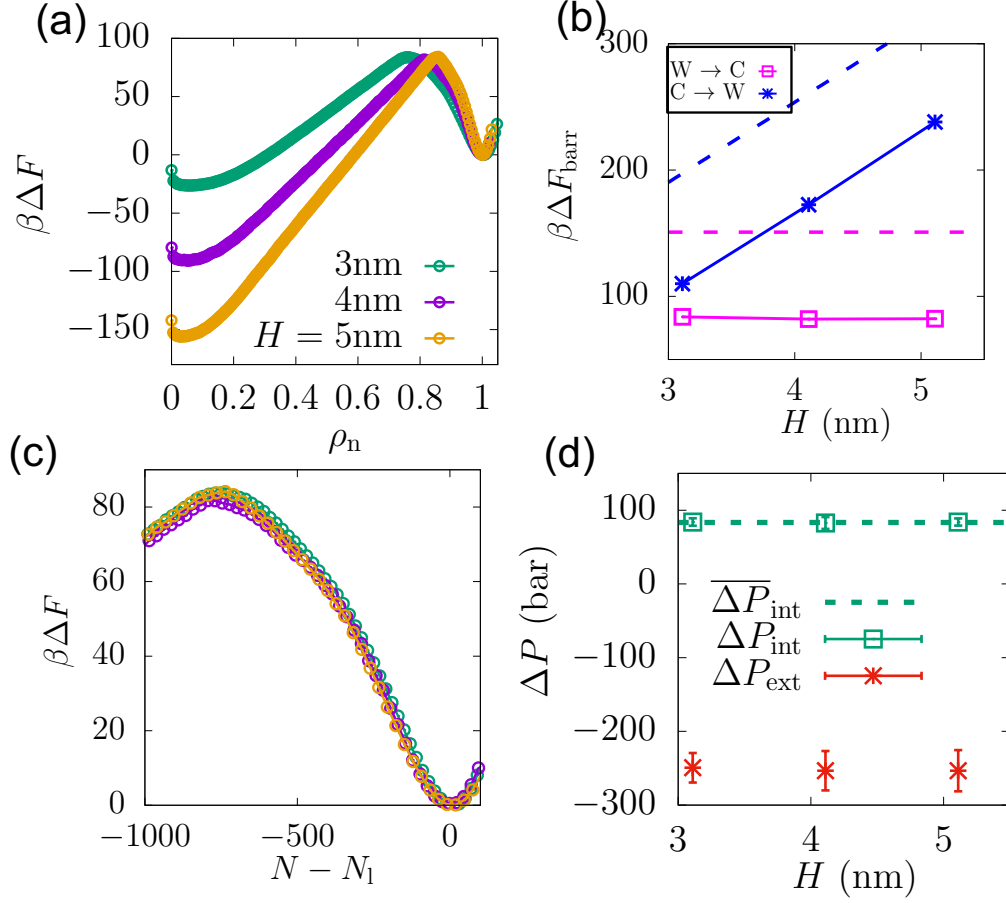


Figure 5.4: Effect of pillar height, H , on free energetics of wetting-dewetting transitions. (a) The simulated free energy, $\Delta F(\rho_n)$ at $\Delta P = 0$ is shown for three systems with different pillar heights, H . For each of the systems the width of the pillars are, $W = 2$ nm and the separation between the pillars are, $S = 4$ nm. $\rho_n \equiv N/N_{\text{liq}}$ is the normalized density in textured region. The free energy curves feature a Cassie state at $\rho_n \approx 0$ and a Wenzel basin at $\rho_n \approx 1$ separated by a barrier. (b) The barriers for the wetting and dewetting transitions are shown here as a function of H . Consistent with macroscopic theory, the wetting barrier, $\Delta F_{\text{C} \rightarrow \text{W}}$ scales linearly with H and the dewetting barrier remains constant. Macroscopic theory over-predicts both the barriers as it does not account for non classical pathway between the barrier and the Wenzel state. (c) Re-plotting the free energy of the systems as a function of $N - N_{\text{liq}}$ highlights that the pathway between the Wenzel state and the barrier state preceding the formation of a nascent vapor-liquid interface, is identical in all the three systems. (d) We also show that the intrusion pressure, ΔP_{int} , pressure above which system must spontaneously transition into the wet Wenzel state is independent of H , consistent with its macroscopic prediction, $\overline{\Delta P}_{\text{int}}$. The extrusion pressure, ΔP_{ext} , pressure below which spontaneous dewetting should occur is also independent of H .

H , also consistent with macroscopic prediction in Equation 5.5. However, the macroscopic theory over-predicts both the barriers as it doesn't take into account the non-classical pathway to dewetting facilitated by fluctuations in water density. The dewetting barrier from simulations lies in the formation of a nascent vapor layer(1 nm thick) followed by a nonclassical path transitioning from one morphology to another and does not depend on H , hence the non-classical barrier to dewetting also does not scale with H .

5.6. Transition from Cassie state to Wenzel state is reversible irrespective of the size of the system

While the pillar heights play no role in determining the superhydrophobicity of the nanopillared surfaces, the width of the pillars, W , and the separation between the pillars, S , strongly dictate the performance (apparent contact angle and contact angle hysteresis) of superhydrophobicity. In particular, Equation 5.1 shows that the apparent contact angle in the Cassie state, θ_{Cassie} , is directly related to S/W of the pillars; as the value of S/W increases, θ_{Cassie} increases. In Figure 5.1b, we plot the apparent contact angle as a function of S/W for a flat contact angle of 123° . Additionally, the fraction of the solid making contact with water in the Cassie state, $\frac{1}{(S/W+1)^2}$, also influences the contact angle hysteresis; as S/W increases, the contact angle hysteresis decreases [50, 32, 16] . However, the measure of robustness of superhydrophobicity, the highest pressure a superhydrophobic material can sustain before collapsing into the wet Wenzel state, the intrusion pressure, ΔP_{int} , decreases with S/W (See equation 5.4). Hence, there is a tradeoff between the performance of a pillared superhydrophobic surface (apparent contact angle and contact angle hysteresis) and its robustness (intrusion pressure), both depending on S/W . However as we demonstrated in Chapter 2, another measure of robustness of superhydrophobicity of the pillared surface is the extrusion pressure, a pressure below which system should spontaneously transition into superhydrophobic Cassie state. Unlike intrusion pressure, which can be well described by macroscopic theory, the extrusion pressure depends on free energetics of complex morphologies near the Wenzel state at $\rho_n \approx 1$. It then becomes an important question to address

that whether increasing S/W would unfavorably affect the extrusion pressure akin to its effect on intrusion pressure. To address this question, we characterize the free energetics of system that has a very high value of $S/W \approx 5$ leading to a an apparent contact angle of $\theta_{\text{Cassie}} = 170^\circ$ for our pillared material.

5.6.1. Free energetics and pathways of wetting-dewetting transitions on a pillared surface with $S = 10 \text{ nm}$ and $W = 2 \text{ nm}$

In Figure 5.5, we plot the free energy as function of ρ_n for a system with $S = 10 \text{ nm}$ and $W = 2 \text{ nm}$ and $H = 3 \text{ nm}$. Instead of obtaining the entire free energy between the Cassie state and the Wenzel state, we obtain $\Delta F(\rho_n > 0.55)$ to reduce the computational cost, as all the non-classical features lie between the barrier state and the Wenzel state. Between the Wenzel state and the barrier, $\Delta F(\rho_n)$ is marked by several kinks, which demarcate five regions with distinct dewetted morphologies (Figure 5.5a). In Figure 5.5b, we plot the derivative of simulated free energy normalized by the textured volume, $\frac{1}{V} \frac{d\Delta F(\rho_n)}{d\rho_n}$, in the units of pressure (bar). Corresponding to the kinks in free energy demarcating different regions, the derivative features abrupt changes in its value or functional forms. As explained in Figure 5.3a, extrusion pressure depends on smallest value of the slope of free energy which lies at the intersection of region-IV (Vapor pockets) and region-V (Gaussian). Whereas the intrusion pressure can be given by the slope of free energy in region-I. The intrusion pressure for this $S = 10 \text{ nm}$ and $W = 2 \text{ nm}$ system is 15 bar, much smaller than that for the $S = 4 \text{ nm}$, $W = 2 \text{ nm}$ systems shown in Figure 5.4d with $\Delta P_{\text{int}} = 83 \text{ bar}$, and is in excellent agreement with its theoretical expectation. However, the extrusion pressure remains at $\Delta P_{\text{ext}} \approx -230 \text{ bar}$, identical to that for the systems shown in Figure 5.4. This invariability of ΔP_{ext} with S/W or S warrants independent study of influence of S and W on ΔP_{ext} .

In Figure 5.5c, we plot the representative configurations corresponding to these regions are shown as interfaces encompassing the dewetted volumes (shown in orange, waters omitted for clarity). The dewetting pathway is almost identical to the one for smaller pillared system

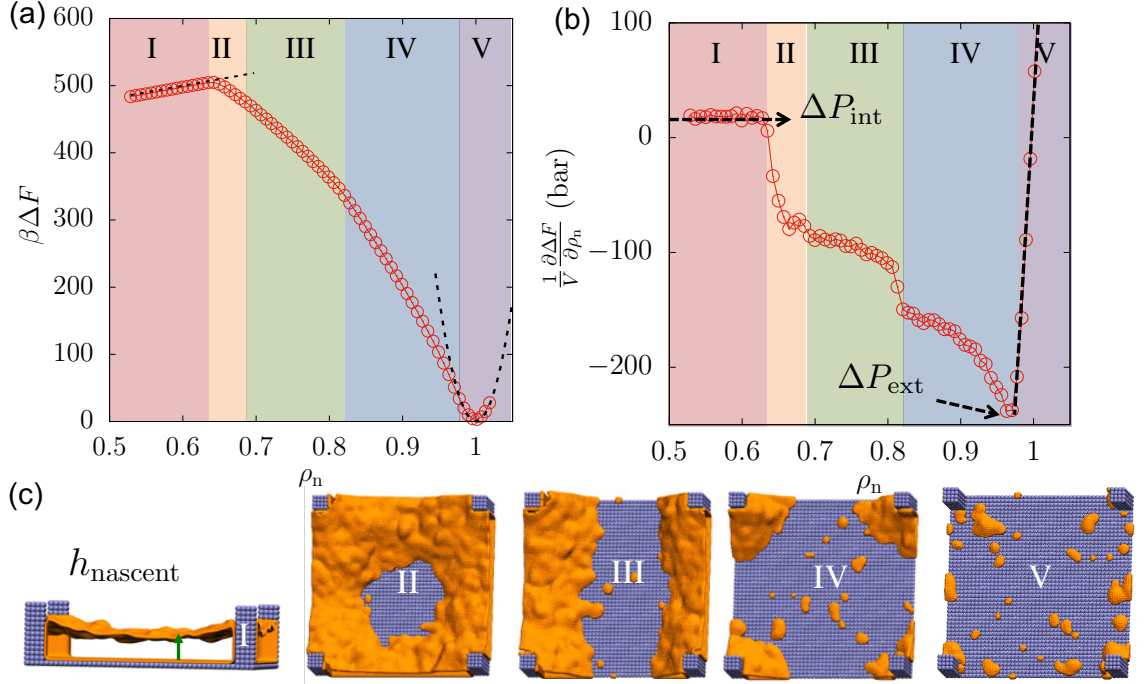


Figure 5.5: Free energetics of wetting-dewetting transitions on a pillared surface with $S = 10$ nm and $W = 2$ nm highlights that dewetting is a nanoscopic phenomena and the transition from Cassie state to Wenzel state is reversible, irrespective of the size of the system. (a) The simulated free energy, $\Delta F(\rho_n)$ at $\Delta P = 0$ as a function of $\rho_n > 0.55$. Between the Wenzel state and the barrier, $\Delta F(\rho_n)$ is marked by several kinks, which demarcate five regions with distinct dewetted morphologies. (b) The derivative of simulated free energy normalized by the textured volume, $\frac{1}{V} \frac{d\Delta F(\rho_n)}{d\rho_n}$, in units of bar is plotted. Corresponding to the kinks in free energy demarcating different regions, the derivative features abrupt changes in its value or functional forms. Extrusion pressure depends on smallest value of the slope of free energy which lies in the region-IV. (c) Representative configurations corresponding to these regions are shown as interfaces encompassing the dewetted volumes (shown in orange, waters omitted for clarity). The dewetting pathway is almost identical to the one for smaller pillared system described in Figure 2.5. Region V ($\rho_n \approx 1$) displays Gaussian fluctuations resulting in a parabolic basin and region IV ($0.82 < \rho_n < 0.96$) is characterized by vapor pockets at the base of the pillars. As ρ_n is reduced, vapor pockets grow, break symmetry, and merge to form a striped vapor layer between the pillars; the stripe expands laterally in Region III ($0.69 < \rho_n < 0.82$) until a nearly intact vapor-liquid interface is formed. Region II ($0.63 < \rho_n < 0.69$) is characterized by water molecules sticking to the center of the cell, and also contains the non-classical barrier, which eventually gives way to the classical Region I at $\rho_n \approx 0.63$. The height of the nascent vapor layer that forms at $\rho_n \approx 0.63^-$ is given by $h_{\text{nascent}} \approx 1.2$ nm.

described in Figure 2.5. Region V ($\rho_n \approx 1$) displays Gaussian fluctuations resulting in a parabolic basin and region IV ($0.82 < \rho_n < 0.96$) is characterized by vapor pockets at the base of the pillars. As ρ_n is reduced, vapor pockets grow, break symmetry, and merge to form a striped vapor layer between the pillars; the stripe expands laterally in Region III ($0.69 < \rho_n < 0.82$) until a nearly intact vapor-liquid interface is formed. Region II ($0.63 < \rho_n < 0.69$) is characterized by water molecules sticking to the center of the cell, and also contains the non-classical barrier, which eventually gives way to the classical Region I at $\rho_n \approx 0.63$. We obtain the height of the nascent vapor layer that forms at $\rho_n \approx 0.63^-$ as follows:

$$h_{\text{nascent}}(\Delta P = 0) = H(1 - \rho_n^{\text{barr}}), \quad (5.6)$$

where, ρ_n^{barr} is the location of the barrier, obtained by locating the maxima in the free energy at $\Delta P = 0$. It is important to note that even though we have increased the size of the basal area four times relative to the system shown in Figure 2.5, the size of the nascent vapor layer is comparable (≈ 1 nm) in both cases. This suggests that the non-classical pathway leading to the formation of this vapor layer is nanoscopic and does not scale as the size of the basal area is increased.

5.6.2. Demonstrating that dewetting is a nanoscopic phenomena

We also examine the height of the nascent vapor layer, $h_{\text{nascent}}(\Delta P = 0)$ (See Equation 5.6) for a 9 different pillared geometries, by varying both S and W and plotting it as a function of basal area, $A_{\text{base}} = S(S + 2W)$ in Figure 5.6. As the basal area scales up, $h_{\text{nascent}}(\Delta P = 0)$ remains almost unchanged and seem to plateau around 1.2 nm. This highlights that the complex dewetting pathway as seen in Figure 5.5 which comprises of various morphological changes leading to the classical region I is nanoscopic irrespective of the size of the system. We can then use the value of $h_{\text{nascent}}^{\infty}(\Delta P = 0)$, value at which $h_{\text{nascent}}(\Delta P = 0)$ plateaued out, to correct the macroscopic prediction to the wetting and dewetting barriers. As shown in Figure 5.6b, and using Equation 5.2, we can obtain the corrected wetting (Cassie $\rightarrow$

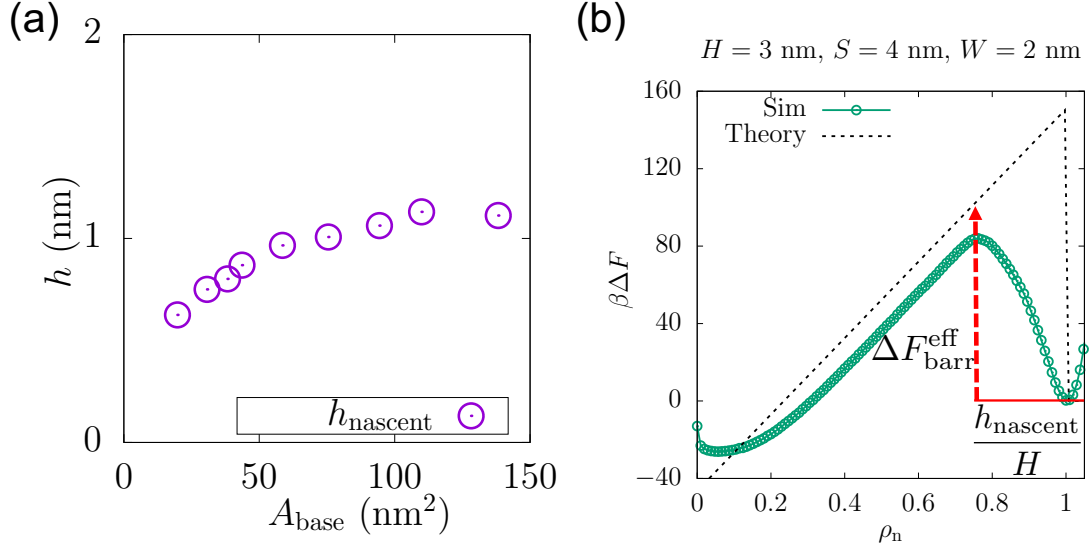


Figure 5.6: Highlighting that dewetting is a nanoscopic phenomena and macroscopic theory will always over-predict the dewetting and wetting barriers even as the system-size is scaled up. (a) Simulated height of the nascent vapor layer, $h_{\text{nascent}}(\Delta P = 0)$ as a function of basal area, $A_{\text{base}} = S(S + 2W)$ for 9 different pillared geometry. As the basal area scales up, $h_{\text{nascent}}(\Delta P = 0)$ remains almost unchanged and seem to plateau around 1.2 nm. This highlights that the complex dewetting pathway as seen in Figure 5.5 which comprises of various morphological changes leading to the classical region I is nanoscopic, irrespective of the size of the system. (b) Using the fact that h_{nascent} is non-zero contrary to the classical macroscopic assumptions, we can explain why macroscopic theory over-predicts the dewetting and wetting barriers and why the discrepancy will scale as system sizes are increased (See Equation 5.7 and 5.8).

Wenzel) barrier as:

$$\overline{\Delta F}_{C \rightarrow W}^{\text{eff}}(\Delta P = 0) = [-(\gamma \cos \theta)4W](H - h_{\text{nascent}}^{\infty}) \quad (5.7)$$

where, the superscript ‘eff’ stands for effective value. Similarly, we can obtain the dewetting barrier by accounting for the non-classical pathway using the value of $h_{\text{nascent}}^{\infty}$ as follows,

$$\overline{\Delta F}_{W \rightarrow C}^{\text{eff}} = \gamma(1 + \cos \theta')S(S + 2W) + [(\gamma \cos \theta)4W]h_{\text{nascent}}^{\infty} \quad (5.8)$$

However, to correct for the barriers at all pressures, prior knowledge on dependence of h_{nascent} on ΔP is needed. Since the various non-classical morphologies leading up to the formation of nascent vapor layer have different ρ_n -ranges and slopes, it’s a non-trivial task to obtain prediction for h_{nascent} at all pressures.

5.7. Separation between the pillars only affects the intrusion but not the extrusion pressure

In previous sections we have established that height of the pillars play no role in the superhydrophobicity (θ_{Cassie}) or on the robustness (ΔP_{int} and ΔP_{ext}) of the superhydrophobicity. While, the dependence of ΔP_{int} on S and W is known through macroscopic theory, which seems in excellent agreement with simulated values in Figure 5.4, little-to-nothing is known about the dependence of ΔP_{ext} on geometry. In this section, we study the effect of S on wetting-dewetting transitions by keeping the value of W constant and vice versa in the following section.

