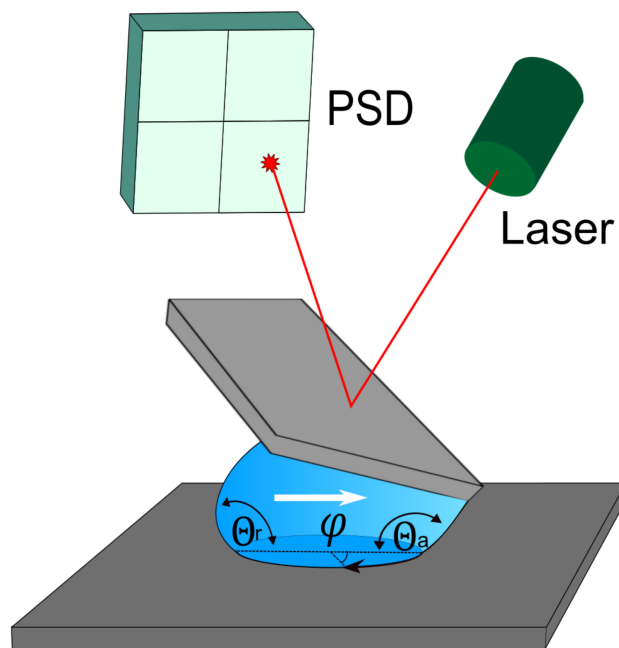


Sliding Drops: Unveiling the Influence of Defects on Dynamic Wetting



Dissertation
zur Erlangung des Grades
"Doktor der Naturwissenschaften" am Fachbereich Physik,
Mathematik und Informatik
der Johannes Gutenberg-Universität
in Mainz

Diego Ignacio Cortés Garcés
Mainz, 2026

Date of exam: 21.08.2026

This work is licensed under a **Creative Commons Attribution 4.0 International License (CC BY 4.0)**.

Abstract

The friction and dynamics of sliding droplets on hydrophobic surfaces are fundamental to numerous industrial and natural processes, ranging from self-cleaning coatings to microfluidic systems. This thesis investigates the microscopic origins of energy dissipation and Contact Angle Hysteresis (CAH) by focusing on the real-time interaction between the triple-phase contact line (CL) and sub-microscopic surface defects. To address this problem, the research is structured around two distinct experimental campaigns.

In the first campaign, detailed in Chapter 3, we utilize a functionalized droplet probe in an Atomic Force Microscope (AFM) to quantify interactions at the nanoscopic scale. By attaching a picoliter-scale droplet ($\approx 30 \mu\text{m}$ diameter) to a tipless cantilever, we measure the lateral friction forces encountered by the CL as it interacts with isolated, well-defined defects. These measurements validate a linear-force model for pinning, demonstrating that the Joanny-de Gennes formalism remains an accurate description of the mechanical restorative forces at these sub-microscopic scales.

The second campaign, presented in Chapter 4, employs a tilted-plate setup coupled with high-speed reflection microscopy to investigate macroscopic drop behavior. Capable of recording at frame rates up to 100,000 fps, this system provides the temporal resolution necessary to observe rapid contact line fluctuations and "stick-slip" dynamics on various hydrophobic substrates. The resulting high-speed datasets are processed through an automated image analysis pipeline, incorporating Canny edge detection, morphological transformations, and iterative polynomial fitting, to extract the precise coordinates of the CL. We quantify the magnitude of pinning through the Deviation (δ), defined as the local distance between the physical CL and its ideal, unperturbed state.

The synthesis of these investigations reveals a significant "Hysteresis Gap". Statistical analysis across various hydrophobic coatings (PFOTS, PFOMS, Teflon, and PS) shows no direct correlation between the density of resolvable nanoscopic defects and the measured macroscopic hysteresis. Even when accounting for sub-diffraction contact line perturbations down to a 50 nm limit, the energy dissipated by individual pinning events remains significantly lower than the total energy associated with macroscopic drop friction. These findings imply that while defects may influence contact angle hysteresis, this effect does not exceed half a degree, a value that is considerably lower than the total hysteresis observed on the studied surfaces.

Keywords: High-speed Imaging, Lateral Force Microscopy, Contact Line Dynamics, Droplet Probe, Pinning Force, Contact Angle Hysteresis.

