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Press

Selin Manukyan

**Fundamental Investigation of  
Forced Wetting on Structured  
Surfaces**

Wetting on 3D Pyramidal Features

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**Selin Manukyan**

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# Nomenclature

## Roman Symbols

$\bar{h}$	Planck's constant
$\bar{n}$	coordinate normal to the wall
$\bar{R}$	capillary length in outer region
$\Delta F$	difference in forces
$\Delta G_s^*$	free energy of surface
$\Delta G_w^*$	molar activation free energy of wetting
$\ell$	mean free path
$\hat{r}$	position of the considered velocity and pressure in outer region
$\vec{k}$	volume force
$\vec{n}$	normal vector
$\vec{i}$	surface force
$f$	fraction of solid surface area wet by the liquid
$G$	Gibbs free energy
$g$	gravity
$h$	profile height
$h_0$	film thickness
$k$	Boltzmann's constant
$L$	characteristic length
$L_\delta$	cut-off length for unbounded force singularity at apparent dynamic wetting line
$L_c$	viscous length
$N$	Avogadro's number
$n$	number of sites per unit area
$P$	pressure

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$p_c$	characteristic pressure
$R$	contact line radius
$R_1/R_2$	mean radii of curvature
$R_a$	average roughness
$r_A$	a variable for advancing contact angle calculation
$r_R$	a variable for receding contact angle calculation
$r_W$	roughness ratio/Wenzel model
$R_x/R_y$	primary radii of curvature
$r_{CB}$	roughness ratio of the wet surface area/Cassie-Baxter model
$T$	temperature
$t_p$	length of plate
$v/U$	velocity
$v_{Wall}$	velocity to the wall
$w$	irreversible work done by the shear stress per unit displacement of length
$W_a$	work of adhesion
$W_c$	work of cohesion
$w_p$	width of plate
$x$	macroscopic length
$x_d/y_d$	data points
$x_t/y_t$	theory points
$F$	force
$F_0$	surface tension force
$F_v$	net force in advancing liquid front per length
$m$	mass
$S$	surface
$s$	slip length
$t$	time
$V$	volume

### **Greek Symbols**

$\alpha$	inclination of the substrate relative to the liquid surface
$\alpha$	phase variable

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$\beta$	slip length
$\delta$	perpendicular distance between the theoretical curve and the experimental
$\delta_x/\delta_y$	small shifting parameters
$\epsilon_x/\epsilon_y$	constants, minimizing the sum $D(\epsilon_x, \epsilon_y)$
$\eta$	viscosity coefficient
$\kappa$	curvature of the free surface
$\kappa_S^0$	frequency of molecular displacement of the surface
$\kappa_W^0$	frequency of molecular displacement in equilibrium
$\lambda$	average length of an individual molecular displacement in the three phase zone
$\mu$	dynamic viscosity
$\Omega$	surface area
$\Phi$	generic flow variable
$\phi$	fraction of solid/liquid interface of drop contact
$\Phi_v$	total dissipation in advancing liquid front
$\Pi$	surface pressure
$\rho$	density
$\sigma$	surface tension
$\sigma_{lg}$	surface tension between liquid and gas
$\sigma_{sg}$	surface tension between solid and gas
$\sigma_{sl}$	surface tension between solid and liquid
$\theta^*$	equilibrium contact angle after imbibition
$\theta_0$	equilibrium contact angle
$\theta_A$	advancing contact angle
$\theta_a$	apparent contact angle
$\theta_D$	dynamic contact angle
$\theta_m$	microscopic contact angle
$\theta_R$	receding contact angle
$\theta_S$	static contact angle
$\theta_W$	static apparent contact angle/Wenzel model
$\theta_w$	microscopic contact

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$\theta_{CB}$	static apparent contact angle/Cassie-Baxter model
$\theta_{crit}$	critical contact angle
$q_{\Phi}$	flow flux