In Figure 5.7a, we plot the simulated value of free energies, $\Delta F(\rho_n)$ at $\Delta P = 0$ for seven systems with different values of S ; for each of the systems $W = 2$ nm. Since, all the complexity of the pathway lies between the Wenzel state and the barrier state, we only plot the free energies for $\rho_n > 0.6$. Each of the free energies feature different values of ρ_n at the barrier, leading to a nanoscopic value of h_{nascent} and finite value of extrusion pressure. The derivative of simulated free energy normalized by the textured volume, $\frac{1}{V} \frac{d\Delta F(\rho_n)}{d\rho_n}$, highlights

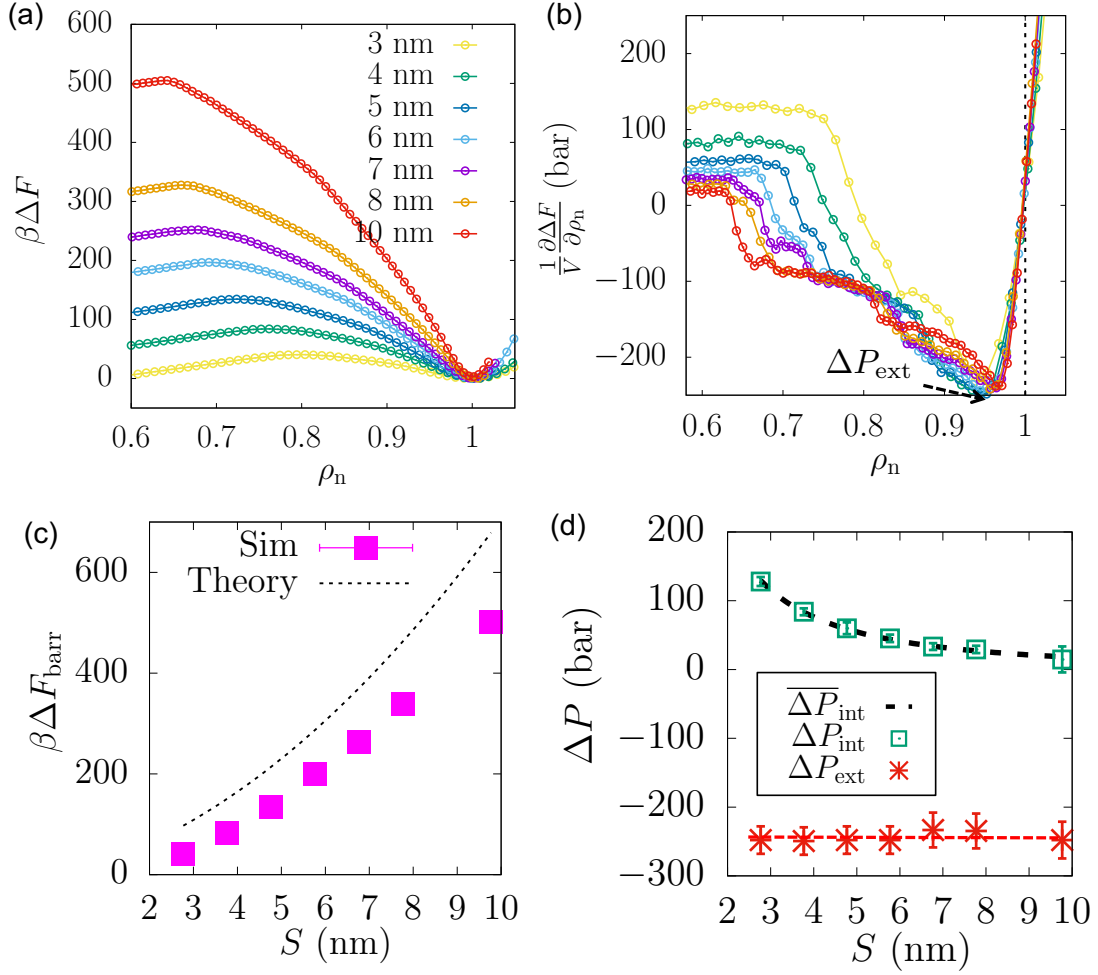


Figure 5.7: Changing the separation between the pillars, S , only affects the intrusion and not the extrusion pressure. (a) The simulated free energy, $\Delta F(\rho_n)$ at $\Delta P = 0$ is shown for seven systems with different values of S . For each of the systems the width of the pillars, $W = 2$ nm. (b) The derivative of simulated free energy normalized by the textured volume, $\frac{1}{V} \frac{d\Delta F(\rho_n)}{d\rho_n}$, in units of bar highlights that each of the system has a complex dewetting pathway between the Wenzel state and the barrier state, marked by multiple abrupt changes in slope. (c) The dewetting barrier is plotted as function of S , highlights that macroscopic theory consistently over-predicts the dewetting barrier as it fails to take the complex dewetting pathway into account. (d) We show that the intrusion pressure, ΔP_{int} is inversely proportional to S , and is in excellent agreement with its macroscopic prediction, $\overline{\Delta P}_{\text{int}}$. Interestingly, the extrusion pressure, ΔP_{ext} , pressure below which spontaneous dewetting occurs, is independent of S . The reason for invariability of ΔP_{ext} on S can be attributed to the fact that extrusion pressure depends on the free energetics of vapor pockets and gaussian fluctuations in the Wenzel basin (at the intersection of region IV and region V in figure 5.5); none of the two morphologies depend on S for their characteristic shape.

that each of the system has a complex dewetting pathway between the Wenzel state and the barrier state, marked by multiple abrupt changes in slope (In Figure 5.7a). Another interesting thing to note is that the smallest value of the derivative is identical for each of these systems, indicating similar value of extrusion pressure, as marked by an arrow. In Figure 5.7d, we show that the extrusion pressure, ΔP_{ext} is indeed independent of S . The reason for invariability of ΔP_{ext} on S can be attributed to the fact that extrusion pressure depends on the free energetics of vapor pockets and gaussian fluctuations in the Wenzel basin (at the intersection of region IV and region V in figure 5.5); none of the two morphologies depend on S for their characteristic shape. We also plot the intrusion pressure, ΔP_{int} , as a function of S , which is in excellent agreement with its macroscopic prediction, $\overline{\Delta P}_{\text{int}}$ and decreases as S decreases, making the system less robust for higher values of S .

5.8. Effect of pillar width on wetting-dewetting transitions

In this section, we explore the effect of pillar width, W , on wetting dewetting transitions. While the intrusion pressure is excellently described by macroscopic theory and decreases as S/W is decreased, the extrusion pressure is not well understood. In the previous sections, we demonstrated that ΔP_{ext} is invariable with both pillar height, H (Figure 5.4), and separation, S (Figure 5.7), and it corresponds to the minimum slope of free energy in region IV (Figure 5.5). In Figure 5.8a, we plot ΔP_{int} and ΔP_{ext} as functions of W ; the simulated ΔP_{int} increases as W is increased, in excellent agreement with its macroscopic expectation (dashed line). Even though larger ΔP_{int} is favorable for creating superhydrophobic surfaces that can withstand larger pressure, the performance of superhydrophobic surfaces (apparent contact angle in Cassie state) decreases due to increased fraction of solid at the top of the pillars. Interestingly, extrusion pressure, ΔP_{ext} , also increases as W is increased, indicating that larger pillar widths are favorable for creating superhydrophobic surfaces that can recover their superhydrophobicity. To understand why ΔP_{ext} increases with W we look at the free energetics of systems with different pillar width. ΔP_{ext} depends on the lowest value of the slope of free energy, in Figure 5.8, we plot the the free energy along with its derivative

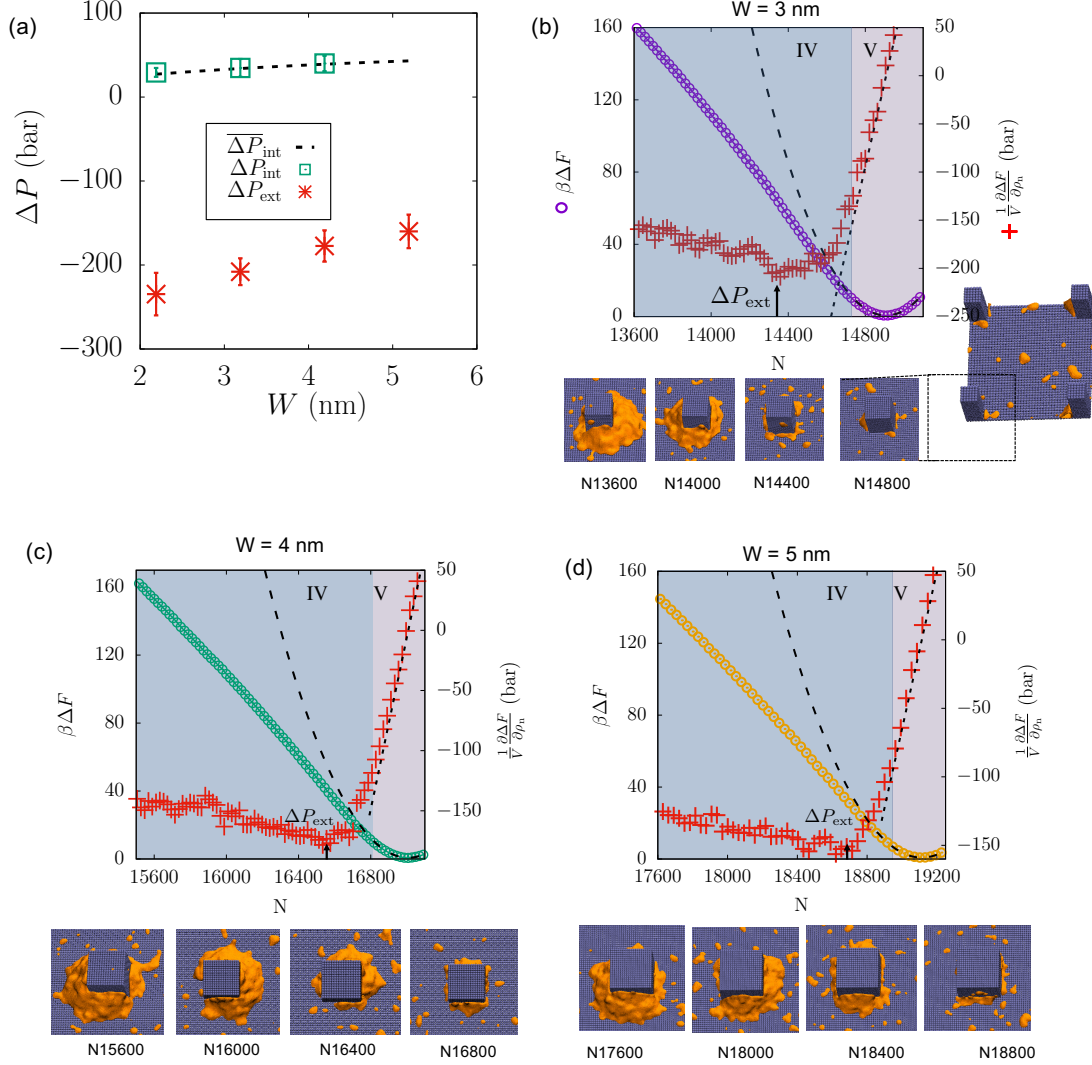


Figure 5.8: Effect of pillar width, W , on free energetics of wetting-dewetting transitions for systems with $S = 8$ nm and $H = 4$ nm. (a) The simulated ΔP_{int} increases as W is increased, in excellent agreement with its macroscopic expectation (dashed line). Extrusion pressure, ΔP_{ext} , also increases as W is increased, indicating that larger pillar widths are favorable for creating more robust superhydrophobic surfaces. Since ΔP_{ext} depends on the lowest value of the slope of free energy, we plot the free energy along with its derivative and representative interfacial snapshots for systems with (b) $W = 3$ nm (c) $W = 4$ nm and (d) $W = 5$ nm. We plot the free energy in the units of $k_B T$ (circles) as a function of N , and its derivative in the units of bar (red-crosses) for each of the 3 systems. Each free energy features a harmonic basin and its derivative features a straight line (corresponding parabola and straight line in black-dashed lines) in the Wenzel state in Region V. As N is decreased the derivative deviates from a straight line and reaches a minimum value corresponding to ΔP_{ext} . The representative snapshots of vapor-liquid interfaces along the path is shown in orange (periodic boundary condition is applied to visualize the pillars as shown in (b)). The pathways indicate that there is a critical size of vapor-pocket, akin to heterogeneous nucleation processes, that corresponds to the lowest slope, and once it forms, subsequent dewetting becomes easier.

and representative interfacial snapshots for three systems with (b) $W = 3$ nm (c) $W = 4$ nm and (d) $W = 5$ nm. Each free energy features a harmonic basin and its derivative features a straight line (corresponding parabola and straight line in black-dashed lines) in the Wenzel state in Region V. As N is decreased the derivative deviates from a straight line and reaches a minimum value corresponding to ΔP_{ext} . The dewetting pathways indicate that there is a critical size of vapor-pocket, akin to heterogeneous nucleation processes, that corresponds to the lowest slope, and once it forms, subsequent dewetting becomes easier. While the exact dependence of the size of critical vapor-pocket on W can be complex, it makes sense that larger values of W provides more hydrophobic areas making the formation of critical vapor pockets easier resulting in larger values of extrusion pressures.

5.8.1. Estimating the dependence of ΔP_{ext} on W using Young's Laplace equation

To understand the dependence of ΔP_{ext} on W , we assume that at their critical size, the vapor pockets take the shape of spherical cap and are comparable to the size of the cross-section of the pillars. As shown in the Figure 5.9a, we can assume that one of the principal radii of the vapor pocket at the basal surface, r_b , is given by:

$$r_b = W/\sqrt{2} + \delta, \quad (5.9)$$

assuming δ is arbitrary small constant that does not depend on W . Using above equation, the largest distance between the vertical face of the pillars and the vapor-liquid interface is $\delta_W = r_b - W/2$ (Figure 5.9a). By assuming that vapor pockets satisfy the contact angle boundary condition, the second principle radius of curvature for the vapor pockets is given by:

$$r_p = \frac{(r_b - W/2)}{\sqrt{2} \cos(\theta - \pi/4)} = \frac{W(\sqrt{2} - 1) + 2\delta}{2\sqrt{2} \cos(\theta - \pi/4)}, \quad (5.10)$$

See Figure 5.9a for a cartoon identifying r_p . According to Young's Laplace equation, the curvatures of a vapor-liquid interface can be related to the pressure difference across the

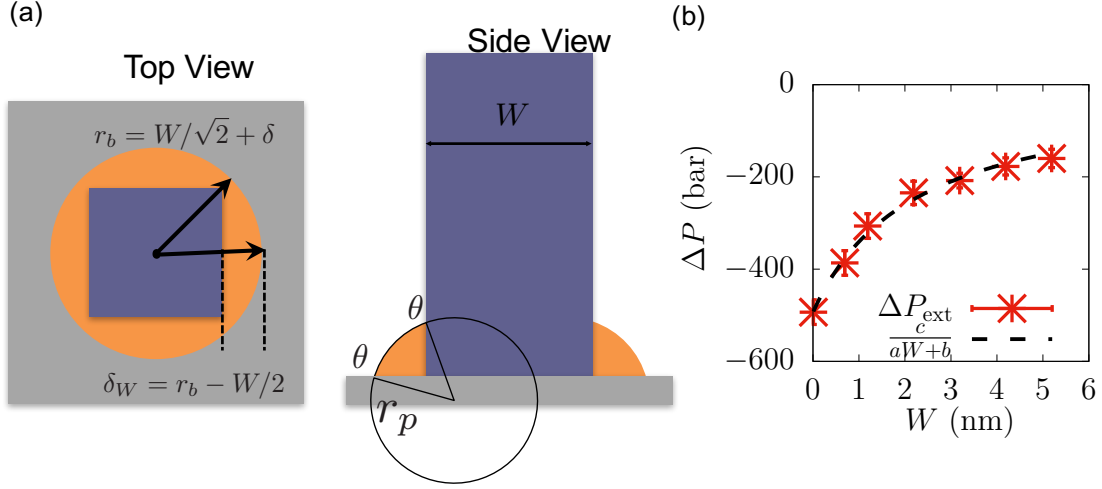


Figure 5.9: A macroscopic model to estimate the influence of W on ΔP_{ext} . (a) Cartoon representing systems morphology at the extrusion pressure, the blue color represent the pillars and the grey color represent the basal surface of the pillars. Vapor pockets are assumed to be a part of spherical cap and are shown in orange. Assuming that the free energetics of vapor pockets of a certain critical size, surrounding the pillars, correspond to the extrusion pressure, we can relate the extrusion pressure to the two principal curvatures of critical vapor pockets. One of the principal radius of curvatures, corresponding to the radius of the three-phase contact line at the basal surface, r_b , is considered to be a value very close to $W/\sqrt{2}$, exceeding it by a constant δ . The other principle radius is obtained by assuming that the vapor pockets satisfy the contact angle boundary conditions. (b) Based on the assumptions in (a), we can relate the extrusion pressure of the system to the sum of the two curvatures using Young's Laplace equation and obtain an inverse dependence on W . We then fit the simulated, ΔP_{ext} for 7 different W -values to our obtained model for extrusion pressure and see excellent agreement.

interface as follows,

$$\Delta P_{\text{vp}} = \gamma \left(\frac{1}{r_b} + \frac{1}{r_p} \right) \propto \frac{1}{W}, \quad (5.11)$$

Using ΔP_{vp} as a proxy for the extrusion pressure, we notice an inverse relationship between the ΔP_{ext} and W . Hence, we fit the simulated value of ΔP_{ext} to a function of $\frac{c}{aW+b}$, and see an excellent fit (see Figure 5.9b). The value of extrusion pressure for $W = 0$, in Figure 5.9b has been obtained from the simulation of a flat plate without any pillars, as shown in Appendix D. Hence the extrusion pressure of the pillars can increase as W is increased ($\Delta P_{\text{ext}}(W \rightarrow \infty) = 0$), however larger values of W will result in more solid fraction on top of the pillars, reducing the superhydrophobicity of the surface.

5.9. Outlook

This study offers insights into the role of the surface geometry in the dewetting process and provides a quantitative basis for designing surfaces that is optimized to inhibit wetting transitions as well as to initiate a reverse dewetting transitions in pillared systems. We studied in detail, the effects of pillar height, the inter-pillar spacing and pillar width, on the wetting-dewetting transitions including the free energy barriers, the pathways and the intrusion and extrusion pressures.

We noted that the pillar-height, H , doesn't affect the superhydrophobicity, the dewetting barrier, the intrusion pressures and is the least important geometric factor in designing robust superhydrophobic surfaces made of square pillars. However, for each of the pillar height, macroscopic theory over-predicted both the wetting and dewetting barriers due to its limitation in describing the non-classical dewetting pathway that consists of formation of multiple non-classical morphology, leading to the formation of the nascent vapor layer. We uncovered that this non-classical dewetting pathway does not depend on pillar height resulting in the invariance of extrusion pressure on H . While the pillar heights play no role in determining the superhydrophobicity of the nano-pillared surfaces, the width of the pillars, W , and the separation between the pillars, S , strongly dictate the performance

(apparent contact angle and contact angle hysteresis) of superhydrophobicity. As S/W increases, the apparent contact angle increases while the contact angle hysteresis decreases, making the surface more superhydrophobic [50, 32, 16]. However, the highest pressure a superhydrophobic material can sustain before collapsing into the wet Wenzel state, ΔP_{int} , decreases with S/W (See equation 5.4), making the surface less robust. Hence, there is a tradeoff between the performance of a pillared superhydrophobic surface (apparent contact angle and contact angle hysteresis) and its robustness (intrusion pressure), both depending on S/W . However, another measure of robustness of superhydrophobicity of the pillared surface is the extrusion pressure, a pressure below which system should spontaneously transition into superhydrophobic Cassie state. Unlike intrusion pressure, which can be well described by macroscopic theory, the extrusion pressure depends on free energetics of complex morphologies near the Wenzel state at $\rho_n \approx 1$. It then becomes an important question to address that whether increasing S/W would unfavorably affect the extrusion pressure akin to its effect on intrusion pressure. To address this question, we characterize the free energetics of system that has a very high value of $S/W = 5$ ($S = 10$ nm and $W = 2$ nm) leading to a an apparent contact angle of $\theta_{\text{Cassie}} = 170^\circ$ for our pillared material. Compared to the surface studied in Chapter 2 with $S/W = 2$ ($S = 4$ nm, $W = 2$ nm), this system with $S/W = 5$ and 4-times larger basal area displayed an identical non-classical path to dewetting; a path that consists of multiple non-classical morphologies (Region II - Region V), leading to the formation of the nascent vapor layer in Region I. Region V ($\rho_n \approx 1$) displays Gaussian fluctuations resulting in a parabolic basin followed by region IV comprising of vapor pockets at the base of the pillars. The slope of the free energy in region IV reaches a minimum value corresponding to the extrusion pressure of the system. As ρ_n is reduced, vapor pockets grow, break symmetry, and merge to form a striped vapor layer between the pillars; the stripe expands laterally in Region III until water molecules stick to the center of the cell, and also contains the non-classical barrier, which eventually gives way to the classical Region I. The height of the nascent vapor layer that forms at the barrier state was $h_{\text{nascent}} \approx 1$ nm. We further demonstrated

that h_{nascent} plotted as a function of basal area plateaus to a non-zero value, explaining why classical macroscopic theory over-predicts the barriers and why the discrepancy between the theoretical and simulated barriers is expected to scale with the area. While the dewetting and wetting barriers are important quantities to study, what is more important, is to understand the pressures (ΔP_{int} and ΔP_{ext}), at which these barriers vanish. Macroscopic theory does an excellent job at predicting the intrusion pressure, which was tested on multiple systems by systematically varying H , S and W . However, classical macroscopic is limited in determination of the extrusion pressure and prescribes that the dewetting transition is not possible. We reveal that not only do we have finite extrusion pressures for all the systems studied, it is independent of both pillar height, H and separation between the pillars, S . We also showed that extrusion pressure scales as $1/W$ by using the famous Young Laplace equation and saw an excellent fit with its simulated values.