Contents

1	Introduction	1
1.1	Historical Overview	2
1.1.1	Early Observations of Liquids and Interfaces	2
1.1.2	Development of Capillarity Concepts in the Seventeenth and Eighteenth Centuries	3
1.1.3	Nineteenth Century: Laplace, Young, and Plateau	3
1.1.4	Late Nineteenth and Early Twentieth Century: Thermodynamics and Measurement	4
1.1.5	Mid- to Late Twentieth Century: Recognition of Dynamic Phenomena	4
1.1.6	Towards Dynamic Contact Line Physics	5
1.2	Overview of thesis	5
1.2.1	Publications associated with this thesis	6
1.3	Interfaces and Surface energy	6
1.3.1	Surface Tension and Surface Energy	7
1.3.2	Contact Angle	8
1.3.3	Young's Equation	9
1.3.4	Dynamic Contact Angle and Hysteresis	9
1.3.5	Furmidge's Equation and Lateral Force Derivation	10
1.3.5.1	Roll Off Angle	11
1.3.6	Young-Laplace Equation	11
1.3.7	Curvature: Differential Approach	12
1.4	Small Perturbation on the Contact Line	13
1.4.1	Localized Force	16
1.4.2	Strong Pinning	16
1.5	Energy dissipation and Contact Angle	18
1.5.1	Hydrodynamic Theory	20
1.5.2	MKT Theory	20
1.5.3	Defect Contribution	21

2	Experimental Methods	23
2.1	Sample Preparation and Characterization	23
2.1.1	Fluorinated Silane Monolayers (PFOTS and PFOMS)	23
2.1.2	Polymer Thin Films (PS and Teflon AF)	24
2.1.3	Polydimethylsiloxane (PDMS) Brushes	24
2.2	Atomic Force Microscopy	24
2.2.1	Operating Modes	25
2.2.1.1	Contact Mode Imaging	25
2.2.1.2	Intermittent Contact Mode	26
2.3	Lateral Force Microscopy (LFM)	26
2.4	Droplet Probe Fabrication	27
2.4.1	Cantilever Preparation	28
2.4.1.1	Fluorination process	28
2.4.2	Sticky Point	28
2.5	Contact Angle Goniometry and Dynamic Wetting	29
2.6	Tilted Plate Setup	31
2.6.1	Inverted Microscopy and Fast Camera	31
3	AFM: Measuring Contact Line-Defect Interactions	33
3.1	Setup	33
3.1.0.1	Sample and Liquid Characterization	34
3.1.0.2	Fixing a Colloid on the Surface	34
3.2	Data Analysis	35
3.2.1	Force Calibration	35
3.2.2	Background Extraction	36
3.3	Results for Smooth Surface	37
3.3.1	Peripheral Thickness and Contact Line Deflection	37
3.4	Sphere Results	38
3.4.1	Azimuthal Dependence	39
3.4.2	Linear Behavior and azimuthal dependence results	40
3.5	Defect-Drop Interaction Model	41
3.5.1	Meniscus Formed by a Sphere	42
3.6	Analysis of Experimental Results	45
3.7	Numerical Simulations	47
3.7.1	Simulation Methodology and Boundary Conditions	47
3.8	Conclusions and Discussion	48

4	Reflection Microscopy: Imaging Contact Line Dynamics	50
4.1	Optical Measurements	51
4.1.1	Experiment	51
4.1.2	Sample Characterization	51
4.2	Image Processing and Data Visualization	52
4.2.1	Preprocessing	53
4.2.1.1	Metadata Extraction and Signal Normalization	53
4.2.1.2	Background Subtraction and Contrast Optimization	54
4.2.1.3	Iterative Edge-Preserving Denoising	54
4.2.1.4	Gaussian smoothing	54
4.2.1.5	Guided Filtering	55
4.2.2	Edge Detection	55
4.2.2.1	Morphological Feature Extraction	55
4.2.3	Analysis and coordinates extraction	56
4.2.3.1	Quantifying the deflection	58
4.3	Results	59
4.3.1	Deflection Maps and Defect Density Distribution	59
4.3.2	Average Deflection and Contact Line Roughness	60
5	Influence of all Size Defects in Friction Forces	64
5.1	Defect Density with AFM Friction Force	66
5.1.1	Natural Defects	66
5.1.2	Special Case: PDMS Brushes	67
5.1.3	Comparison of AFM and Optical Results	68
5.1.4	Thermal Activation and Minimum Interaction	70
5.2	Chemical Defects	71
5.2.1	Rectangular Patch	72
5.3	Interpreting the Results	74
6	Conclusions and Outlook	76
6.1	Final Remarks on Energy Dissipation	77
6.2	Outlook and Future Directions	77
	Bibliography	83
	Appendix A: Use of AI Tools	84
A	“Use of AI tools”	84
	Curriculum Vitae	85