### **Abbreviations**

Bo	Bond number
Ca	capillary number
CMOS	complementary metaloxidesemiconductor
Fr	Froude number
Oh	Ohnesorge number
PDMS	trimethylsiloxy terminated polydimethylsiloxane
PP	physical properties number
Re	Reynolds number
We	Weber number



# Contents

<b>Nomenclature</b>	<b>i</b>
<b>1 Introduction</b>	<b>1</b>
1.1 Motivation	1
1.2 Organization of the Study	2
<b>2 Essentials of Wetting Kinetics</b>	<b>5</b>
2.1 Wetting on Ideal Surfaces	7
2.1.1 No-Slip Condition	8
2.2 Static Wetting on Non-Ideal Rough Solid Surfaces	9
2.2.1 Wenzel's Model	9
2.2.2 Cassie-Baxter Model	9
2.2.3 Cassie-Baxter to Wenzel Transition	10
2.3 Phenomena on Dynamic Contact Angles	12
2.3.1 Molecular Kinetics at the Contact Line	13
2.3.2 Hydrodynamics of Wetting	14
2.3.3 Empirical Models	17
2.3.4 Exclusion of Cut-off Region	18
2.4 Chemical Heterogeneity	18
2.5 Summary	20
<b>3 Dip Coating</b>	<b>23</b>
3.1 Previous Studies	24
3.1.1 Characteristics of the Wedge Flow Near a Moving Contact Line	25
3.2 Equilibrium Liquid Shape of a Liquid-Solid Interface	28
3.2.1 Inertial and Viscous Effects on Dynamic Wetting	30
3.2.2 Determining the Film Thickness by Dip Coating of Homogeneous Surfaces	31

3.3 Experiments . . . . .	32
3.3.1 Experimental Setup . . . . .	32
3.3.2 Image Processing . . . . .	34
3.4 Validation of Fitting on Flat surfaces . . . . .	36
3.4.1 Fitting of the Data for the Meniscus Shape . . . . .	36
3.4.2 Contact Angle Measurements on Flat Smooth Surfaces . . . . .	37
3.5 Results and Discussion . . . . .	40
3.5.1 Definition of Contact Angle on Very Rough Surfaces . . . . .	43
3.5.1.1 Static and Dynamic Meniscus Shapes on Dry 3D Pyramidal Arrays . . . . .	43
3.5.2 Dynamic Advance On Dry 3D Pyramidal Arrays (10cSt PDMS) . . . . .	48
3.5.2.1 2mm Pyramidal Features . . . . .	48
3.5.2.2 1mm Pyramidal Features . . . . .	53
3.5.2.3 0.5mm Pyramidal Features . . . . .	56
3.5.2.4 Comparison of Observations for Dynamic Advancing Con- tact Line . . . . .	58
3.5.3 Receding of Wetted 3D Pyramidal Arrays (10cSt PDMS) . . . . .	63
3.5.3.1 2mm Pyramidal Features . . . . .	63
3.5.3.2 1mm Pyramidal Features . . . . .	65
3.5.3.3 0.5mm Pyramidal Features . . . . .	68
3.5.3.4 Comparison of Observations for Receding Contact Line . . . . .	70
3.5.4 Dynamic Advance On Dry 3D Pyramidal Arrays (100cSt PDMS) . . . . .	74
3.5.4.1 2mm Pyramidal Features . . . . .	74
3.5.4.2 1mm Pyramidal Features . . . . .	76
3.5.4.3 0.5mm Pyramidal Features . . . . .	78
3.5.4.4 Comparison All Observation for Advancing Contact line . . . . .	79
3.5.5 Receding of Wetted 3D Pyramidal Arrays (100cSt PDMS) . . . . .	83
3.5.5.1 2mm Pyramidal Features . . . . .	83
3.5.5.2 1mm Pyramidal Features . . . . .	83
3.5.5.3 0.5mm Pyramidal Features . . . . .	86
3.5.5.4 Comparison of Observations for Receding Contact Line . . . . .	87