These results helped us identify the factors that can be important in designing superhydrophobic surfaces using square pillars. Depending on the specific application of superhydrophobic materials, we have handle on increasing apparent contact angle (by increasing S/W), increasing robustness by increasing intrusion pressure (by decreasing S/W) or increasing robustness by increasing extrusion pressure (by increasing W). However, as also evident from the results, square pillars give little flexibility in controlling the superhydrophobicity independent of the robustness, due to their contrasting dependence on S/W and warrants study of other texture-shapes such as cones or spheres.

CHAPTER 6 : Spontaneous Recovery of Superhydrophobicity on Pillared Surfaces Augmented with Spherical Nanoparticles: Effects of Scaling the Feature Size

Superhydrophobicity stems from the presence of texture on a surface in the Cassie state in which a water droplet resides on the top of the surface asperities. One major impediment in creating superhydrophobic surfaces is the loss of superhydrophobicity upon the wetting of the surface texture in the Wenzel state. Moreover, this loss of superhydrophobicity is widely considered irreversible due to the presence of large kinetic barriers that impede the Wenzel-to-Cassie transition. To facilitate the recovery of superhydrophobicity and to afford reversible control over surface properties, significant efforts have focused on inducing the reverse Wenzel-to-Cassie dewetting transition. In previous chapters we showed that an understanding of the Cassie-Wenzel transition pathway on simple pillared surfaces facilitates the rational design of surfaces with superior superhydrophobicity. By identifying the pathways to dewetting, and in particular, the regions that are hardest to dewet, we were able to inform the location of sites where the introduction of additional texture would be optimal. Additionally, the geometry of the introduced texture required three strict criteria to be fulfilled, (i) a confined (negative curvature) region of nanoscopic dimensions to nucleate a vapor bubble, (ii) the nucleated vapor bubble must grow to a large enough size to facilitate the formation of an intact vapor-liquid interface or nascent vapor layer (iii) the vapor-liquid interface must not be pinned by surface features as it rises along the pillars. We employ macroscopic theory to model dewetting pathways taken in steps (i) through (iii) for the pillared system augmented with spherical nanoparticles, to study the effect of scaling the features on the spontaneous recovery of superhydrophobicity on such systems.

6.1. Introduction

Presence of textures on hydrophobic surfaces can render the surface superhydrophobic, endowed with useful properties such as self-cleaning, no-slip, anti-fouling etc [7]. Thousands

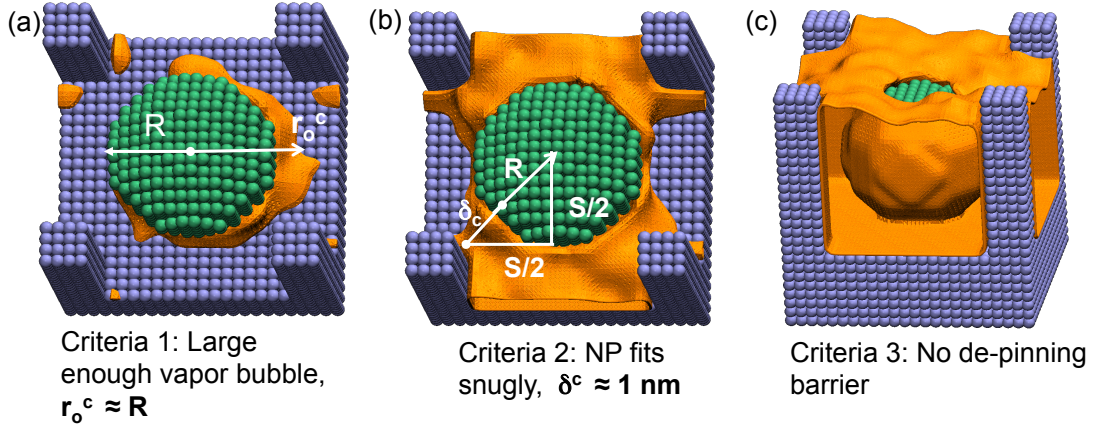


Figure 6.1: For spontaneous recovery of superhydrophobicity in pillared system, augmented with spherical nanoparticle, we pictorially show the three criteria that need to be fulfilled. In each of the case, pillars are shown in blue, the nanoparticle is shown in green, the vapor interfaces are shown in orange and water molecules are hidden for clarity. (a) Criteria 1: the nanoparticle of radius, R , must spontaneously nucleate a vapor bubble; the vapor bubble must be large enough such that its radius on the basal surface, r_o^c , is comparable to R . (b) Criteria 2: The nanoparticle should be not too far away from the pillars, *i.e.* $\delta_c \approx 1 \text{ nm}$, so that the vapor formed underneath the nanoparticle interacts with vapor pockets formed at the base of the pillars to form an intact vapor-liquid interface. (c) Criteria 3: There should be very small or no barrier in the process of the vapor interface detaching from the top of the nanoparticle.

of plant and animal species have been observed to have superhydrophobic surfaces and all these surfaces seem to have roughness at multiple sizes in the micron-submicron range [61, 50]. Superhydrophobicity stems from the presence of texture on a surface in the Cassie state in which a water droplet resides on the top of the surface asperities. One major impediment in creating superhydrophobic surfaces is the loss of superhydrophobicity upon the wetting of the surface texture in the Wenzel state [71, 52]. Moreover, this loss of superhydrophobicity is widely considered irreversible due to the presence of large kinetic barriers that impede the Wenzel-to-Cassie transition. [71] To facilitate the recovery of superhydrophobicity and to afford reversible control over surface properties, significant efforts have focused on inducing the reverse Wenzel-to-Cassie dewetting transition [18, 44, 83, 12, 60]. In previous chapters we showed that an understanding of the Cassie-Wenzel transition pathway on simple pillared surfaces facilitates the rational design of surfaces with superior superhydrophobicity. By identifying the pathways to dewetting, and in particular, the regions that are hardest to dewet, we were able to inform the location of sites where the introduction of additional texture would be optimal. Additionally, the geometry of the introduced texture required three strict criteria to be fulfilled, which we reassess in the context of a pillared system augmented with a spherical nanoparticle as follows:

1. A confined (negative curvature) region of nanoscopic dimensions to nucleate a vapor bubble: A (hydrophobic) spherical nanoparticle can barrierlessly nucleate a vapor bubble at the basal surface, however it is important to understand if the size of the bubble it nucleates is large enough. In particular, we ask, how does the radius of the vapor bubble on the basal surface compare with the radius of nanoparticle?
2. The nucleated vapor bubble must grow to a large enough size to facilitate the formation of an intact vapor-liquid interface or nascent vapor layer: For the pillared system augmented with spherical nanoparticles, the NP should be not too far away from the pillars for their vapor pockets to combine and form an intact vapor-liquid interfaces.
3. The vapor-liquid interface must not be pinned by surface features as it rises along

the pillars: This implies that there should be very small or no barrier in the process of vapor interface detaching from the top of the nanoparticle. To understand this, we characterize the free energy of the hybrid pillars+NP system using macroscopic theory and predict the barrier for vapor-liquid interface to detach from the top of the nanoparticle.

Each of these criteria is pictorially shown in Figure 6.1. We employ macroscopic theory to model dewetting pathways taken in steps (i) through (iii) to study the effect of texture-parameters such as the radius of the nanoparticle, R , the height, H , width, W and inter-pillar separation, S , of the pillars on their ability spontaneously recover their superhydrophobicity. While appreciating the fact that fluctuations in water density are extremely enhanced in such confined hydrophobic textures and macroscopic theory tends to overestimate the barriers, it can still be powerful in studying the qualitative effects of scaling the geometric features such as the radius of the nanoparticle and the height, width and inter-pillar spacing of the pillars on the three steps.

6.2. Criteria 1: Barrierless Nucleation of Vapor Bubble Underneath a Spherical Nanoparticle

In this section we use a macroscopic framework to model dewetting underneath a spherical nanoparticle in contact with a plane. For the setup shown in the Figure 6.2, we can express the free energy of a partially dewetted state relative to a wet Wenzel state as follows:

$$\Delta F = \gamma A_{vl} + \gamma \cos \theta A_{sv} + \Delta P V_v, \quad (6.1)$$

where γ is the vapor-liquid surface tension, and $\Delta\gamma \equiv \gamma \cos \theta$ is the difference between the solid-vapor and solid-liquid surface tensions with θ being the contact angle of both the sphere and the plane. A_{vl} and A_{sv} are the vapor-liquid and the solid-vapor interfacial areas, respectively, in the partially wet state, and ΔP is the difference between the pressures of the liquid and the vapor phases. For the geometry shown in Figure 6.2b, the two interfacial

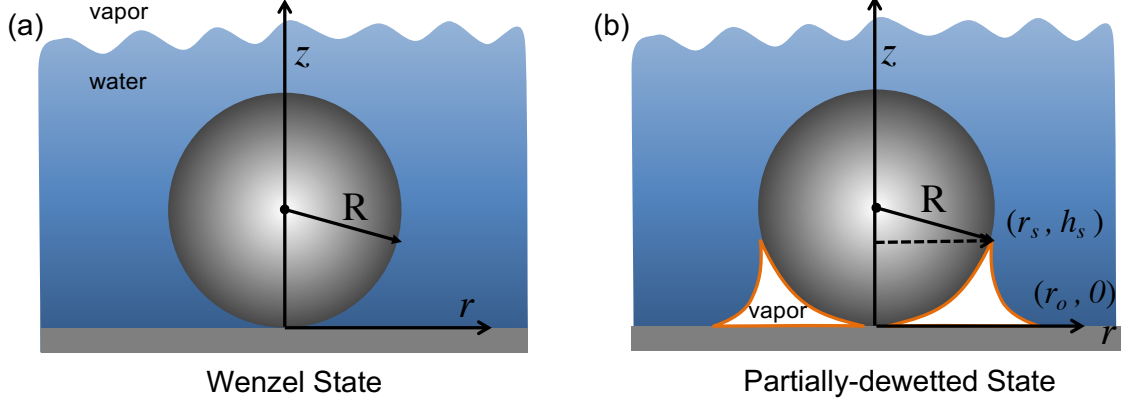


Figure 6.2: Schematic showing a spherical nanoparticle of radius, R , in contact with a plane (perpendicular to the z -axis) in a wet Wenzel state and in a partially dewetted state. (a) In the Wenzel state, the fluid shown in blue wets the texture. (b) In a partially dewetted state, a ring of vapor forms at the intersection of the sphere and the plane. For (r, z) as the cylindrical coordinates as depicted, the location of the vapor-liquid interface is given by $r(h)$ with its location at the plane is $h = 0, r = r_o$ and at the surface of the sphere is $h = h_s, r = r_s$.

areas and the volume terms can be expressed in terms of the location of the vapor-liquid interface, (h, r) as below:

$$\begin{aligned} \Delta F = & \gamma \int_0^{h_s} 2\pi r \sqrt{dr^2 + dh^2} \\ & + \gamma \cos \theta (\pi r_o^2 + 2\pi R h_s) \\ & + \Delta P \left[\int_0^{h_s} \pi r^2 \sqrt{dr^2 + dh^2} - (\pi/3) h^2 (3R - h) \right]. \end{aligned}$$

By using dimensionless variables, $h \equiv h/R$, $r \equiv r/R$, $\Delta f = \Delta F / \gamma \pi R^2$ and assuming that the system is at co-existence pressure, $\Delta P = 0$, we obtain

$$\Delta f \{h, r(h), \dot{r}(h), r_o, h_s; \cos \theta\} = 2 \int_0^{h_s} dh \, r(h) \sqrt{1 + \dot{r}(h)^2} + \cos \theta (r_o^2 + 2h_s), \quad (6.2)$$

where $\dot{r}(h) \equiv dr(h)/dh$.

An Euler Lagrange minimization of Equation 6.2, leads to:

$$\frac{\partial L}{\partial r} = \frac{d}{dh} \frac{\partial L}{\partial \dot{r}} \quad (6.3)$$

where, $L = r(h)\sqrt{1 + \dot{r}(h)^2}$ leading to:

$$\dot{r}^2 - r\ddot{r} + 1 = 0 \quad (6.4)$$

Since Equation 6.4 doesn't have a well known analytical form and involves incomplete elliptic integrals of the first and second kinds, we simply use numerical optimization to obtain the shape of the vapor-liquid interface and the free energy.

6.2.1. Numerical optimization of the free energy

We can recast Equation 6.2 into a numerical optimization problem as follows:

1. We choose M values of h_s for $0 \leq h_s \leq 1$ with the k^{th} -value as h_s^k .
2. We divide the distance between, $h = 0$ to $h = h_s^k$ into $N \equiv h_s^k/\delta_h$ grids, where $\delta_h \ll h_s^k$.
3. We obtain N-set of variables, $\{h_i, r_i\}$ ($i = 0, 1, \dots, N$), with the boundary condition, $r_N = r_s = \sqrt{1 - (1 - (h_s^k)^2)}$.
4. Minimize the free energy functional, $\Delta f\{r_0, r_1, \dots, r_{N-1}; h_s^k\}$ using the partial derivative of free energy (Equation 6.6 and Equation 6.7) by employing a 4th-order RK method, to obtain the optimal values of $\{h_i, r_i\}$.
5. Repeat Steps 2-5 for all M-values of h_s^k and obtain the free energy as a function of h_s^k , per Equation 6.5.

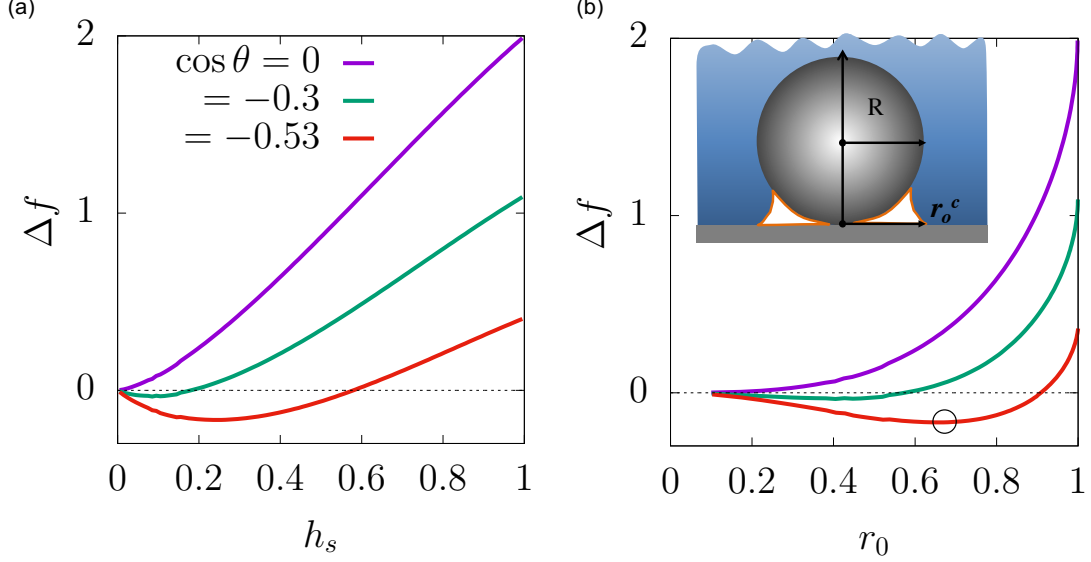


Figure 6.3: Free energetics of the system containing spherical nanoparticle of radius R , in contact with a plane. (a) We plot the dimension-less free energy, $\Delta f(h) \equiv \Delta F / \gamma \pi R^2$ as a function of h_s for three values of $\cos \theta$. $h_s \equiv h_s / R$ corresponds to the z-position of the vapor-liquid interface at the point of contact with the sphere (see Figure 6.2) and $h_s = 0$ corresponds to a wet Wenzel state. Results highlight that for hydrophobic nanoparticles ($\cos \theta < 0$) a vapor bubble of certain size can barrierlessly nucleate until the free energy reaches its minimum value at, h_s^c , upon further dewetting the free energy increases. Changing contact angle, θ affects the location of the minima in free energy, larger the θ , larger the value of h_s^c . (b) We also plot the free energy as a function of the radius of vapor-pocket at the basal surface, $r_o \equiv r_o / R$, indicating the size of the largest vapor pocket that can form with a barrier r_o^c increases with θ . For the system with $\cos \theta = -0.53$, which is the contact angle for our simulated systems in chapters 2 through 5, $r_o^c = 0.66$. As a rule of thumb, we would want $R(1 - r_o^c) < \approx 1$ nm, hence for systems with $\cos \theta = -0.53$, $R \leq R_{\max}^{(1)}$ with $R_{\max}^{(1)} \approx 3$ nm. (We use the superscript (1) to refer that it derives from criteria 1)

The numerical expression for the free energy, $\Delta f\{r_0, r_1, \dots, r_N - 1; h_s^k\}$ can be obtained from Equation 6.2 as follows:

$$\Delta f\{r_0, r_1, \dots, r_N - 1; h_s^k\} = \cos \theta (r_o^2 + 2h_s^k) + 2 \sum_{i=0}^{N-1} \delta_h r_i \sqrt{1 + (r_{i+1} - r_i)^2 / \delta_h^2} \quad (6.5)$$

The partial derivative of the free energy with respect to each of the variable, r_i , is obtained to perform a numerical optimization.

$$\mu_i \equiv \frac{\partial \Delta f}{\partial r_i} = 2 \left[\frac{-r_i(r_{i+1} - r_i)}{\sqrt{(\delta_h^2 + (r_{i+1} - r_i)^2)}} + \sqrt{(\delta_h^2 + (r_{i+1} - r_i)^2)} \right]; \quad i = 1, 2, \dots, N - 1 \quad (6.6)$$

$$\mu_0 = 2 \cos \theta r_0 + 2 \left[\frac{-r_0(r_1 - r_0)}{\sqrt{(\delta_h^2 + (r_1 - r_0)^2)}} + \sqrt{(\delta_h^2 + (r_1 - r_0)^2)} \right] \quad (6.7)$$

In Figure 6.3a, we plot the dimensionless free energy, $\Delta f(h) \equiv \Delta F / \gamma \pi R^2$ as a function of h_s for three values of $\cos \theta$. $h_s \equiv h_s / R$ corresponds to the z-position of the vapor-liquid interface at the point of contact with the sphere (see Figure 6.2) and $h_s = 0$ corresponds to a wet Wenzel state. Results highlight that for hydrophobic nanoparticles ($\cos \theta < 0$) a vapor bubble of certain size can barrierlessly nucleate until the free energy reaches its minimum value at, h_s^c , upon further dewetting the free energy increases. In Figure 6.3b, we replot the free energy as a function of the radius of vapor-pocket at the basal surface, $r_o \equiv r_o / R$, indicating the size of the largest vapor pocket that can form with a barrier r_o^c increases with θ . For the system with $\cos \theta = -0.53$, which is the contact angle for our simulated systems in chapters 2 through 5, $r_o^c = 0.66$. As a rule of thumb, we would want $R(1 - r_o^c) \lesssim 1$ nm, hence for systems with $\cos \theta = -0.53$, $R^{(1)} \lesssim 3$ nm (We use the superscript (1) to refer that it comes from criteria 1).

$$R^{(1)} \lesssim 3 \text{ (nm)} \quad (6.8)$$

This is an important result, as it really restricts the size of the nanoparticle that can be used to nucleate vapor bubbles, however, this can only work as a conservative estimate

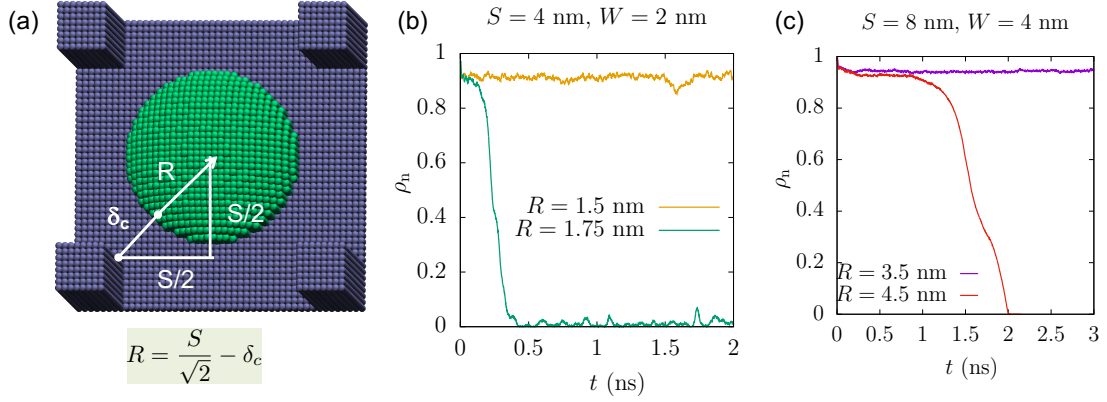


Figure 6.4: Demonstrating that simply scaling all the parameters of the system (S , W and R) for the system that spontaneously dewetted does not ensure dewetting, maintaining $\frac{S}{\sqrt{2}} - R \approx 1$ nm, does. (a) Schematic showing the parameter, δ_c characterizing how snugly a nanoparticle of radius, R , fits in a pillared system of pillar height, H , width of the pillars, W , and inter-pillar spacing, S . (b) The density of water in the textured volume, ρ_n , plotted as a function of time, as obtained from unbiased simulations (also previously shown in Figure 3.4.2). When initialized in the Wenzel state, the surface with $R = 1.5$ nm is unable to undergo complete dewetting, whereas the surface with $R = 1.75$ nm spontaneously dewets to the Cassie state. For each of the surface, $S = 4$ nm and $W = 2$ nm, providing $\delta_c(R = 1.5) \approx 1.3$ nm whereas $\delta_c(R = 1.75) \approx 1$ nm. $\delta_c = \frac{S}{\sqrt{2}} - R \lesssim 1$ nm then seems like a necessary condition to achieve spontaneous dewetting. (c) Even though the system with $S = 4$ nm, $W = 2$ nm and $R = 1.75$ nm dewetted, simply scaling all the parameters twice in system with $S = 8$ nm, $W = 4$ nm and $R = 3.5$ nm (purple) does not dewet. But the system with $S = 8$ nm, $W = 4$ nm and $R = 4.5$ nm and $\delta_c = 1$ nm spontaneously dewets to the Cassie state. Hence, as a rule of thumb, to fulfill criteria-2, $R^{(2)} \gtrsim \frac{S}{\sqrt{2}} - 1$ (nm).

of $R^{(1)}$ because dewetting in such confined spaces are extremely non-classical phenomena and macroscopic theory often over-predicts the barriers. In fact in Figure 6.4c, we show that a system with $R = 4.5$ nm was able to barrierlessly nucleate a vapor bubble which then was able to collapse with bubble underneath the neighboring pillars and eventually led to complete and spontaneous dewetting of the system. In future, it might be useful to characterize r_o^c from simulation to get a more realistic estimate of the $R^{(1)}$.