List of Figures

1.1	Surface Tension Schematic.	8
1.2	Contact Angle and Interfacial Tensions.	8
1.3	Dynamic Contact Angle.	9
1.4	Differential force contribution on a sliding drop.	11
1.5	Representation of curvature in a liquid meniscus.	12
1.6	Small Perturbation on the Contact Line.	15
1.7	Strong Pinning.	17
1.8	Regimes on the contact line.	19
2.1	AFM Illustration.	25
2.2	Friction force AFM.	26
2.3	Sequence: Preparing droplet probe.	28
2.4	Scanning Electron Microscopy image of hydrophilic spot on a treated cantilever.	29
2.5	Goniometer.	30
2.6	Experimental setup for high-speed reflection microscopy.	31
3.1	Setup description.	34
3.2	Drop friction single line Scan.	35
3.3	Friction Map before and after background extraction.	37
3.4	Colloid on teflon surface.	38
3.5	Illustrating friction rings.	39
3.6	Drop-sphere interaction curves.	40
3.7	Force, Slope and Work v/s Azimuthal Angle.	41
3.8	Meniscus formed on the semi-spherical defect.	42
3.9	Force expressed in terms of ϕ	43
3.10	Sequence of events when the drop passes a spherical defect.	44
3.11	Contribution of small localized pinning on the contact line.	45
3.12	Calculated dependency of CAH versus the density of hemispherical defects.	46
3.13	Visual representation of the Surface Evolver Simulation.	47
3.14	Contact line-defect interaction on different parts.	48

3.15	Surface Evolver results.	49
4.1	Setup reflection microscopy.	51
4.2	Example of optical results.	53
4.3	Workflow for image analysis and defect quantification.	53
4.4	Representation of the two approaches for edge extraction.	55
4.5	Visual representation of how the coordinates are extracted.	56
4.6	Deflection maps and defect size distribution.	57
4.7	Density extraction procedure.	58
4.8	Density of optically resolvable defects.	59
4.9	Results for the average contact line deflection and roughness.	60
4.10	Surface plot of the contact line perturbation.	61
4.11	Time evolution of the energy density for the receding contact line.	62
5.1	Friction Force Maps of the smooth surfaces.	65
5.2	Droplet-probe AFM results.	66
5.3	Friction force map of a drop scanning PDMS brushes.	67
5.4	Comparison of AFM and Optical Results.	68
5.5	Distribution of contact line deflections measured by reflection microscopy and AFM, for different substrates.	69
5.6	Critical boundary radius for thermal activation.	71
5.7	Schematic of a drop moving over a hydrophobic and hydrophilic patch.	73
5.8	Timeline of a square patch pinning.	74
5.9	Defect energy density of the five samples studied versus the contact angle hysteresis.	75

Chapter 1

Introduction

Wetting interactions are ubiquitous in human life and across the natural world. A deeper understanding of these processes has driven the development of increasingly efficient technologies [1, 2], enabling a wide range of applications in textiles, materials science, food science, and agronomy. Precision control over wetting properties is a cornerstone of modern technology, spanning from the production of waterproof fabrics and self-cleaning surfaces to specialized coatings designed to either promote or suppress liquid spreading.

In parallel, biological systems [3], including animals, plants, and fungi, have evolved tissues with highly specialized wetting properties, refined over millions of years of evolution. Notable examples include water-repellent lotus leaves [4], adhesive insect pads, and antifouling marine surfaces [5]. Despite the significant technological advances inspired by these natural systems and the progress made through biomimetic engineering, many fundamental questions remain unanswered. In particular, the microscopic mechanisms governing drop friction and the resistance to motion on solid surfaces are still not fully understood.

Since the formalization of wetting and drop dynamics as a field of study, various theoretical frameworks have been proposed to explain the origins of drop friction. From a hydrodynamic perspective [6], friction is often attributed to viscous dissipation within the drop, which leads to geometric deformation and an imbalance in interfacial tensions. Similarly, from a molecular point of view, specific interactions at the interface can affect the interfacial tension in a comparable manner, manifesting as a force opposing the motion. While these hydrodynamic and molecular approaches provide valuable insights, they are generally limited to specific cases and often fail to account for the overall complexity of friction forces [7].

A widely discussed cause of drop friction is the continuous interaction between the sliding contact line and microscopic surface defects [8]. These defects lead to contact angle hysteresis, a phenomenon where the energy required to overcome chemical heterogeneities or topographical protrusions and holes is dissipated as the drop moves. Although other mechanisms, such as charge deposition and surface adaptation, also contribute to the total resistive force, this research focuses on the defect approach to quantify its specific relevance to drop friction. By

characterizing the different surfaces involved in this study, we find that despite having similar topography and static contact angle, the friction force of sliding drops differ considerably between each other. To address this discrepancy, this doctoral research explores new methods for probing liquid-solid interactions at the micro- and nanoscales. We combine complementary experimental techniques, including Atomic Force Microscopy (AFM) and optical microscopy coupled with high-speed imaging. These experimental observations are integrated with numerical simulations and theoretical modeling. Together, this approach provides a comprehensive framework to investigate how microscopic chemical and topographic defects influence the dynamics of the three-phase contact line for liquid drops sliding over solid surfaces. Our results will demonstrate that contact angle hysteresis (CAH) does not occur solely through pinning and depinning processes; rather, these events account for only a small fraction of the total CAH.