3.5.6 Comparison of Amplitudes (Capillary Rise Height) and Periods of Dynamic Advancing and Dynamic Receding . . . . .	91
3.5.7 Change in Plate Orientation . . . . .	94
3.5.8 Transferability of Feature Size, Dipping Velocity and Feature Orientation . . . . .	95
3.6 Summary and Future Work . . . . .	98
<b>4 Wetting on Structured Surfaces with Dynamic Volume Change</b>	<b>101</b>
4.1 Dynamic Contact Angle Measurement on Advancing Liquid Volume . . .	103
4.1.1 Experimental Setup . . . . .	103
4.1.2 Image Processing . . . . .	104
4.1.3 Features of Surface Wetting . . . . .	106
4.1.3.1 Surface Coating . . . . .	106
4.1.3.2 Features of Test Liquids and Structured Substrates . . . . .	107
4.1.4 Experimental Results . . . . .	108
4.1.4.1 Water . . . . .	108
4.1.4.2 Glycerin-Water Mixture (85%-15% vol.) . . . . .	112
4.1.4.3 Silicon Oil Variations (5/10/20/50 cSt) . . . . .	112
4.1.5 Discussion . . . . .	122
4.2 Numerical Simulations . . . . .	128
4.2.1 Fundamentals of Numerical Simulations with OpenFOAM® . . . . .	128
4.2.2 Numerical Parameters Used in Computation . . . . .	130
4.2.3 Numerical Results and Comparisons with Experiments . . . . .	131
4.2.4 Discussion . . . . .	137
4.3 Summary and Future Work . . . . .	137
<b>5 Conclusion</b>	<b>141</b>
<b>A Physical Meaning of Dimensionless Numbers</b>	<b>143</b>
<b>B Properties of Test Liquids</b>	<b>145</b>
<b>C Scheimpflug Principle</b>	<b>147</b>
<b>D Complimentary Data Plots</b>	<b>151</b>

Contents

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D.1 Fluctuation Decay Graphs (related to Chapter 3) .....151

D.2 Contact Angle and Radius Measurements on Pyramidal Arrays (related to Chapter 4) .....151

**Bibliography** ..... **155**

# Chapter 1

## Introduction

### 1.1 Motivation

Wetting is the ability of a liquid to maintain contact with a solid surface, resulting from intermolecular interactions when the two are brought together. Wetting is important in the bonding or adherence of two materials. The degree of wettability is determined by a force balance between adhesive and cohesive forces. In coating operations, adhesion, detergency, lubrication, and other operations in which liquids are applied directly onto the solid surfaces; wettability plays a very crucial role which cannot be ignored. Wettability affects the spontaneous imbibitions of fluids into porous media and controls the separability of particulate solids by flotation.

The fundamentals of wetting are used very often and widely in painting, coating, lubrication and printing applications. The non-perfect nature of surfaces used in industrial applications, such as metal, glass and plastic surfaces of cars and planes or paper, require more complicated dynamic models than existing static models.

In literature the significance of wettability has been recognized, but is often discussed only in terms of measured contact angles of various liquids on various substrates. In 1805 Thomas Young [16] defined a contact angle equation taking into consideration the surface energies of the existing media at the intersection point. Unfortunately it is only applicable for the static case on perfectly flat and rigid surfaces, which in real world barely exist. In 1878 Gibbs [15] tried to express the contact angle relation with thermodynamical approach, again for static case. In 1960 Zisman [99] observed that contact angle decreases directly proportional to the surface tension of the liquid. In 1975 Hoffmann [47] postulated for the first time that if the equilibrium contact angle in the static case on a flat surface is zero, then the apparent dynamic contact angle depends solely on the capillary number ( $Ca$ ).