6.3. Criteria 2: Barrierless Formation of an Intact Vapor-liquid Interface in Pillared System Augmented with Nanoparticle

Once the 1st criteria is fulfilled and the vapor bubble underneath a nanoparticle roughly reaches the size of the radius of the nanoparticle, for a pillared system containing nanoparticles, the vapor bubble underneath the nanoparticle and vapor pockets underneath the pillars must combine to form an intact vapor-liquid interface. To obtain the criteria for the intact vapor-liquid interface to form, we run equilibrium simulations on 4 test systems, each consisting of pillared system augmented with a spherical nanoparticle. In Figure 6.4, we demonstrate that for the vapor-pockets underneath the nanoparticle and the vapor pockets at the pillared system to interact the following criteria needs to be satisfied,

$$R^{(2)} \gtrsim \frac{S}{\sqrt{2}} - 1 \text{ (nm)} \quad (6.9)$$

where R is the radius of the nanoparticle, S is separation between the pillars and the subscript (2) refers to criteria number 2.

6.4. Criteria 3: Barrierless De-pinning of Vapor-Liquid Interface from the top of the Nanoparticle

Once Criteria 1 and 2 are satisfied, we must find out the criteria for the vapor-liquid interface to not get pinned at the top of the nanoparticle. For the system shown in Figure 6.5a, the free energy of a partially wet state relative to the free energy of the Wenzel state is given by:

$$\Delta F(h_{vl}) = \gamma A_{vl}(h_{vl}) + \Delta\gamma A_{sv}(h_{vl}) + \Delta P V_v(h_{vl}), \quad (6.10)$$

where γ is the vapor-liquid surface tension, and $\Delta\gamma$ is the difference between the solid-vapor and solid-liquid surface tensions; according to the Young's equation, $\Delta\gamma = \gamma \cos \theta$. A_{vl} and A_{sv} are the vapor-liquid and the solid-vapor interfacial areas, respectively, in the partially

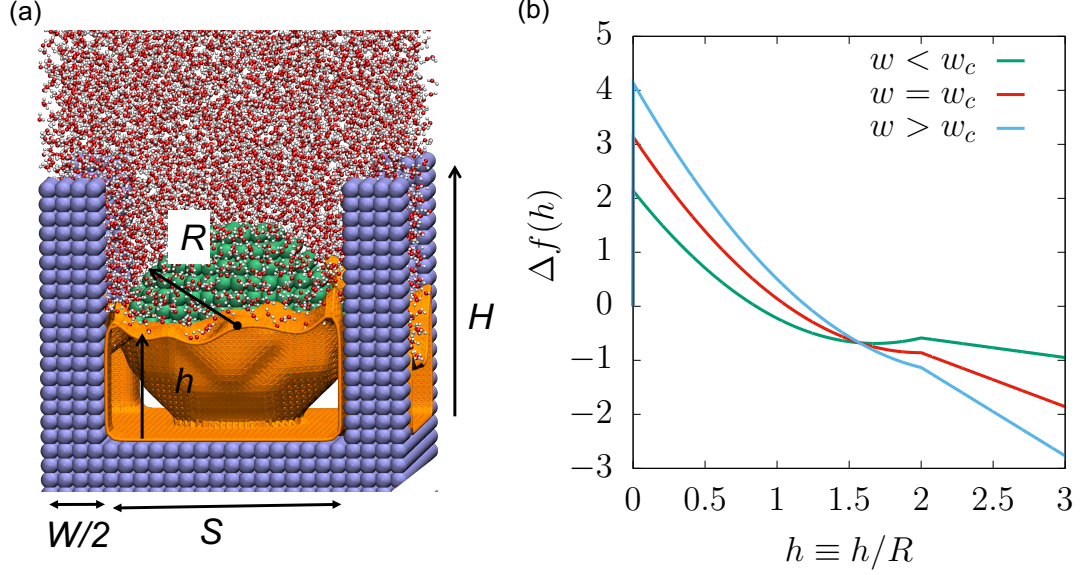


Figure 6.5: A partially wet state in a pillared system augmented with spherical nanoparticle can be characterized by a flat vapor-liquid interface at height, h_{vl} , rising along the pillars. plotting the free energy as a function of h , provides the criteria for barrier-less depinning of the interface at the top of the nanoparticle (a) Schematic showing a pillared surface with pillar height, H , pillar width, W and interpillar separation, S , augmented with a spherical nanoparticle of radius, R . In the partially dewetted state, we assume a flat interface lying at height, $h \equiv h/R$. (b) Dimensionless free energy of the system, $\Delta f \equiv \Delta F/\gamma\pi R^2$ as a function of h for three systems with changing the ratio of pillar-width to the radius of the nanoparticle, $w \equiv W/R$. The critical value of w is given by Equation 6.13 provides the criteria, $w > w_c$ for the de-pinning barrier to vanish. The free energy of the system with $w = w_c$ (green curve) features a local minimum $h_{\min} < 2$, giving rise to a barrier associated with the detaching the vapor-liquid interface from $h = h_{\min}$; the expressions for $h_{\min}$ and the barrier are provided in Equation 6.11 and Equation 6.12, respectively. However for each $w = w_c$ (red curve), and $w \geq w_c$ (purple curve), there is no barrier associated with the detaching the vapor-liquid interface from the nanoparticle.

wet state, and ΔP is the difference between the pressures of the liquid and the vapor phases. At co-existence pressure, $\Delta P = 0$ and by substituting the expressions for the interfacial areas according to the geometry in Figure 6.5a, considering the pillars height, H , width, W and inter-pillar separation, S and the radius of the nanoparticle, R , we get:

$$\begin{aligned}\Delta F(h_{\text{vl}} \leq 2R) &= \gamma(A_{\text{base}} - \pi r(h_{\text{vl}})^2) + \gamma \cos \theta (A_{\text{base}} + 2\pi R h_{\text{vl}} + 4W h_{\text{vl}}) \\ \Delta F(h_{\text{vl}} \geq 2R) &= \gamma A_{\text{base}} + \gamma \cos \theta (A_{\text{base}} + 4\pi R^2 + 4W h_{\text{vl}})\end{aligned}$$

where, h_{vl} is the height of the vapor-liquid interface shown in Figure 6.5a, $A_{\text{base}} = S(S+2W)$ is the basal area and $r(h_{\text{vl}})^2 = R^2 - (R - h_{\text{vl}})^2 = 2R h_{\text{vl}} - h_{\text{vl}}^2$. We can use dimensionless quantities, by normalizing all the length-scale units by R , such as $h \equiv h_{\text{vl}}/R$, $w = W/R$, $a_b = A_{\text{base}}/\pi R^2$ and obtain the dimensionless free energy as, $\Delta f \equiv \Delta F/\gamma \pi R^2$ given by:

$$\begin{aligned}\Delta f(h \leq 2) &= (a_b - 2h + h^2) + \cos \theta (a_b + 2h + 4wh/\pi) \\ \Delta f(h \geq 2) &= a_b + \cos \theta (a_b + 4 + 4wh/\pi)\end{aligned}$$

To obtain the minimum in Free energy, we then obtain the derivative of free energy as:

$$\begin{aligned}\frac{d\Delta f(h \leq 2)}{dh} &= \pi(2h - 2) + \cos \theta (2 + 4w/\pi) \\ \frac{d\Delta f(h \geq 2)}{dh} &= \cos \theta (4w/\pi)\end{aligned}$$

The derivative of the free energy has a minimum at h_{min} , given by:

$$\frac{d\Delta f(h \leq 2)}{dh} = 0 \equiv h_{\text{min}} = 1 - \cos \theta (1 + \frac{2w}{\pi}) \quad (6.11)$$

The barrier for the system to detach the vapor-liquid interface lying at $h = h_{\text{min}}$ is then

given by:

$$\Delta f_{\text{depinning}} = \Delta f(h = 2) - \Delta f(h = h_{\min}) = (2 - h_{\min})^2 \quad (6.12)$$

As clear from the above equation, the de-pinning barrier vanishes at $h_{\min} \geq 2$ given by,

$$w \geq w_c \equiv \frac{\pi (1 + \cos \theta)}{2 (-\cos \theta)} \quad (6.13)$$

In Figure 6.5b, we plot the free energy as a function of h for three values of w . Since, $w \equiv W/R$, the above equation can be rewritten as following, providing us with constraints for the third criteria,

$$R^{(3)} \leq \frac{2W(-\cos \theta)}{\pi(1 - \cos \theta)} \quad (6.14)$$

However, as is the case of macroscopic framework, this criteria is only a conservative estimate of radius that can be used. For instance, in our simulated system shown in Figure 6.4b, the value of $W = 2$ nm and $\cos \theta = -0.53$ would recommend $R \leq 1.43$ nm, however, our system with $R = 1.75$ nm observes no barrier in the detachment of the vapor-liquid interface at the top of the nanoparticle and spontaneously dewets.

6.5. Outlook & Future Work

Although numerous methods have been suggested for texturing hydrophobic surfaces, from top-down fabrication to bottom-up self-assembly techniques [36, 77, 26], a key bottleneck in their widespread adoption has been the fragility of the superhydrophobic Cassie state and the associated irreversible breakdown of superhydrophobicity upon wetting [7]. Chapters 2 through 5 took a major step in addressing this challenge, highlighting the importance of water density fluctuations in stabilizing non-classical pathways on nanotextured surfaces, which reduce dewetting barriers and enable the spontaneous recovery of superhydrophobicity. In particular, our results in Chapter 3, also suggested a general strategy for augmenting

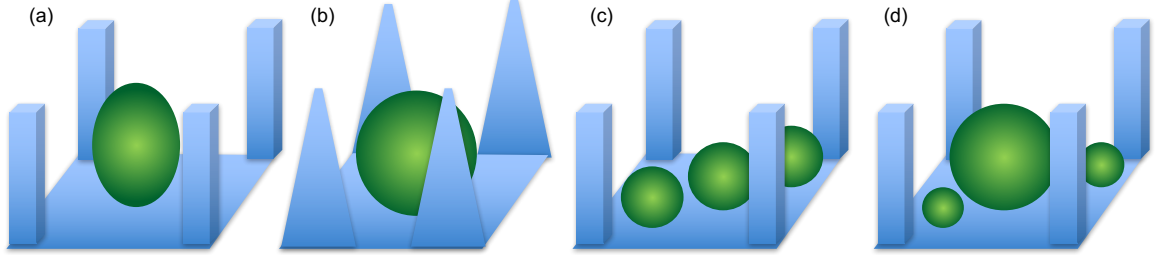


Figure 6.6: Future ideas to overcome the restrictions inherent in square-pillared system augmented with single nanoparticle (a) Using a ellipsoidal nanoparticle can be favorable in satisfying criteria 1 and 3 listed in Figure 6.1. (b) Conical pillars can be extremely helpful in both criteria 1 and 2, while maintaining a high apparent contact angle. (c) Using multiple nanoparticles or (d) nanoparticles of multiple sizes could be useful as we scale the system size up to maintain criteria 1.

the design of existing nanotextured surfaces. By identifying the pathways to dewetting, and in particular, the regions that are hardest to dewet, we were able to inform the location of sites, where the introduction of additional texture would be optimal. In addition, the geometry of the introduced texture required three strict criteria to be fulfilled, (i) a confined (negative curvature) region of nanoscopic dimensions to nucleate a vapor bubble, (ii) the nucleated vapor bubble must grow to a large enough size to facilitate the formation of an intact vapor-liquid interface or nascent vapor layer (iii) the vapor-liquid interface must not be pinned by surface features as it rises along the pillars. In this chapter we use macroscopic frameworks combined with our simulation results to obtain constraints for each of the criteria. While overcoming each criteria system becomes more and more robust as we saw in Chapter 3, however, each of the criteria restrict the radius of the nanoparticle, R , relative to the width, W , and inter-pillar spacing, S in different ways. While it is favorable to have small R for it to nucleate the vapor in criteria (i) and small R/W to have a barrierless depinning of the vapor-liquid interface in criteria (iii), it needs to snugly fit in the space between the pillars, for criteria (ii). All of these restrictions makes it important to explore different shapes of the pillars and variety of nucleating sites, in future, to design robust surfaces at larger length-scales. In Figure 6.6, we present some of the interesting future ideas to overcome the restrictions inherent in square-pillared system augmented with single nanoparticle.

CHAPTER 7 : Dewetting on Surfaces with Re-entrant Geometries: Implications for the Design of Superoleophobic Surfaces

Fluids with low surface tension, such as oils and alkanes, in contact with a rough solid surface, have their lowest free energy in the fully wetted Wenzel state. As a result the effective contact angle is lower than that on the flat substrate. For applications in which nonwetting by these oily fluids is desired, wetting barrier must be introduced to maintain the non-wetted composite state. One way to create this free-energy barrier to wetting is to fabricate roughness with re-entrant geometry; such geometries have curvatures that vary with the height of the texture, allowing liquids of different contact angles to sit in composite states at different heights.

The free energetics of wetting transitions in one of the most common re-entrant geometry, consisting of spherical nanoparticles, has been extensively explored by various researchers [77, 78, 28]. However, due to the rarity of observing dewetting or Wenzel-to-Cassie transition in such surfaces, the phenomena of dewetting remains largely unexplored. In Chapter 2 through Chapter 5, we showed that an understanding of the dewetting pathways of the pillared system can lead us to design novel textures that can spontaneously dewet. In this chapter, we show that in contrast to the dewetting proceeding through the formation of vapor at the basal surface in the case of square pillared surface, formation of vapor layer at the closest separation between the nano particles can facilitate dewetting more optimally. We demonstrate that the likelihood of observing such a pathway increases with decreasing value of contact angle, θ , as well as with decreasing value of ratio of separation between the nanoparticles to the radius of the nanoparticles, S/R . Since the surface tensions of most oils are much lower than that of water, oil droplets are more likely to display relatively smaller contact angles on most flat surfaces and therefore oil is more likely to dewet through this novel pathway.

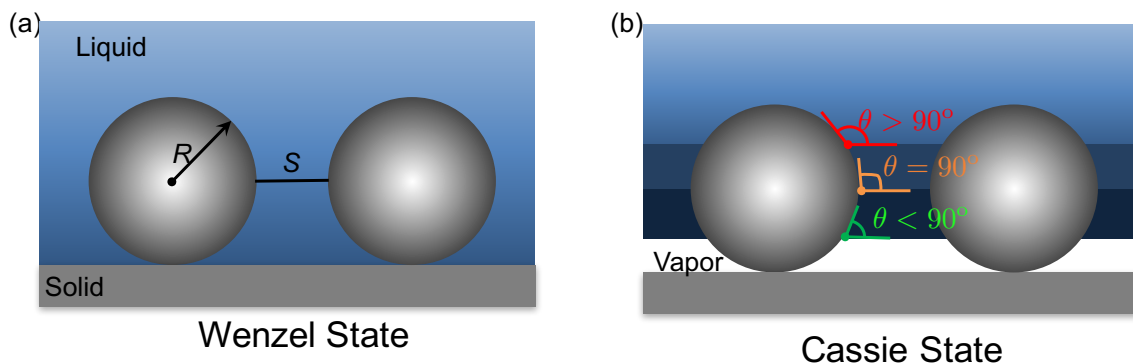


Figure 7.1: (a) In the Wenzel state, the fluid wets the texture and for the fluids with contact angle (θ) $< 90^\circ$, the apparent contact angle will be even lower as prescribed by the Wenzel's equation. (b) In the Cassie state, fluid is unable to penetrate the surface texture and sits atop a cushion of air, leading to a small contact angle hysteresis and a large contact angle, which are critical in conferring superhydrophobicity or superoleophobicity to the surface. Different liquids (with different contact angle, θ) sit at different fill-levels, characterized by the height of the vapor-liquid interface, h ; a characteristic quality of re-entrant geometries making them useful for creating oleophobic surfaces.

7.1. Introduction

Extreme oil repellency, “superoleophobicity”, is a desirable surface property for a wide range of applications including anti-fouling, anti-fogging, anti-smudge, and lab-on-chip applications [23, 4]. However, superoleophobicity is difficult to accomplish as the surface tensions of most oils are much lower than that of water, meaning oil droplets are more likely to display contact angles $< 90^\circ$ on most flat surfaces and therefore adding roughness to the surface will lower this angle further in the Wenzel state. Another challenge in creating superoleophobic surfaces is that most of their applications require the surfaces to be superhydrophobic as well. Thanks to the class of surfaces commonly known as the re-entrant surfaces, in which, high effective contact angles with both oil and water can be achieved even when the flat surface contact angle is low [77, 78, 28]. Structures with re-entrant curvature (spherical, cylindrical, oval etc.) are able to support high droplet contact angles for various liquids with at contact angles, θ , since it is possible to draw multiple tangents of a corresponding flat surface, as demonstrated in Figure 7.1c. Therefore liquids with various contact angles

can wet the re-entrant curvature to different extents to achieve a favorable vapor-liquid interface shape; allowing for a surface to behave both oleophobic and hydrophobic.

Our work builds upon recent theoretical studies, which have characterized the free energetics of wetting-transitions on surfaces made of spherical nanoparticles and have explored the effect of radius of the nanoparticles and the separation between the nanoparticles. Based on our understanding on pillared systems, that even when classical macroscopic theory prescribes that a dewetting transition from the wet Wenzel state to the Cassie state is not possible, the actual dewetting barriers can be smaller and can vanish at an extrusion pressure. Dewetting transition becomes possible because the formation of the nascent vapor layer at the basal surface is actually a non-classical process proceeding through multiple morphological transitions, with each transition lowering the barrier to dewetting. An understanding of the dewetting pathway allowed us to design practical surface that could spontaneously dewet under ambient conditions. In this chapter, we show that in contrast to the dewetting proceeding through the formation of vapor at the basal surface in the case of square pillared surface, formation of vapor layer at the closest separation between the nano particles can facilitate dewetting more optimally. We demonstrate that the likelihood of observing such a pathway increases with decreasing value of contact angle, θ , as well as with decreasing value of ratio of separation between the nanoparticles to the radius of the nanoparticles, S/R . Since the surface tensions of oily fluids are often much lower than that of water, oil droplets are more likely to display relatively smaller contact angles on most flat surfaces and therefore oil is more likely to dewet through this novel pathway.

7.2. Macroscopic Theory for Wetting-dewetting transitions

For the system shown in Figure 7.2, the free energy of a partially wet state relative to the free energy of the Wenzel state is given by:

$$\Delta F(h_{vl}) = \gamma A_{vl}(h_{vl}) + \Delta\gamma A_{sv}(h_{vl}) + \Delta PV_v(h_{vl}), \quad (7.1)$$

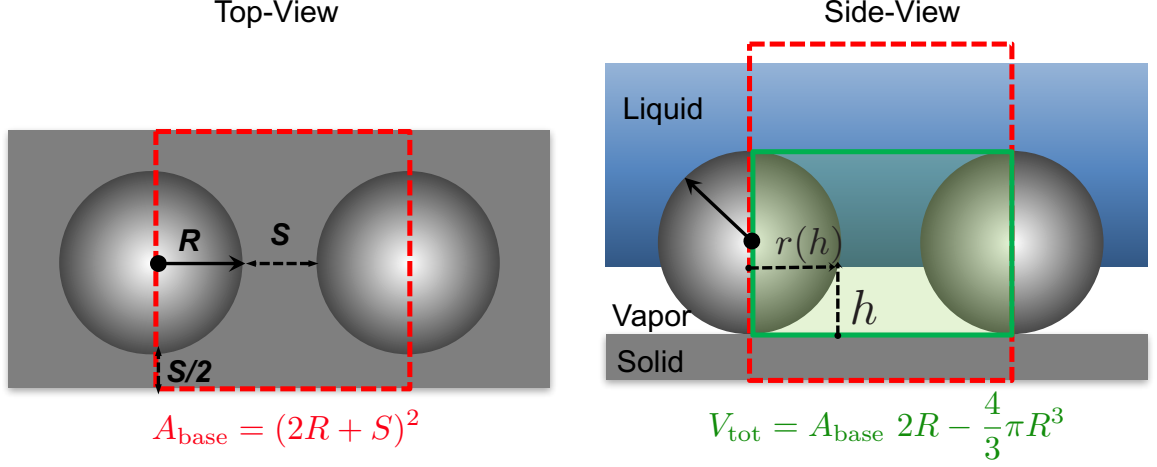


Figure 7.2: The dimensions that characterize the re-entrant surface decorated with spherical nanoparticles (NPs), are the radius of the NPs, R , and the inter-particle spacing, S . The red dashed-lines highlight the box which has periodic boundary conditions replicating the content of the box in both x and y-directions. A partially dewetted state is characterized by the height of the vapor-liquid interface that is parallel to, and at a distance, h (normalized by R), away from the basal surface. The area of the basal surface in the box is then given by, $A_{\text{base}} = (2R + S)^2$ and the texture-volume (shown in green in side-view snapshot) is given by, $V_{\text{tot}} = A_{\text{base}} 2R - \frac{4}{3}\pi R^3$.

where γ is the vapor-liquid surface tension, and $\Delta\gamma$ is the difference between the solid-vapor and solid-liquid surface tensions; according to the Young's equation, $\Delta\gamma = \gamma \cos \theta$. A_{vl} and A_{sv} are the vapor-liquid and the solid-vapor interfacial areas, respectively, in the partially wet state, and ΔP is the difference between the pressures of the liquid and the vapor phases. Assuming that a partially wet state on the surface is characterized by a flat vapor-liquid interface at h_{vl} -distance from the basal surface, we obtain, $A_{\text{vl}} = A_{\text{base}} - \pi r_{\text{vl}}^2$, is independent of h_{vl} , whereas $A_{\text{sv}} = A_{\text{base}} + 2\pi R h_{\text{vl}}$, increases linearly with h_{vl} . Also, using the geometry described in Figure 7.2, $A_{\text{base}} = (S + 2R)^2$ and $V_v = A_{\text{base}} h_{\text{vl}} - (\pi/3) h_{\text{vl}}^2 (3R - h_{\text{vl}})$ the Free energy from Equation 7.1 can be rewritten as:

$$\Delta F(h_{\text{vl}}) = \gamma(A_{\text{base}} - \pi r_{\text{vl}}^2) + \gamma \cos \theta (A_{\text{base}} + 2\pi R h_{\text{vl}}) + \Delta P (A_{\text{base}} h_{\text{vl}} - (\pi/3) h_{\text{vl}}^2 (3R - h_{\text{vl}})) \quad (7.2)$$

We can use define dimension less quantities such as, $h = h_{vl}/R$, $r = r_{vl}/R$, $s = S/R$, $a_b = A_{base}/\pi R^2 = (s + 2)^2/\pi$, and $p = \Delta PR/\gamma$

$$\Delta F(h_{vl})/\gamma\pi R^2 \equiv \Delta f(h) = a_b - r^2 + \cos\theta(a_b + 2h) + p(h^3/3 - h^2 + a_b h), \quad (7.3)$$

Also using the geometry described in Figure 7.2, we get $r^2 = 2h - h^2$, we obtain,

$$\Delta f(h) = (1 + \cos\theta)a_b - 2h(1 - \cos\theta) + h^2 + p(h^3/3 - h^2 + a_b h), \quad (7.4)$$

One key feature of the above equation is that there is one local minimum at $h = 0$ (at the Wenzel state) and there could be 2 more local minima as the equation is cubic in h . Before we begin to explore what these minima are and study the effect of pressure on the free energy, we first study the simple case of system lying at the co-existence pressure.

7.2.1. Effect of contact angle, $\cos\theta$, and separation between the particles, s , on the free energy at co-existence pressure, $\Delta f(h; p = 0)$

For a system at the co-existence pressure, $p = 0$, hence, the free energy described in Equation 7.4 can be reduced to:

$$\Delta f(h; p = 0) = (1 + \cos\theta)a_b - 2h(1 - \cos\theta) + h^2 \quad (7.5)$$

There are only two local minima of the this free energy equation, corresponding to the Wenzel state at $h_w = 0$ and corresponding to the partially-filled Cassie state at $h_c = (1 - \cos\theta)$. We can also obtain the barrier to wetting and dewetting as:

$$f_{barr}(W \rightarrow C) = (1 + \cos\theta)a_b \quad ; \quad f_{barr}(C \rightarrow W) = (1 - \cos\theta)^2 \quad (7.6)$$

As evident from the above expressions, the wetting barrier only depends on contact angle, $\cos\theta$ whereas, the dewetting barrier depends on both $\cos\theta$ and the basal surface area, $a_b = A_{base}/\pi R^2 = (S/R + 2)^2/\pi$.

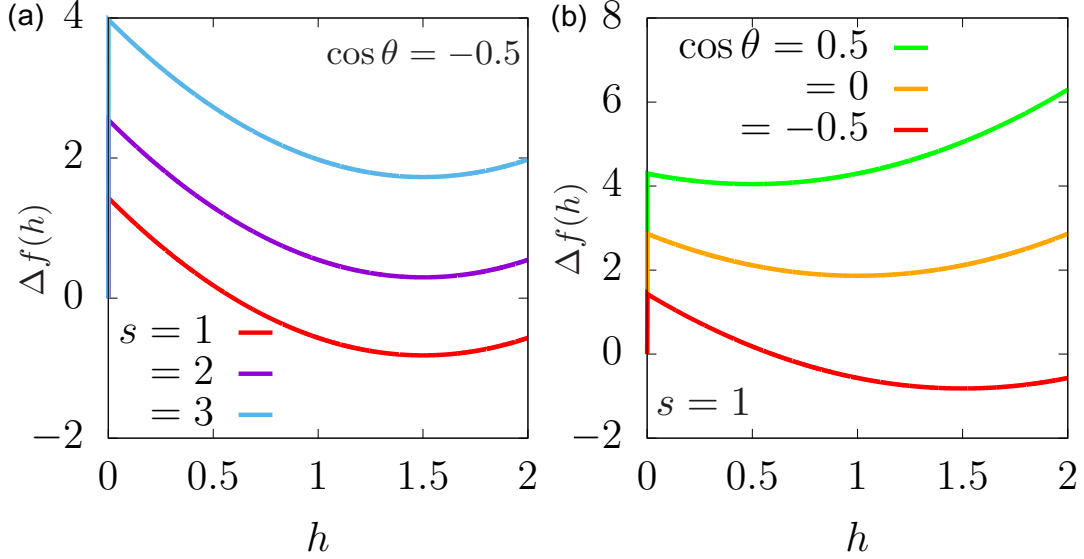


Figure 7.3: Effect of separation between the particles, s , and contact angle, $\cos \theta$, on the free energy at co-existence pressure, $\Delta f(h; p = 0)$. (a) We plot the dimension-less free energy, $\Delta f(h) \equiv \Delta F / \gamma \pi R^2$ as a function of dimensionless height of vapor-liquid interface, $h \equiv h_{\text{vl}} / R$ for three values of $s \equiv S / R$; the contact angle is identical ($\cos \theta = -0.5$) for each of the three systems. Macroscopic theory (Equation 7.5) predicts a barrier to the dewetting (Wenzel-to-Cassie) transition at $h = 0$; this dewetting barrier corresponds to the work of adhesion that must be performed to nucleate a vapor-liquid interface at the basal surface and hence, depends on the basal area, $a_b = (s + 2)^2 / \pi$. Rest of the free energy profiles, $\Delta f(h > 0; p = 0)$ for the three values of s , are parallel, and consequently, the location of the Cassie basin as well as the wetting barrier is identical in each of the three cases. (b) Changing contact angle, θ affects the location of the Cassie basin, given by, $h_c = (1 - \cos \theta)$ highlighting why different fluids on the same surface would prefer to sit at different fill-level (See Figure 7.1b). Changing θ affects both the wetting and dewetting barriers according to Equation 7.6.

7.2.2. Effect of pressure on free energy

As per equation 7.4, the dewetting barrier doesn't change with pressure, a limitation inherent in flat-interface-macroscopic models. For all values of pressure the dewetting barrier is given by $f_{\text{barr}}(W \rightarrow C) = (1 + \cos \theta)a_b$. However the barrier to wetting, $f_{\text{barr}}(W \rightarrow C)$ changes with pressure and depends on the location of Cassie state. To obtain the location of the Cassie state, *i.e.* the minimum in free energy, we first obtain the derivative of free energy with respect to h as follows:

$$d\Delta f(h)/dh = -2(1 - \cos \theta) + 2h + p(h^2 - 2h + a_b) = ph^2 + 2(1 - p)h + pa_b - 2(1 - \cos \theta). \quad (7.7)$$

Since the derivative is quadratic in h , free energy can have more than one extremum for $0 < h < 2$ for each root of $d\Delta f(h)/dh$ given by,

$$h_{\text{extremum}} = \frac{(p - 1) \pm \sqrt{p^2(1 - a_b) - 2p \cos \theta + 1}}{p} \quad (7.8)$$

In Figure 7.4 and Figure 7.5, we explore the effect of pressure on the free energy, the location of the Cassie state, the location of the second local extremum (a maxima).

To study the effect of $\cos \theta$ and s on location of the extremum, we plot the location of h_{min} and h_{max} as function of pressure for various values of $\cos \theta$ and s in Figure 7.6.

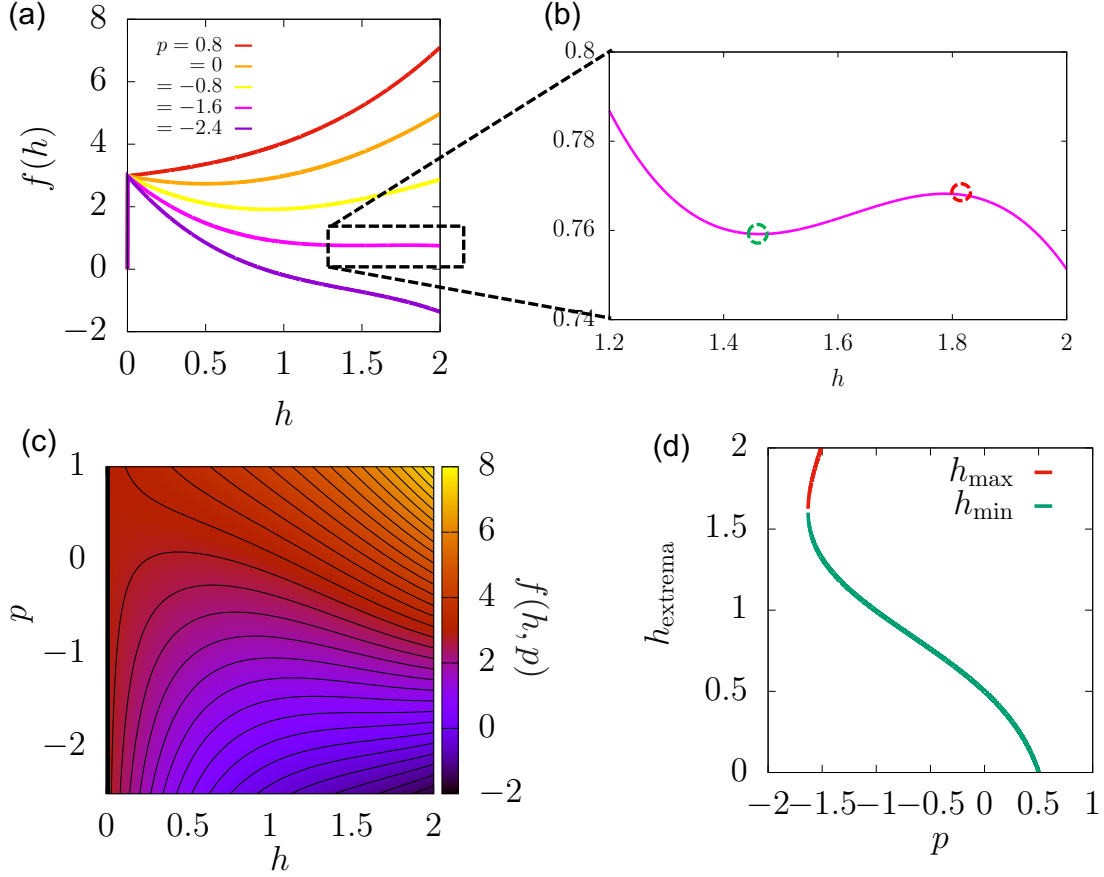


Figure 7.4: Effect of pressure on free energy for a system with separation between the nano-particles, $s = 0.5$ and $\cos \theta = 0.5$. (a) $\Delta f(h)$ as a function of height of vapor-liquid interface, h (Equation 7.4) for various values of dimensionless pressure, $p \equiv \Delta PR/\gamma$. While the dewetting barrier and the local minimum corresponding to Wenzel state remain invariant with p , for the Cassie state, both its location and the wetting barrier in transitioning into the Wenzel state, change with pressure. As pressure increases, system favors states with higher density and consequently the location of local minima corresponding to the Cassie state, $h_{\min}$, decreases with p . Eventually, for pressures larger than the intrusion pressure, Cassie state is destabilized (red curve) and system should spontaneously transition to the Wenzel state. Analogously, upon decreasing the pressure, the location of the Cassie state, $h_{\min}$, increases, and the fluid will sit higher-up between the nanoparticles. Eventually, the local minima at intermediate values of h vanishes, and Cassie state becomes the stable state at $h = 2$ (purple curve); however the invariance of the dewetting barrier would still impede a transition from the metastable wenzel state to the Cassie state. (b) Interestingly, at some intermediate value of the pressure, free energy displays a local maxima, $h_{\max}$, posing a second barrier for the system. (c) We plot free energy as function of both h and p to show the free energy landscape; while its clear to observe the behavior of local minima, $h_{\min}$, the local maxima is difficult to observe due to its relatively smaller range. (d) Plotting the values of $h_{\min}$ and $h_{\max}$ as a function of p highlight the small range of p -values for which the local maximum in free energy appears; the results also highlight that $h_{\max} \geq h_{\min}$.

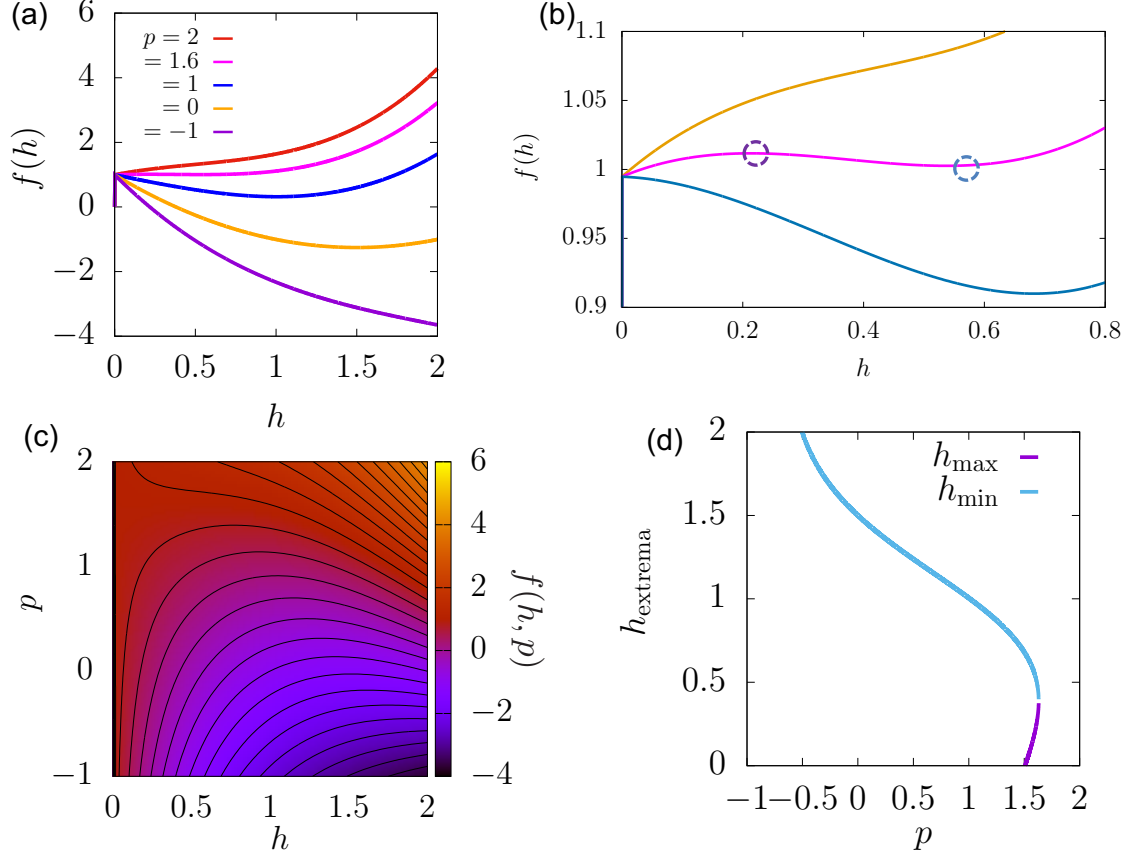


Figure 7.5: Effect of pressure on free energy for a system with separation between the nanoparticles, $s = 0.5$ and $\cos \theta = -0.5$ ($\theta = 120^\circ$). (a) $\Delta f(h)$ as a function of h (Equation 7.4) for various values of pressures, p . Qualitatively, the results are very similar to that of a low contact angle system shown in Figure 7.4, only major difference is that the local minima corresponding to the Cassie state, $h_{\min}$ spans over higher values of h and can go upto $h = 2$. (b) For intermediate values of pressures, free energy displays a local maxima, $h_{\max}$, posing a second barrier for the system. (c) We plot free energy as function of both h and p to show the free energy landscape. (d) In contrast with the system with $\cos \theta > 0$ in Figure 7.4d, $h_{\max} \leq h_{\min}$ and $h_{\max}$ spans a range of positive and higher values of pressures. A direct consequence of this result is that the system has an additional barrier to wetting as pressure increases.

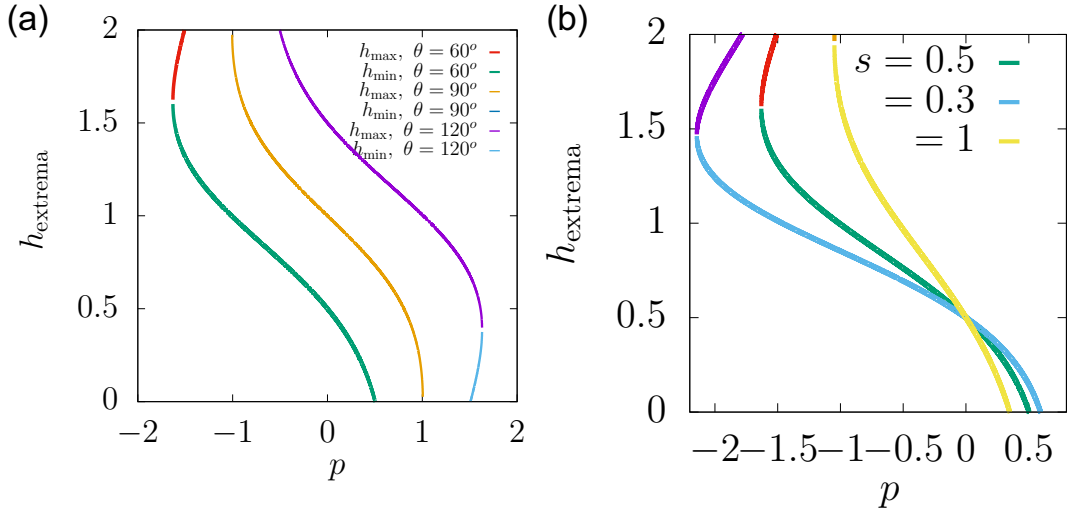


Figure 7.6: Effect of contact angle and basal area on the location of the extrema in free energy. (a) Location of the Cassie state (local minima) and the local maxima highlighted in Figure 7.4b and Figure 7.5b as a function of pressure for 3 different values of θ ; each of the plots had $s = 0.5$. (b) For system with $\cos \theta = 0.5$, we plot the extrema as a function of the separation between the nanoparticle, $s \equiv S/R$ to highlight that the local maxima tends to vanish in the limit of large s .