Until now there have been many publications about static wettability of Newtonian fluids on various surfaces but there is a lack of experimental and theoretical research addressing dynamic wetting combined with complex surfaces. Dynamic wetting on chemically heterogeneous and physically rough surfaces show unexpected phenom-

ena. The special dynamical behaviors between the liquid and the solid such as low adhesion, giant hydrodynamic slip, frictionless motion, and rebounds after impacts generates the super-hydrophobicity. Moreover understanding the physics of dynamic wetting between the oxidated steel sheets and the melted zinc is necessary to improve the performance of the hot dip galvanization. With modern experimental methods it is possible to comprehend the controlling mechanism of the interactions between the chemical or physical structure of a substrate and the morphology of its wetting layer to be able to manipulate the system. This allows controlling the process of shape formation of the complex fluids such as colloidal solutions or biological cells. On the other side, forced dynamic wetting, which is applied for gravure printing processes, is investigated broadly to hinder the air entrainment and ribbing as the substrates speed overcomes the liquid speed. All above mentioned application areas are the proofs of the timelessness of this topic.

The present study aims to enlighten the unapparent nature of complex dynamic wetting. The complexity of contact angle variation on structured surfaces with respect to ideal surfaces is presented and the phenomenon of contact angle hysteresis and pinning on structured surfaces is discussed in detail.

### 1.2 Organization of the Study

This study comprises three main chapters excluding the introduction and conclusion chapters. The final chapter summarizes the results and concludes the work presented here.

In Chapter 2 the essentials of wetting kinetics, hydrodynamics of wetting, phenomena and theories on dynamic contact angle are introduced and a general literature survey is given.

Chapter 3 addresses vertical forced wetting (dip coating). The dip coating experiments are realized with very small capillary numbers on very rough structured substrates compared to industrial applications to understand the underlying physics behind it. Current fitting methods are examined and alternative fitting methods are suggested. The experimental results on flat and structured three-dimensional surfaces in static and dynamic cases are studied and compared with the existing models.

The second part of the study, chapter 4, is about horizontal forced wetting by dynamic volume change. The same structured features are placed horizontally on a surface and by pumping liquid through a hole in the middle of the substrate, the contact angle change is observed in dependence on increasing liquid volume. The results are compared to the dip coating experiments and correlations are formulated.

The final chapter summarizes the results and conclusions on forced wetting in horizontal and vertical configurations. Moreover this chapter gives an outline for possible

## 1.2. Organization of the Study

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characterization and modeling methods of dynamic wetting on structured surfaces for possible future research to improve the understanding of dynamic wetting application.

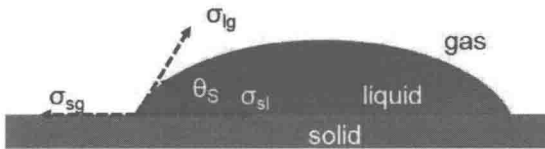




## Chapter 2

# Essentials of Wetting Kinetics

Wetting is the interaction of a liquid with a solid under vacuum, gas or another liquid. The intersection line of these three media is called contact-, wetting- or three phase-line. This interaction might be spreading of a liquid over a surface, penetration of a liquid into a porous medium, or displacement of one liquid by another. The contact angle expresses wettability quantitatively as a feature and helps to characterize a surface and determine the interactions between solids and liquids [1]. It is mostly measured using a sessile or resting drop. From the thermodynamic point of view, wettability is the balance between the adhesive forces, between the liquid and solid, and the cohesive forces within the liquid. The contact angle is determined by the difference of these two forces (Figure 2.1). The static equilibrium contact angle ( $\theta_s$ ) of the drop on the solid surface determines the wettability; a low contact angle is a sign of high wettability and a high contact angle is a sign of low wettability.



**Figure 2.1:** Contact angle of a liquid droplet on a rigid solid surface.

Wettability plays a major role in a wide range of industrial and biological applications such as lab-on-a-chip systems, polymer bonding for protective coatings, high speed coating/painting applications, inhibition of liquids into porous media, condensation heat transfer, food (taste) perception on the tongue and palate, eye drops (artificial tears), printing technologies, nucleation control, lubrication and friction reduction. Being able to characterize, describe and manipulate the wetting properties of a substrate for a specific liquid or a group of target liquids are at the focus of many industrial and biological applications [2].

When a liquid displaces another fluid or gas from a solid surface, this is called *dy-*