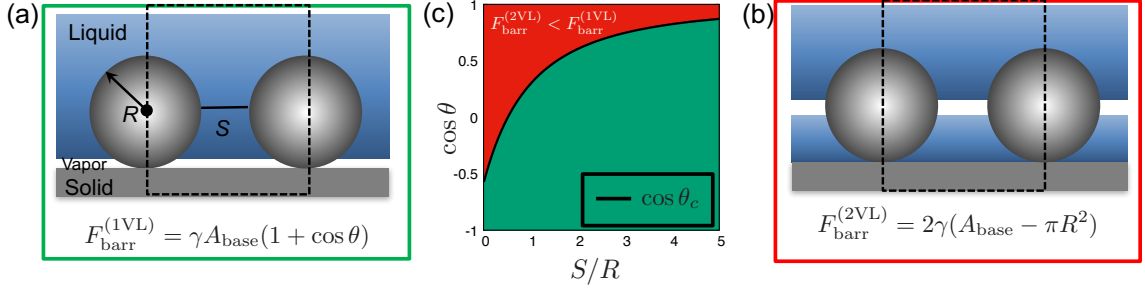


Figure 7.7: (a) Classical macroscopic theory envisions dewetting to proceed through the formation of nascent vapor layer at the basal surface, with a dewetting barrier of $F_{\text{barr}}^{(1\text{VL})} = \gamma A_{\text{base}}(1 + \cos \theta)$ (1VL corresponds to the presence of a single intact vapor-liquid interface in this model). (b) However, a more viable dewetting path can be the formation of nascent vapor layer at the closest separation between the nano particles with a dewetting barrier given by, $F_{\text{barr}}^{(2\text{VL})} = 2\gamma(A_{\text{base}} - \pi R^2)$ (2VL corresponds to the two vapor-liquid interfaces). (c) $\cos \theta_c$ as a function of S/R (black line) is obtained by comparing the barrier for both pathways (See Equation 7.9). In the red region, for systems with $\cos \theta > \cos \theta_c$, the dewetting barrier is lower for the 2VL-pathway whereas the reverse is true for the green region. Therefore, for systems with relatively lower values of contact angle, θ , which is true for most oily fluids, and for systems with relatively lower values of S/R , dewetting is more likely to proceed through nucleation of vapor at the closest distance between the nanoparticles and not at the basal surface.

7.3. An alternate, Less Expensive Path to Dewetting on Re-entrant Surfaces

The free energetics of wetting transitions in the re-entrant geometry consisting of spherical nanoparticles using the macroscopic models described in Section 6.2 has been extensively explored by various researchers [77, 78, 28]. However, due to the rarity of observing dewetting or Wenzel to Cassie transition in such surfaces, the phenomena of dewetting remains largely unexplored. In Chapter 2 through Chapter 5, we showed that an understanding of the dewetting pathways of the pillared system led us to design novel textures that can spontaneously dewet. In this section, we show that in contrast to the dewetting proceeding through the formation of vapor at the basal surface in the case of square pillared surface, a lower cost dewetting path can be formation of vapor layer at the closest separation between the nano particles (See Figure 7.7c). The dewetting barrier for the pathway shown in Figure 7.7a is provided by Equation 7.6 as $f_{\text{barr}}^{(1\text{VL})} = a_b(1 + \cos \theta)$ (in the dimension-less units); the superscript (1VL) represents that dewetting proceeds through formation of 1-vapor liq-

uid interface. Whereas, the barrier for dewetting through pathway shown in Figure 7.7c is given by, $f_{\text{barr}}^{(2\text{VL})} = 2(a_b - 1)$. In systems with $f_{\text{barr}}^{(2\text{VL})} > f_{\text{barr}}^{(1\text{VL})}$ or $\cos \theta > \cos \theta_c$, dewetting is more likely to proceed through the formation of vapor layer at the bottom of the nanoparticles. Where, $\cos \theta_c$ is a critical value of $\cos \theta$ obtained as function of $s \equiv S/R$ as below:

$$[f_{\text{barr}}^{(2\text{VL})} = f_{\text{barr}}^{(1\text{VL})}] \equiv [\cos \theta_c = 1 - \frac{2}{a_b} = 1 - \frac{2\pi}{(s+2)^2}] \quad (7.9)$$

As shown in Figure 7.7, for systems with relatively lower values of contact angle, θ , (or larger values of $\cos \theta$) and smaller ratio of separation to the radius, $s \equiv S/R$ this alternate pathway imposes smaller barrier to dewetting. This is a very important result as closely-packed nanoparticles ($s \rightarrow 0$) are routinely employed in creation of superhydrophobic and superoleophobic surfaces. The in following sections, we explore the influence of this novel nucleation mechanism on the entire free energy pathway for systems with $\cos \theta < \cos \theta_c$.

7.3.1. Free energetics of wetting-dewetting transition using the 2VL pathway: Demonstrating that the formation of vapor at the closest separation between the nanoparticles is most favorable

Assuming that a partially wet configuration following the 2VL dewetting pathway (See Figure 7.7c) is characterized by two flat vapor-liquid interfaces lying at h_1 and h_2 (such that $0 \leq h_1 \leq h_2 \leq 2$) as shown in Figure 7.8a. The free energy of such a partially dewetted state relative to a wet Wenzel state is then given by:

$$\begin{aligned} \Delta f(h_1, h_2; p, \cos \theta, s) = & (a_b - 2h_2 + h_2^2) + (a_b - 2h_1 + h_1^2) \\ & + \cos \theta \, 2(h_2 - h_1) \\ & + p[(h_2^3/3 - h_2^2 + a_b h_2) - (h_1^3/3 - h_1^2 + a_b h_1)] \end{aligned}$$

where the first term corresponds to the (unfavorable) contribution from the two vapor-liquid interfacial areas, the second term corresponds to the contribution from the vapor-

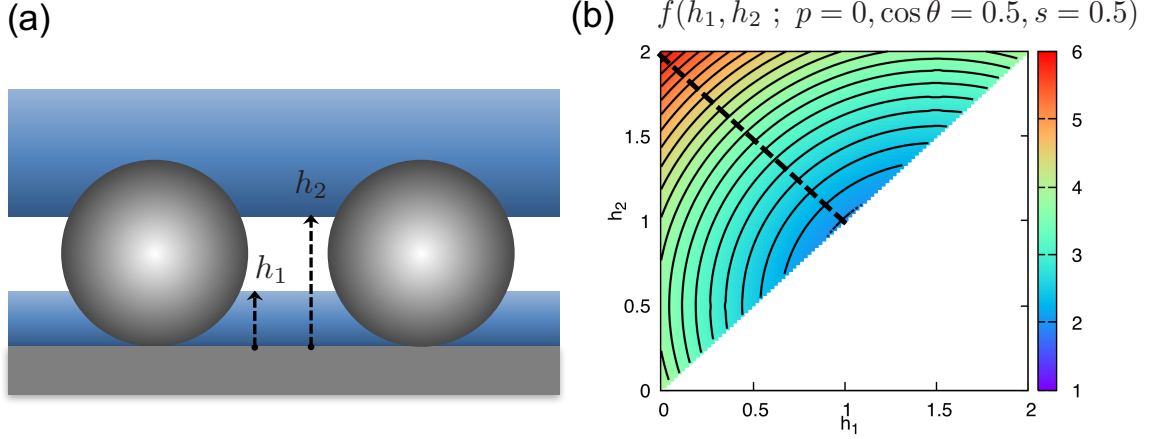


Figure 7.8: (a) A partially wet configuration following the 2VL dewetting pathway (See Figure 7.7c) is characterized by two flat vapor-liquid interfaces lying at h_1 and h_2 (such that $0 \leq h_1 \leq h_2 \leq 2$). (b) The free energy plotted as a function of h_1 and h_2 highlights that the minimum values of free energy lies at $h_1 = h_2 = 1$, and along the black dashed line ($h_1 + h_2 = 2$) suggesting why it is most favorable for the nascent vapor layer to form at $h_1 = h_2 = 1$.

solid interfacial areas, and the third term corresponds to the contribution from PV -term, to the free energy. Consistent with the macroscopic theory in section 6.2, all the length-scale parameters are normalized by radius of the spheres, R , $\Delta f \equiv \Delta F/(\gamma\pi R^2)$, $a_b \equiv (S + 2R)^2/(\pi R^2)$ and $p \equiv \Delta PR/\gamma$. For the simpler case of system as co-existence pressure, the free energy can be expressed as:

$$\Delta f(h_1, h_2; p = 0, \cos \theta, s) = (a_b - 2h_2 + h_2^2) + (a_b - 2h_1 + h_1^2) + \cos \theta \, 2(h_2 - h_1) \quad (7.10)$$

In Figure 7.8b, we plot $\Delta f(h_1, h_2)$ for $p = 0$, $s = 0.5$ and $\cos \theta = 0.5$; the plot highlights that the most optimal path follows the formation of nascent vapor layer at the closest distance between the nanoparticles at $h_1 = h_2 = 1$, and then proceeding the dewetting through following $h_1 + h_2 = 2$ as h_1 decreases from 1 to 0.

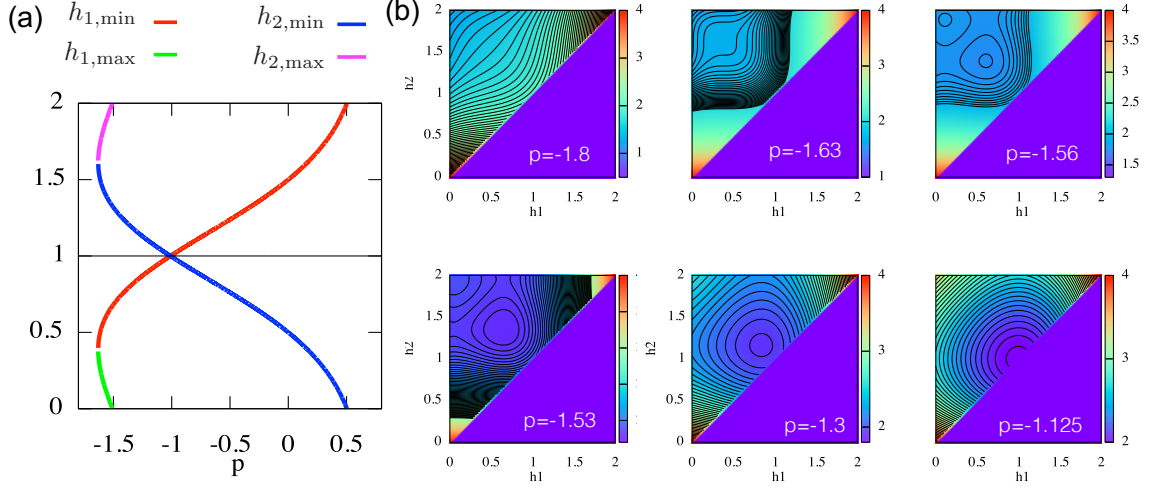


Figure 7.9: Effect of pressure on free energy, $f(h_1, h_2)$, for a system with separation between the nano-particles, $s = 0.5$ and $\cos \theta = 0.5$ following the pathway described in Figure 7.8. (a) Plotting the values of $h_{1,\min}$ and $h_{2,\min}$ as a function of p shows the effect of pressure on the free energy minima; for all values of p , it follows that $h_{1,\min} + h_{2,\min} = 2$. For intermediate values of p a local maxima is present also following $h_{1,\max} + h_{2,\max} = 2$. (c) We plot free energy as function of both h_1 and h_2 for various values of p .

7.3.2. Effect of pressure on free energy, $f(h_1, h_2)$

In order to study the effect of pressure on the free energy of the system, and on the wetting and dewetting barriers, we first obtain the location of the local extremum in free energy.

The partial derivatives of the free energy with respect to h_1 and h_2 is given by:

$$\frac{\partial \Delta f(h_1, h_2)}{\partial h_1} = -ph_1^2 + 2(1+p)h_1 - (2 + 2\cos \theta + pa_b)$$

$$\frac{\partial \Delta f(h_1, h_2)}{\partial h_2} = ph_2^2 + 2(1-p)h_2 - (2 - 2\cos \theta - pa_b)$$

Since the derivative is quadratic in both h_1 and h_2 , free energy can have more than one extremum for $0 \leq h_1 \leq h_2 \leq 2$ given by,

$$h_{1,\text{extremum}} = \frac{(p+1) \pm \sqrt{p^2(1-a_b) - 2p\cos \theta + 1}}{p} \quad (7.11)$$

$$h_{1,\text{extremum}} = \frac{(p-1) \pm \sqrt{p^2(1-a_b) - 2p \cos \theta + 1}}{p} \quad (7.12)$$

For both the minima and maxima, it turns out that,

$$h_{1,\text{extremum}} + h_{2,\text{extremum}} = 2 \quad (7.13)$$

In Figure 7.9, we plot the free energy and location of the minima and maxima in free energy as a function of pressure for a set of system with $\cos \theta = 0.5$ and $s = 0.5$.

7.4. Comparison of free energetics of wetting-dewetting transition using the 1VL and 2VL pathways

In Section 6.3 we showed that for systems with relatively larger values of contact angle, $\cos \theta > \cos \theta_c$ pathway proceeding through formation of 2VL interfaces (or through formation of a nascent vapor layer at $h_1 = h_2 = 1$) imposes smaller barrier to dewetting as compared to conventionally studied macroscopic models in Section 6.2. In this section we compare the free energy as function of density in the textured volume given by, $\rho_n \equiv V_{\text{liq}}/V_{\text{tot}}$ for the two methods. The expression for ρ_n for the the 1VL pathway is given by:

$$\rho_n = 1 - \frac{h^3/3 - h^2 + a_b h}{2a_b - 4/3}, \quad (7.14)$$

where, h is the height of the vapor-liquid interface as shown in Figure 7.2. Similarly, the expression for ρ_n for the two 2VL pathways corresponding to the two vapor-liquid interfaces lying at h_1 and h_2 as shown in Figure 7.8 is given by:

$$\rho_n = 1 - \frac{(h_2^3/3 - h_2^2 + a_b h_2) - (h_1^3/3 - h_1^2 + a_b h_1)}{2a_b - 4/3} ; h_2 = 2 - h_1. \quad (7.15)$$

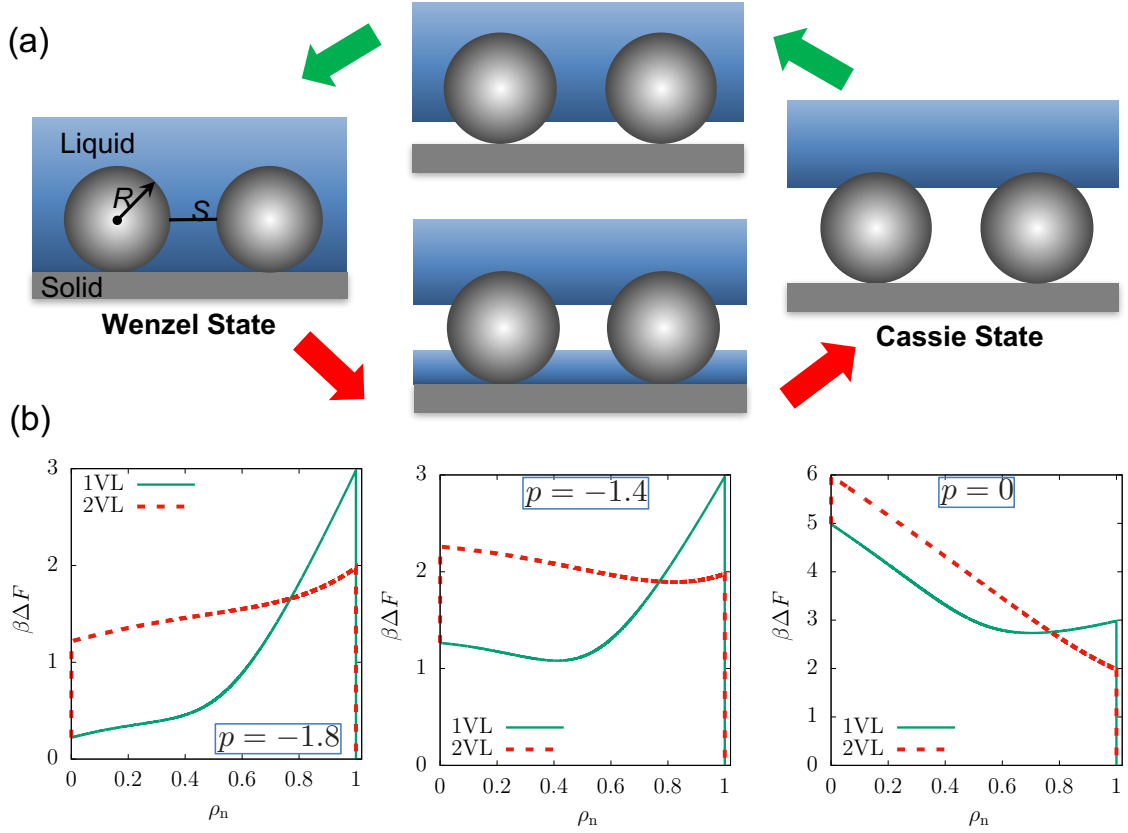


Figure 7.10: (a) Schematic showing the most likely pathway to wetting and dewetting transitions for systems with $\cos \theta > \cos \theta_c$ (Equation 7.9). The wetting transition from the Cassie state to the Wenzel state should occur through the single vapor-liquid interface descending along the nanoparticles until it reaches the basal surface (green arrows). However the dewetting transition from the wet Wenzel state to the Cassie state is more likely to occur through formation of nascent vapor layer at the closest distance between the nanoparticles (red arrows). (b) Free energy according to both the pathways, as functions of density, $\rho_n \equiv V_{\text{liq}}/V_{\text{tot}}$, in the textured volume, V_{tot} (See Figure 7.2) for three different values of pressure. We use the fact that the most optimal pathway follows $h_1 + h_2 = 2$, to obtain the free energy and density corresponding to the 2VL pathway. Each of the free energy profile features a Cassie state at $\rho_n = 0$ and Wenzel state at $\rho_n = 1$; in each case the 2VL pathway offers a lower resistance to dewetting whereas the 1VL pathway offers a lower resistance to wetting transition.

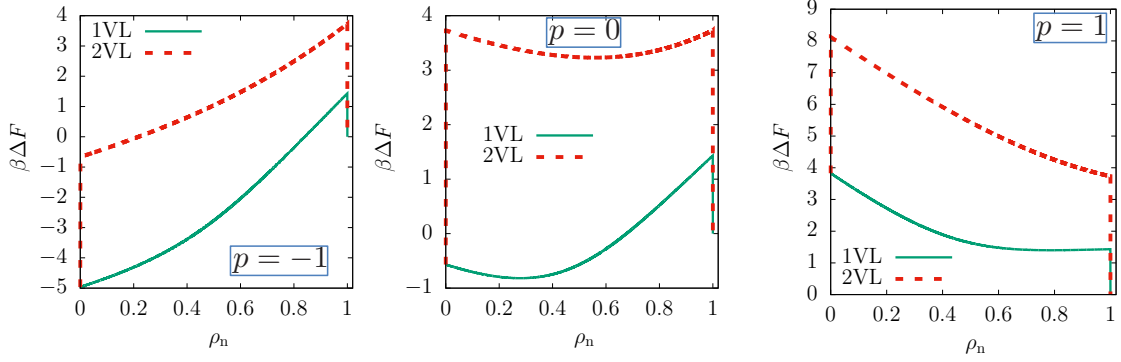


Figure 7.11: We compare the free energy corresponding to the 1VL and 2VL pathways, for a system with $\cos \theta < \cos \theta_c$ ($\cos \theta = -0.5$, $s = 1.0$) for three different values of pressure. In contrast with systems with $\cos \theta > \cos \theta_c$ shown in figure 7.10, these systems would follow the 1VL pathway for both wetting and dewetting transitions.

We also use the fact that most optimal value of the interfaces follow, $h_2 = 2 - h_1$ as shown in Section 6.3. The expression of free energy using $h_2 = 2 - h_1$ then becomes,

$$\begin{aligned} \Delta f(h_1; p, \cos \theta, s) = & (2a_b - 4h_1 + 2h_1^2) \\ & + \cos \theta \, 2(2 - 2h_1) \\ & + p[(2 - h_1)^3/3 - h_1^3/3 - +2(2h_1 - 2) + a_b(2 - 2h_1)] \end{aligned}$$

In Figure 7.10 and Figure 7.11, we then compare the free energy for the 1VL pathway from Equation 7.4 and free energy from the 2VL pathway as obtained from Equation above.

For Figure 7.10, we have chosen a system with $\cos \theta > \cos \theta_c$ (Equation 7.9), such that the 2VL pathway offers lesser barrier to the dewetting transition. Whereas, for system with $\cos \theta < \cos \theta_c$, the free energy for 1VL is consistently lower than that of 2VL pathway for all values of density and pressures.

7.5. Outlook

Omniphobicity is an extreme situation where a variety of liquid stay at the top of rough surfaces, in the so-called Cassie state. Owing to the dramatic reduction of solid/liquid

contact, such states lead to many applications, such as antifouling, droplet manipulation, hydrodynamic slip, and self-cleaning. This field of research has been very active for about 20 years, with theoretical, experimental, and computational viewpoints and it has been established that a re-entrant geometry offers potential for a variety of liquids to stay in a partially dewetted Cassie state. In many studies, model re-entrant texture made of spherical nanoparticles have been explored for their performance and robustness [77, 78, 28]. However, most such studies are focussed on creating robust surfaces that can remain in the Cassie state for a wide range of conditions by preventing the transition to the wet Wenzel state. Since macroscopic models prescribe that the dewetting transition is not possible (as it is impeded by the work of adhesion in the formation of a nascent vapor layer at the basal surface), the free energetics from a perspective of dewetting transition remains largely unexplored. In Chapter 2 through Chapter 5, we showed that dewetting transition is possible as the actual dewetting pathway is more complex and consists of various changes in morphology before the nascent vapor layer forms. An understanding of the dewetting pathways of the pillared system also led us to design novel textures that can spontaneously dewet under ambient conditions. Hence, in this study we tried to explore the free energetics of wetting-dewetting transitions on a re-entrant surface decorated with spherical nanoparticles, with an emphasis on understanding dewetting. We reveal show that contrasting with the dewetting proceeding through the formation of vapor at the basal surface in pillared surfaces, for the nano-particle system, formation of vapor layer at the closest separation between the nano particles can facilitate dewetting more optimally. We demonstrate that the likelihood of observing such a pathway increases with decreasing value of contact angle, θ , as well as with decreasing value of ratio of separation between the nanoparticles to the radius of the nanoparticles, S/R ; there exists a critical contact angle for each value of S/R demarcating systems that have a preference of one dewetting pathway over the other. Since the surface tensions of most oils are much lower than that of water, oil droplets are more likely to display relatively smaller contact angles on most flat surfaces and therefore oil is more likely to dewet through this novel pathway. However, lacking in this macroscopic model,

is an understanding of the “extrusion” pressure, which depends on the free energetics of complex morphologies forming prior to the formation of nascent vapor layer. As a future study, the free energy calculations from Chapter 2 through Chapter 5 can be repeated for these systems to uncover the actual dewetting pathways and inform more robust designs of re-entrant surfaces.

APPENDIX A : INDUS Method

A.1. INdirect Umbrella Sampling (INDUS) calculations

The INDUS method entails biasing the number of waters, N , in a volume, V , of interest, indirectly through a coarse-grained water number, $\tilde{N}$, that is closely related to N . Because N changes discontinuously when a particle crosses the boundary of V , biasing N can lead to impulsive forces. In contrast, $\tilde{N}$ is a continuous function of the particle positions. To coarse-grain N , we use a Gaussian function with a standard deviation of 0.01 nm that is truncated at 0.02 nm and shifted down; this choice of parameters allows the resultant $\tilde{N}$ and N to remain strongly correlated. To sample N over the entire range between the Cassie and the Wenzel basins, we run a series of simulations with different harmonic biasing potentials $U_j(\tilde{N}) = \frac{\kappa}{2}(\tilde{N} - \tilde{N}_j^*)^2$ ($j = 1, 2, \dots, n_w$), with $\kappa = 0.03$ kJ/mol and the $\tilde{N}_j^*$ -values chosen to allow sufficient overlap between adjacent windows. The INDUS simulations enable us to sample the biased joint distribution function, $P_V^j(N, \tilde{N})$, which represents the probability of observing N waters and $\tilde{N}$ coarse-grained waters in V , in the presence of the biasing potential, $U_j(\tilde{N})$. We then unbias and stitch together the n_w biased joint distribution functions using the weighted histogram analysis method (WHAM) [75, 57]. Finally, we integrate the resultant unbiased joint distribution function over $\tilde{N}$ to obtain the probability, $P_V(N)$, of observing N waters in V .

For each of the textured surfaces studied, we choose the textured volume, V (e.g., see Figure 1.2b for pillared system), as the probe volume for INDUS simulations. We use the symbol V to refer to the probe volume region, and also to quantify the volume of that region. To compare partially wet states across different surfaces, we define a normalized water density, $\rho_n \equiv N/N_{\text{liq}}$, with N being the number of water molecules in V in the partially wet state, and N_{liq} being the corresponding value in the fully wet (Wenzel) state; that is, N_{liq} corresponds to the location of the liquid basin maximum in $P_V(N)$. The free energy, $\Delta F(\rho_n)$, of the system in a partially wet state with normalized density ρ_n , relative

to that in the Wenzel state, which we report in the main text, is then obtained as:

$$\beta\Delta F(\rho_n) = -\ln [P_V(N)/P_V(N_{\text{liq}})], \quad (\text{A.1})$$

where $\beta^{-1} = k_B T$ is the thermal energy, and k_B is the Boltzmann constant.

A.2. Estimating dependence of $\Delta F(\rho_n)$ on ΔP

For the pure water system studied here, as the surface texture dewets, the region vacated by liquid water is replaced with water-vapor. Thus, the difference in pressures between the liquid and vapor phases, $\Delta P \equiv P_{\text{liq}} - P_{\text{vap}}$, can be obtained by setting the pressure of the vapor phase to be equal to the vapor-liquid coexistence pressure at the system temperature, i.e., $P_{\text{vap}} = P_{\text{coex}}(T)$. Further, because our simulations are performed in the NVT ensemble with a vapor-liquid interface in the simulation box (situated far from the textured surface), we ensure that liquid water is in co-existence with its vapor, and $P_{\text{liq}} = P_{\text{coex}}(T)$ [45]. The free energy profiles, $\Delta F(\rho_n)$, that we estimate in our simulations, are thus at $\Delta P = 0$. However, increasing pressure favors configurations with higher densities in a well-defined manner; free energy profiles at other pressures can thus be readily estimated (to within an additive constant) by reweighting the simulation results obtained at the co-existence pressure as follows: Free energy $F(N; \Delta P)$ at a pressure ΔP is obtained by:

$$\beta F(N; \Delta P) = -\ln P_v(N; \Delta P) = -\ln \frac{P_v(N) e^{-\beta \Delta P ((N_{\text{liq}} - N)/\rho_b)}}{\sum_{N=0}^{\infty} P_v(N) e^{-\beta \Delta P (N_{\text{liq}} - N)/\rho_b}}, \quad (\text{A.2})$$

where $\beta = k_B T$ is the thermal energy of the system, ρ_b is the bulk water density and $\beta F(N; \Delta P = 0) = -\ln P_v(N)$ is the free energy of system at saturation pressure. Using $\rho_n = N/N_{\text{liq}}$ we obtain:

$$\beta F(\rho_n; \Delta P) = \beta F(\rho_n; \Delta P = 0) + \beta \Delta P V (1 - \rho_n) + C, \quad (\text{A.3})$$

where $C = \ln \sum_{N=0}^{\infty} P_v(N) e^{\beta \Delta P V \rho_n}$ is the normalization constant.

The net result is the addition of a term linear in ρ_n , analogous to the last term in Equation 2.1. Assuming the liquid basin to be the zero of energy at each pressure, we get, free energy of any state with respect to the wet Wenzel state as:

$$\Delta F(\rho_n; \Delta P) = \Delta F(\rho_n; \Delta P = 0) + \Delta PV(1 - \rho_n). \quad (\text{A.4})$$

Note that typical experiments are performed with atmospheric air surrounding the water droplet; if this air enters the region vacated by the water, P_{vap} will increase from $P_{\text{coex}}(T)$ to P_{atm} leading to a corresponding decrease in ΔP . However, such small changes in pressure are expected to have subtle quantitative effects on $\Delta F(\rho_n)$. For example, as P_{vap} changes from $P_{\text{coex}}(T = 300K) \approx 0.03$ bar to $P_{\text{atm}} \approx 1$ bar, ΔP decreases by 0.97 bar; as seen in Figure 2.5c changes in wetting/dewetting barriers resulting from such small changes in ΔP are minimal.

APPENDIX B : Offsets in Geometric Parameters

B.1. Estimating Offsets in Geometric Parameters

The values of the pillar width W , its height H and the inter-pillar separation S , reported in the Chapters 2 through 5, correspond to the distances between the centers of the corresponding surface atoms. To compare our simulations with macroscopic theory, here we obtain more refined estimates of these geometric parameters. In particular, we use the fact that the effective volume of the textured region, V_{eff} , ought to be related to N_{liq} (the number of waters in V with the system in the liquid basin), through the simple expression, $V_{\text{eff}} = N_{\text{liq}}/\rho_{\text{B}}$, where ρ_{B} is the bulk liquid density. For instance, we estimate N_{liq} (and thereby, V_{eff}) by running equilibrium simulations for 10 different geometries ($S = 3, 4$ nm and $H = 2, 3, 4, 4.5, 5$ nm). We then assume that V_{eff} is related to effective values of the geometric parameters as $V_{\text{eff}} = S_{\text{eff}}(S_{\text{eff}} + 2W_{\text{eff}})H_{\text{eff}}$. Consistent with this assumption, we find that N_{liq} is a linear function of H for both $S = 3$ nm and $S = 4$ nm, as shown in Fig. B.1. Further, the x -intercepts obtained from both the corresponding fits are identical, allowing us to estimate the effective height as $H_{\text{eff}} = H + 0.11$ nm. The two fitted slopes are then used to obtain $S_{\text{eff}} = S - 0.23$ nm and $W_{\text{eff}} = W + 0.19$ nm respectively. These effective values of W , H and S are used in all comparisons to macroscopic theory that are described in Chapters 2 through 5 as well as in the main text; the subscript ‘eff’, however, is dropped from all equations for the sake of simplicity.

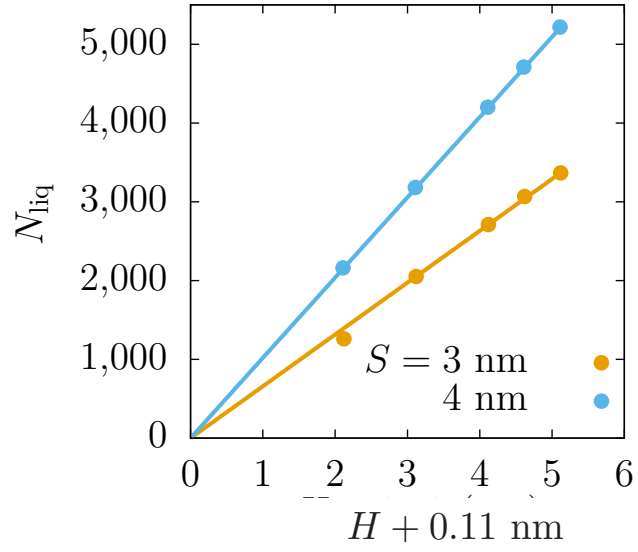


Figure B.1: Linear fits to N_{liq} as a function of the pillar height, H , plus an offset of 0.11 nm, pass through the origin. Thus, $H_{\text{eff}} = H + 0.11 \text{ nm}$. The slopes of the fitted lines enable us to similarly determine the offsets in pillar width, W , and the inter-pillar separation, S .

APPENDIX C : Coarse-grained density and Interface Calculations

C.1. Algorithm for Estimating Instantaneous Interfaces

Our procedure for calculating instantaneous interfaces closely follows that prescribed by Willard and Chandler [87], and builds upon it. In addition to using Gaussian smearing functions to obtain a spatially coarse-grained water density, we also incorporate a coarse-grained density of the surface atoms to obtain an overall normalized coarse-grained density as:

$$\tilde{\rho}_{\text{total}}(x, y, z) = \frac{\tilde{\rho}_{\text{water}}(x, y, z)}{\rho_{\text{B}}} + \frac{\tilde{\rho}_{\text{surface}}(x, y, z)}{\rho_{\text{surface}}^{\text{max}}}, \quad (\text{C.1})$$

where $\tilde{\rho}_{\alpha}$ is the coarse-grained density field of species α , and $\rho_{\text{surface}}^{\text{max}}$ is the maximum in $\tilde{\rho}_{\text{surface}}(x, y, z)$ for a flat surface consisting of 1 layer of surface atoms. $\tilde{\rho}_{\alpha}$ is obtained using:

$$\tilde{\rho}_{\alpha}(x, y, z) = \sum_{i=1}^{N_{\alpha}} \phi(x - x_i) \phi(y - y_i) \phi(z - z_i), \quad (\text{C.2})$$

where α represents either the water oxygen atoms or the surface atoms, N_{α} is the number of atoms of type α , and (x_i, y_i, z_i) correspond to the co-ordinates of atom i . $\phi(x)$ is chosen to be Gaussian with standard deviation, σ , and is truncated at $|x| = c$, shifted down and normalized:

$$\phi(x) = k[e^{-x^2/2\sigma^2} - e^{-c^2/2\sigma^2}] \Theta(c - |x|), \quad (\text{C.3})$$

where $\Theta(x)$ is the Heaviside step function and k is the normalization constant. We choose $\sigma = 0.16$ nm for the surface atoms, $\sigma = 0.24$ nm for water oxygens, and $c = 0.7$ nm for both. We define the instantaneous interface encapsulating the dewetted regions as the $\tilde{\rho}_{\text{total}}(x, y, z) = 0.5$ isosurface, and employ the Marching Cubes algorithm to identify that isosurface [40]. While the precise location and the shape of the instantaneous interface depend on the values of the parameters employed to calculate it, we do not expect the qualitative insights obtained to be sensitive to the particular choice of parameters. A detailed discussion of how the parameters affect the instantaneous interface calculation is

beyond the scope of this work, and will be the subject of a separate publication.

Algorithm for Estimating Average Interfaces

The average interfaces are obtained by simply time averaging the coarse grained density described in Equation C.1 and then obtaining the isosurface by employing the Marching Cubes algorithm.

APPENDIX D : Calculating work of adhesion, $\gamma(1 + \cos \theta)$

D.1. Obtaining $\gamma(1 + \cos \theta)$ using interface potential calculation

We compute the value of $\gamma(1 + \cos \theta)$, to eventually obtain the surface tension, γ , of our water model, and the Young's contact angle, θ , of the pillared atoms, to make comparisons with macroscopic theory. To this end, we build upon the interface potential approach developed by Rane et. al. [63] which involves characterizing the free energy of creating an intact vapor layer next to a wet non-polar substrate. To be able to make exact comparison between macroscopic theory and simulations we choose an appropriate substrate equivalent to the basal surface of the pillared surfaces. For systems in Chapter 2, we choose a substrate that is 1 nm thick, as the Lennard Jones interaction between pillar atoms and water molecules are cut-off at 1 nm, and any thicker substrate ought to have identical interaction strength and consequently same contact angle. We then perform simulations on a 4 nm $\times$ 4 nm $\times$ 1 nm substrate, wet by a thick water slab made with 3140 water molecules. This water slab was additionally followed by a sufficiently thick vapor layer, which was then followed by a purely repulsive wall, such that water in all the configurations at all times remains in co-existence with its vapor; hence maintaining the pressure of the system at vapor pressure of water at $T=300\text{K}$ (Figure D.1a). To characterize the free energy of creating a vapor layer at the surface, we perform INDUS simulation in a 4 nm $\times$ 4 nm $\times$ 4 nm probe volume, v , adjacent to the surface as shown in Figure D.1. In Figure D.1b, we plot $\Delta F/L^2$ as a function of $N \in v$; as N is decreased, first vapor bubbles first form at the surface, eventually giving way to form an intact vapor layer. Once the vapor layer has been formed, further reducing N results in rising of the vapor-liquid interface without any penalty. The difference in free energy between the states containing this vapor-liquid interface, ($N < 1700$), and the wet state, is $\Delta F = A_{vl}\gamma + A_{sv}\gamma_{sv} - A_{sl}\gamma_{sl}$ (Figure D.1b). On further assuming that the vapor-liquid interfacial area, $A_{vl} = A_{sv} = A_{sl} \approx L^2$ and upon using the Young's equation, we obtain $\Delta F/L^2 = \gamma(1 + \cos \theta)$. We obtain $\gamma(1 + \cos \theta) = 5.97 \pm 0.0006 \text{ } k_B T/\text{nm}^2$ by fitting a constant to $\Delta F/L^2$ for $N < 1700$ in Figure D.1, where the reported error the standard

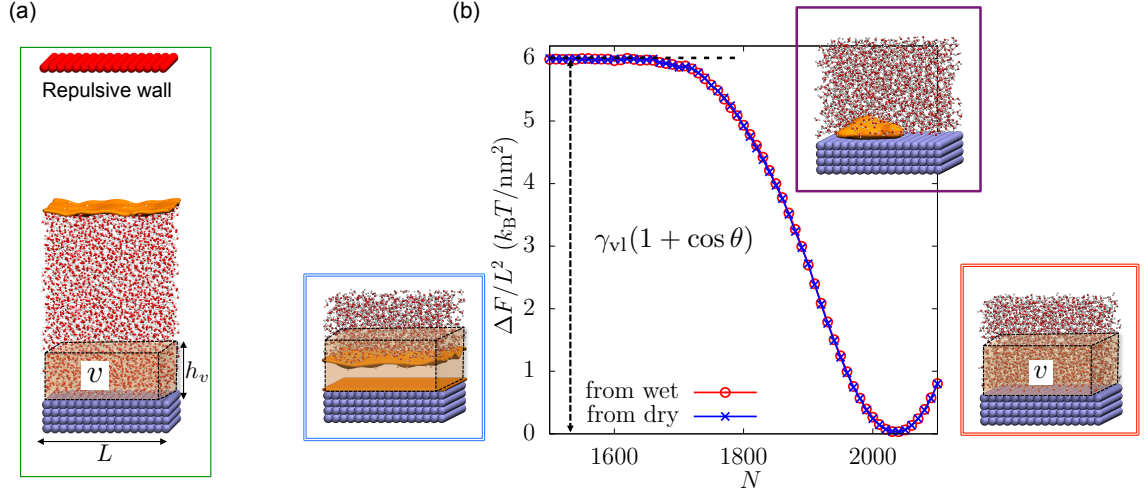


Figure D.1: Obtaining $\gamma(1 + \cos \theta)$ using interface potential calculation. (a) To perform interface potential calculations, we employ INDUS method to characterize free energy, F , as a function of number of waters, N , in the probe volume v (shown by dashed lines). INDUS method allows us to obtain, $\Delta F \equiv F - F_{\text{liq}}$ as function of N , where the subscript 'liq' denotes the fully wet state. (b) Dewetting in volume, v , proceeds through transition between various morphologies, reflected in the transition between different functional forms in $\Delta F(\rho_n)$ as ρ_n is decreased from 1; one such morphology for $N = 1900$ featuring a vapor bubble at the surface is shown. Eventually, an intact vapor-liquid interface forms at $N \approx 1700$ and on further reducing N this vapor-liquid interface rises with no energetic penalty. The free energy of creating this intact vapor-liquid interface is then given by $\Delta F = \gamma(1 + \cos \theta)L^2$, where L^2 is the cross sectional area of the plate; we fit $\Delta F/L^2$ for $\rho_n < 1700$, to extract the value of $\gamma(1 + \cos \theta) = 5.97 \pm 0.0006 \text{ } k_B T/\text{nm}^2$. We perform the free energy calculations starting from both dry and wet initial conditions to ensure there is no barrier in any coordinate orthogonal to N and get the same result.

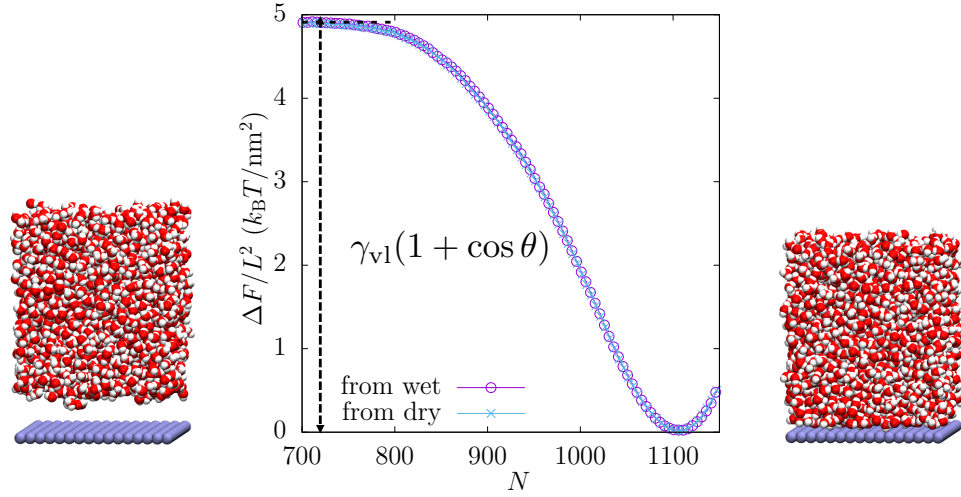


Figure D.2: Obtaining $\gamma(1 + \cos \theta)$ using interface potential calculation on a substrate made of single layer of atoms. We fit $\Delta F/L^2$ for $\rho_n < 750$, to extract the value of $\gamma(1 + \cos \theta) = 4.91 \pm 0.001 \text{ } k_B T/\text{nm}^2$.

error in averaging over all the data for $1500 < N < 1700$.

For systems in Chapter 5, we have pillared surfaces with basal surface made of single layer of atoms, resulting in slightly smaller value of $\gamma(1 + \cos \theta) = 4.91 \pm 0.001 \text{ } k_B T/\text{nm}^2$ as shown in Figure D.2. The system setup and INDUS simulation for this calculation is identical to that shown in Figure D.1a, the height of the probe volume is 2 nm and the plate dimension was 4 nm×4 nm. The smaller value of $\gamma(1 + \cos \theta)$ is expected because of the reduced strength of Lennard-Jones attraction between water molecules and surface made of single layer of atoms as opposed to substrate made of 4 layers of atoms.

BIBLIOGRAPHY

- [1] H. Acharya, S. Vembanur, S. N. Jamadagni, and S. Garde. Mapping hydrophobicity at the nanoscale: Applications to heterogeneous surfaces and proteins. *Faraday Discuss.*, 146:353–365, 2010.
- [2] G. Azimi, R. Dhiman, H.-M. Kwon, A. T. Paxson, and K. K. Varanasi. Hydrophobicity of rare-earth oxide ceramics. *Nature Mater.*, 12(4):315–320, 2013.
- [3] H. J. C. Berendsen, J. R. Grigera, and T. P. Straatsma. The missing term in effective pair potentials. *J. Phys. Chem.*, 91:6269–6271, 1987.
- [4] B. Bhushan. Biomimetics inspired surfaces for drag reduction and oleophobicity/philicity. *BEILSTEIN JOURNAL OF NANOTECHNOLOGY*, 2:66–84, FEB 1 2011.
- [5] D. Bonn, J. Eggers, J. Indekeu, J. Meunier, and E. Rolley. Wetting and spreading. *Rev. Mod. Phys.*, 81(2):739–805, 2009.
- [6] J. B. Boreyko and C. P. Collier. Dewetting Transitions on Superhydrophobic Surfaces: When Are Wenzel Drops Reversible? *J. Phys. Chem. C*, 117(35):18084–18090, 2013.
- [7] E. Bormashenko. Progress in understanding wetting transitions on rough surfaces. *Adv. Coll. Interface Sci.*, 222:92–103, 2015.
- [8] G. Bussi, D. Donadio, and M. Parrinello. Canonical sampling through velocity rescaling. *J. Chem. Phys.*, 126(1):014101, 2007.
- [9] H.-J. Butt, D. Vollmer, and P. Papadopoulos. Super liquid-repellent layers: The smaller the better. *Adv. Coll. Interface Sci.*, 222(104 - 109), 2014.
- [10] A. Cassie and S. Baxter. Wettability of porous surfaces. *Trans. Faraday Soc.*, 40:546–551, 1944.
- [11] D. Chandler. Interfaces and the driving force of hydrophobic assembly. *Nature*, 437:640–647, 2005.
- [12] A. Checco, B. M. Ocko, A. Rahman, C. T. Black, M. Tasinkevych, A. Giacomello, and S. Dietrich. Collapse and reversibility of the superhydrophobic state on nanotextured surfaces. *Phys. Rev. Lett.*, 112:216101, 2014.
- [13] C. Cottin-Bizonne, J.-L. Barrat, L. Bocquet, and E. Charlaix. Low-friction flows of liquid at nanopatterned interfaces. *Nature Mater.*, 2(4):237–240, 2003.
- [14] P.-G. De Gennes, F. Brochard-Wyart, and D. Quéré. *Capillarity and wetting phenomena: drops, bubbles, pearls, waves*. Springer Science & Business Media, 2013.

- [15] R. D. Deegan, O. Bakajin, T. F. Dupont, G. Huber, S. R. Nagel, and T. A. Witten. Capillary flow as the cause of ring stains from dried liquid drops. *Nature*, 389(6653):827–829, 10 1997.
- [16] H. Y. Erbil, A. L. Demirel, Y. Avc, and O. Mert. Transformation of a simple plastic into a superhydrophobic surface. *Science*, 299(5611):1377–1380, 02 2003.
- [17] U. Essmann, L. Perera, M. L. Berkowitz, T. Darden, H. Lee, and L. G. Pedersen. A smooth particle mesh ewald method. *J. Chem. Phys.*, 103:8577–8593, 1995.
- [18] P. Forsberg, F. Nikolajeff, and M. Karlsson. Cassie–Wenzel and Wenzel–Cassie transitions on immersed superhydrophobic surfaces under hydrostatic pressure. *Soft Matter*, 7:104–109, 2011.
- [19] A. Giacomello, M. Chinappi, S. Meloni, and C. M. Casciola. Metastable wetting on superhydrophobic surfaces: continuum and atomistic views of the cassie-baxter-wenzel transition. *Phys. Rev. Lett.*, 109(22):226102, 2012.
- [20] A. Giacomello, S. Meloni, M. Müller, and C. M. Casciola. Mechanism of the cassie-wenzel transition via the atomistic and continuum string methods. *J. Chem. Phys.*, 142(10):104701, 2015.
- [21] R. Godawat, S. N. Jamadagni, and S. Garde. Characterizing hydrophobicity of interfaces by using cavity formation, solute binding, and water correlations. *Proc. Natl. Acad. Sci. U.S.A.*, 106:15119 – 15124, 2009.
- [22] B. Hess, C. Kutzner, D. van der Spoel, and E. Lindahl. Gromacs 4: Algorithms for highly efficient, load-balanced, and scalable molecular simulation. *J. Chem. Theory Comp.*, pages 435 – 447, 2008.
- [23] J. A. Howarter and J. P. Youngblood. Self-cleaning and anti-fog surfaces via stimuli-responsive polymer brushes. *ADVANCED MATERIALS*, 19(22):3838+, NOV 19 2007.
- [24] J. N. Israelachvili. *7 - Repulsive Steric Forces, Total Intermolecular Pair Potentials, and Liquid Structure*, pages 133–149. Academic Press, 2011.
- [25] S. N. Jamadagni, R. Godawat, and S. Garde. Hydrophobicity of proteins and interfaces: Insights from density fluctuations. *Ann. Rev. Chem. Biomol. Engg.*, 2(1):147–171, 2011.
- [26] S.-M. Kang, S. Hwang, S.-H. Jin, C.-H. Choi, J. Kim, B. J. Park, D. Lee, and C.-S. Lee. A rapid one-step fabrication of patternable superhydrophobic surfaces driven by marangoni instability. *Langmuir*, 30(10):2828–2834, 2014.
- [27] T. Koishi, K. Yasuoka, S. Fujikawa, T. Ebisuzaki, and X. C. Zeng. Coexistence and transition between cassie and wenzel state on pillared hydrophobic surface. *Proc. Natl. Acad. Sci. U.S.A.*, 106(21):8435–8440, 2009.

- [28] A. K. Kota, G. Kwon, and A. Tuteja. The design and applications of superomniphobic surfaces. *NPG Asia Mater*, 6:e109–, 07 2014.
- [29] T. N. Krupenkin, J. A. Taylor, E. N. Wang, P. Kolodner, M. Hodes, and T. R. Salamon. Reversible wetting–dewetting transitions on electrically tunable superhydrophobic nanostructured surfaces. *Langmuir*, 23(18):9128–9133, 08 2007.
- [30] V. Kumar and J. R. Errington. Impact of small-scale geometric roughness on wetting behavior. *Langmuir*, 29(38):11815–11820, 2013.
- [31] V. Kumar, S. Sridhar, and J. R. Errington. Monte carlo simulation strategies for computing the wetting properties of fluids at geometrically rough surfaces. *J. Chem. Phys.*, 135(18):184702, 2011.
- [32] A. Lafuma and D. Quéré. Superhydrophobic states. *Nature Mater.*, 2(7):457–460, 2003.
- [33] W. Lei, Z.-H. Jia, J.-C. He, T.-M. Cai, and G. Wang. Vibration-induced wenzel-cassie wetting transition on microstructured hydrophobic surfaces. *Appl. Phys. Lett.*, 104(18):181601, 2014.
- [34] F. Leroy and F. Mueller-Plathe. Rationalization of the behavior of solid-liquid surface free energy of water in cassie and wenzel wetting states on rugged solid surfaces at the nanometer scale. *Langmuir*, 27(2):637–645, 2011.
- [35] X.-M. Li, D. Reinhoudt, and M. Crego-Calama. What do we need for a superhydrophobic surface? a review on the recent progress in the preparation of superhydrophobic surfaces. *Chem. Soc. Rev.*, 36:1350–1368, 2007.
- [36] X.-M. Li, D. Reinhoudt, and M. Crego-Calama. What do we need for a superhydrophobic surface? a review on the recent progress in the preparation of superhydrophobic surfaces. *Chem. Soc. Rev.*, 36:1350–1368, 2007.
- [37] Y. Li and W. Ren. Numerical study of vapor condensation on patterned hydrophobic surfaces using the string method. *Langmuir*, 30(31):9567–9576, 08 2014.
- [38] G. Liu, L. Fu, A. V. Rode, and V. S. J. Craig. Water Droplet Motion Control on Superhydrophobic Surfaces: Exploiting the Wenzel-to-Cassie Transition. *Langmuir*, 27(6):2595–2600, 2011.
- [39] Y. Liu, X. Chen, and J. H. Xin. Can superhydrophobic surfaces repel hot water? *J. Mater. Chem.*, 19(31):5602–5611, 2009.
- [40] W. E. Lorensen and H. E. Cline. Marching cubes: A high resolution 3d surface construction algorithm. In *Proceedings of the 14th Annual Conference on Computer Graphics and Interactive Techniques*, SIGGRAPH '87, pages 163–169, New York, NY, USA, 1987. ACM.

- [41] K. Lum, D. Chandler, and J. D. Weeks. Hydrophobicity at small and large length scales. *J. Phys. Chem. B*, 103:4570–4577, 1999.
- [42] P. Lv, Y. Xue, H. Liu, Y. Shi, P. Xi, H. Lin, and H. Duan. Symmetric and asymmetric meniscus collapse in wetting transition on submerged structured surfaces. *Langmuir*, 31(4):1248–1254, 02 2015.
- [43] L. Maibaum and D. Chandler. A coarse-grained model of water confined in a hydrophobic tube. *J. Phys. Chem. B*, 107(5):1189–1193, 2003.
- [44] G. Manukyan, J. M. Oh, D. van den Ende, R. G. H. Lammertink, and F. Mugele. Electrical Switching of Wetting States on Superhydrophobic Surfaces: A Route Towards Reversible Cassie-to-Wenzel Transitions. *Phys. Rev. Lett.*, 106(1):014501, 2011.
- [45] T. Miller, E. Vanden-Eijnden, and D. Chandler. Solvent coarse-graining and the string method applied to the hydrophobic collapse of a hydrated chain. *Proc. Natl. Acad. Sci. U.S.A.*, 104:14559–14564, 2007.
- [46] J. Mittal and G. Hummer. Static and dynamic correlations in water at hydrophobic interfaces. *Proc. Nat. Acad. Sci.*, 105:20130–20135, 2008.
- [47] S. Moulinet and D. Bartolo. Life and death of a fakir droplet: Impalement transitions on superhydrophobic surfaces. *Eur. Phys. J. E*, 24(3):251–260, 2007.
- [48] M. Nosonovsky and B. Bhushan. Patterned Nonadhesive Surfaces: Superhydrophobicity and Wetting Regime Transitions. *Langmuir*, 24(4):1525–1533, 2008.
- [49] M. Nosonovsky and B. Bhushan. Patterned nonadhesive surfaces: Superhydrophobicity and wetting regime transitions. *Langmuir*, 24(4):1525–1533, 02 2008.
- [50] M. Nosonovsky and B. Bhushan. Superhydrophobic surfaces and emerging applications: Non-adhesion, energy, green engineering. *Curr. Opin. Colloid Interface Sci.*, 14(4):270–280, 2009.
- [51] G. Pallares, M. E. M. Azouzi, M. A. González, J. L. Aragonés, J. L. Abascal, C. Valeriani, and F. Caupin. Anomalies in bulk supercooled water at negative pressure. *Proc. Natl. Acad. Sci. U.S.A.*, 111(22):7936–7941, 2014.
- [52] P. Papadopoulos, L. Mammen, X. Deng, D. Vollmer, and H.-J. Butt. How superhydrophobicity breaks down. *Proc. Natl. Acad. Sci. U.S.A.*, 110(9):3254–3258, 2013.
- [53] N. A. Patankar. Transition between superhydrophobic states on rough surfaces. *Langmuir*, 20(17):7097–7102, 2004.
- [54] N. A. Patankar. Transition between superhydrophobic states on rough surfaces. *Langmuir*, 20(17):7097–102, Aug 2004.

- [55] N. A. Patankar. Consolidation of hydrophobic transition criteria by using an approximate energy minimization approach. *Langmuir*, 26(11):8941–8945, 2010.
- [56] A. J. Patel, P. Varilly, and D. Chandler. Fluctuations of water near extended hydrophobic and hydrophilic surfaces. *J. Phys. Chem. B*, 114:1632–1637, 2010.
- [57] A. J. Patel, P. Varilly, D. Chandler, and S. Garde. Quantifying density fluctuations in volumes of all shapes and sizes using indirect umbrella sampling. *J. Stat. Phys.*, 145:265–275, 2011.
- [58] A. J. Patel, P. Varilly, S. N. Jamadagni, H. Acharya, S. Garde, and D. Chandler. Extended surfaces modulate hydrophobic interactions of neighboring solutes. *Proc. Natl. Acad. Sci. U.S.A.*, 108:17678 – 17683, 2011.
- [59] A. J. Patel, P. Varilly, S. N. Jamadagni, M. F. Hagan, D. Chandler, and S. Garde. Sitting at the edge: How biomolecules use hydrophobicity to tune their interactions and function. *J. Phys. Chem. B*, 116:2498 – 2503, 2012.
- [60] S. Prakash, E. Xi, and A. J. Patel. Spontaneous recovery of superhydrophobicity on nanotextured surfaces. *Proc. Nat. Acad. Sci. U.S.A.*, 113(20):5508–5513, 2016.
- [61] D. Quéré. Wetting and Roughness. *Annu. Rev. Mater. Res.*, 38:71–99, 2008.
- [62] Y. Rahmawan, L. Xu, and S. Yang. Self-assembly of nanostructures towards transparent, superhydrophobic surfaces. *J. Mater. Chem. A*, 1(9):2955–2969, 2013.
- [63] K. S. Rane, V. Kumar, and J. R. Errington. Monte carlo simulation methods for computing the wetting and drying properties of model systems. *The Journal of Chemical Physics*, 135(23):234102, 2011.
- [64] R. C. Remsing, E. Xi, S. Ranganathan, S. Sharma, P. G. Debenedetti, S. Garde, and A. J. Patel. Pathways to dewetting in hydrophobic confinement. *Proc. Natl. Acad. Sci. U.S.A.*, 112(27):8181–8186, 2015.
- [65] W. Ren. Wetting transition on patterned surfaces: Transition states and energy barriers. *Langmuir*, 30(10):2879–2885, 03 2014.
- [66] B. Rotenberg, A. J. Patel, and D. Chandler. Molecular explanation for why talc surfaces can be both hydrophilic and hydrophobic. *J. Am. Chem. Soc.*, 133:20521 – 20527, 2011.
- [67] J.-P. Ryckaert, G. Ciccotti, and H. J. C. Berendsen. Numerical integration of the cartesian equations of motion of a system with constraints: molecular dynamics of n-alkanes. *J. Comp. Phys.*, 23(3):327 – 341, 1977.
- [68] K. Rykaczewski. Microdroplet Growth Mechanism during Water Condensation on Superhydrophobic Surfaces. *Langmuir*, 28(20):7720–7729, 2012.

- [69] E. S. Savoy and F. A. Escobedo. Molecular simulations of wetting of a rough surface by an oily fluid: Effect of topology, chemistry, and droplet size on wetting transition rates. *Langmuir*, 28(7):3412–3419, 2012.
- [70] E. S. Savoy and F. A. Escobedo. Simulation study of free-energy barriers in the wetting transition of an oily fluid on a rough surface with reentrant geometry. *Langmuir*, 28(46):16080–16090, 2012.
- [71] M. Sbragaglia, A. M. Peters, C. Pirat, B. M. Borkent, R. G. H. Lammertink, M. Wessling, and D. Lohse. Spontaneous breakdown of superhydrophobicity. *Phys. Rev. Lett.*, 99:156001, 2007.
- [72] A. Shahraz, A. Borhan, and K. A. Fichthorn. A theory for the morphological dependence of wetting on a physically patterned solid surface. *Langmuir*, 28(40):14227–14237, 2012.
- [73] A. Shahraz, A. Borhan, and K. A. Fichthorn. Wetting on physically patterned solid surfaces: The relevance of molecular dynamics simulations to macroscopic systems. *Langmuir*, 29(37):11632–11639, 2013.
- [74] A. Shahraz, A. Borhan, and K. A. Fichthorn. Kinetics of droplet wetting mode transitions on grooved surfaces: Forward flux sampling. *Langmuir*, 30(51):15442–15450, 2014.
- [75] M. Souaille and B. Roux. Extension to the weighted histogram analysis method: combining umbrella sampling with free energy calculations. *Computer Phys. Comm.*, 135:40–57, 2001.
- [76] P. R. ten Wolde and D. Chandler. Drying-induced hydrophobic polymer collapse. *Proc. Natl. Acad. Sci. U.S.A.*, 99:6539–6543, 2002.
- [77] A. Tuteja, W. Choi, M. Ma, J. M. Mabry, S. A. Mazzella, G. C. Rutledge, G. H. McKinley, and R. E. Cohen. Designing Superoleophobic Surfaces. *Science*, 318:1618–1622, 12 2007.
- [78] A. Tuteja, W. Choi, G. H. McKinley, R. E. Cohen, and M. F. Rubner. Design parameters for superhydrophobicity and superoleophobicity. *MRS bulletin*, 33(08):752–758, 2008.
- [79] P. Varilly and D. Chandler. Water evaporation: A transition path sampling study. *J. Phys. Chem. B*, 117(5):1419–1428, 2013.
- [80] P. Varilly, A. J. Patel, and D. Chandler. An improved coarse-grained model of solvation and the hydrophobic effect. *J. Chem. Phys.*, 134:074109, 2011.
- [81] C. Vega and E. De Miguel. Surface tension of the most popular models of water by using the test-area simulation method. *J. Chem. Phys.*, 126(15):154707, 2007.

- [82] S. Vembanur, A. J. Patel, S. Sarupria, and S. Garde. On the thermodynamics and kinetics of hydrophobic interactions at interfaces. *The Journal of Physical Chemistry B*, 117(35):10261–10270, 2013.
- [83] T. Verho, J. T. Korhonen, L. Sainiemi, V. Jokinen, C. Bower, K. Franze, S. Franssila, P. Andrew, O. Ikkala, and R. H. A. Ras. Reversible switching between superhydrophobic states on a hierarchically structured surface. *Proc. Natl. Acad. Sci. U.S.A.*, 109(26):10210–10213, 06 2012.
- [84] R. N. Wenzel. Resistance of solid surfaces to wetting by water. *Ind. Eng. Chem.*, 28(8):988–994, 1936.
- [85] A. P. Willard and D. Chandler. The role of solvent fluctuations in hydrophobic assembly. *J. Phys. Chem. B*, 112:6187–6192, 2008.
- [86] A. P. Willard and D. Chandler. The role of solvent fluctuations in hydrophobic assembly. *J. Phys. Chem. B*, 112:6187–6192, 2008.
- [87] A. P. Willard and D. Chandler. Instantaneous liquid interfaces. *J. Phys. Chem. B*, 114(5):1954–1958, 2010.
- [88] L. Xu, R. G. Karunakaran, J. Guo, and S. Yang. Transparent, superhydrophobic surfaces from one-step spin coating of hydrophobic nanoparticles. *ACS Appl. Mater. Interfaces*, 4(2):1118–1125, 2012.
- [89] H. Yaghoubi, A. Dayerizadeh, S. Han, M. Mulaj, W. Gao, X. Li, M. Muschol, S. Ma, and A. Takshi. The effect of surfactant-free tio 2 surface hydroxyl groups on physico-chemical, optical and self-cleaning properties of developed coatings on polycarbonate. *Journal of Physics D: Applied Physics*, 46(50):505316, 2013.
- [90] X. Zhang, F. Shi, J. Niu, Y. Jiang, and Z. Wang. Superhydrophobic surfaces: from structural control to functional application. *J. Mater. Chem.*, 18:621–633, 2008.
- [91] Y. Zhang and W. Ren. Numerical study of the effects of surface topography and chemistry on the wetting transition using the string method. *J. Chem. Phys.*, 141(24):244705, 2014.