1.1 Historical Overview

Before starting the discussion on interfaces, wetting and dynamic drops, it is essential to review the historical timeline of interface science. Just as the development of physics, the case of interfaces began with early speculations and evolved into the comprehensive knowledge we possess today.

1.1.1 Early Observations of Liquids and Interfaces

Water and its behavior have fascinated observers for centuries, long before formal scientific theories were developed. Ancient scholars noted how liquids rise in narrow tubes and interact with solid boundaries, hinting at interfacial phenomena that would only be understood much later. For example, Leonardo da Vinci made some of the first recorded observations of capillary rise and fluid motion in small cracks and channels, recognizing that liquid could climb against gravity [9]. Similarly, *Galileo Galilei* made early qualitative observations of fluid behavior, including the rise and suspension of liquids in confined spaces, illustrating an intuitive grasp of surface effects long before scientific formalism existed [10].

In the ancient world, Greek engineers such as *Hero of Alexandria* (active c. 1st century AD) developed sophisticated pneumatic and hydraulic devices that exploited the behavior of fluids and gases within confined spaces [11, 12]. Although Hero did not formulate a theory of capillarity, his descriptions of mechanisms where liquid displacement occurred as a result of thermal expansion of air demonstrate practical engagement with fluid–air interfaces. Other ancient observers, including naturalists such as Pliny the Elder (23–79 AD), recorded how substances like oil altered the appearance and behaviour of water surfaces, which can be interpreted as early qualitative observations related to surface phenomena [13]. These empirical insights laid the groundwork for later quantitative investigations into interfacial forces and capillarity that

emerged in the seventeenth and eighteenth centuries.

1.1.2 Development of Capillarity Concepts in the Seventeenth and Eighteenth Centuries

After early empirical observations by Renaissance thinkers, the seventeenth and eighteenth centuries saw the first detailed studies of liquid rise in narrow tubes and related interfacial effects. Experimental work by *Francis Hauksbee* in the early 1700s noted that liquids ascend more in narrower tubes and that the phenomenon was not appreciably altered by vacuum conditions, indicating an intrinsic effect of the fluid and its interaction with the solid surface [14,15]. These careful observations were followed between 1718 and 1719 by the British physician and scientist James Jurin, who quantified this effect in what is now known as *Jurin's law*: the maximum height of liquid rise in a capillary tube is inversely proportional to the tube diameter [16]. This provided one of the earliest quantitative expressions related to capillarity.

Later in the eighteenth century, *Johann Andreas Segner* and others recognized that surface phenomena behave as if liquid interfaces possess an effective “tension,” laying conceptual foundations for later theories of surface energy [15]. These seventeenth and eighteenth century investigations established capillary rise as a reproducible physical phenomenon and prepared the ground for the formal theoretical treatments that would follow at the start of the nineteenth century.

1.1.3 Nineteenth Century: Laplace, Young, and Plateau

A major advance in the scientific understanding of interfacial phenomena occurred in the early nineteenth century with the work of *Thomas Young* and *Pierre-Simon Laplace*. In 1805 Thomas Young published one of the first theoretical treatments linking capillary action to surface tension and introduced the idea that the contact angle formed between a liquid and a solid is determined by an equilibrium of interfacial forces [15,17]. Young's insight provided a qualitative framework for understanding wetting and laid the conceptual foundation for later mathematical formalism.

Pierre-Simon Laplace (1749–1827) built on Young's work by developing the mathematical expression that relates the curvature of a fluid interface to the pressure difference across it. The resulting relation, now known as the Young–Laplace equation, quantitatively describes how surface tension and the principal radii of curvature determine the capillary pressure at a liquid–air or liquid–liquid interface [17,18]. This combination of Young's conceptual contact angle and Laplace's curvature principle remains central to modern surface and interfacial science.

In the mid-nineteenth century, Belgian physicist *Joseph Plateau* (1801–1883) undertook extensive experimental studies of surface tension in soap films, drops, and bubbles. Plateau's meticulous investigations of soap film shapes and his formulation of what became known as *Plateau's laws* provided empirical evidence of how surface tension governs minimal surfaces

and foams [19]. His work helped bridge the gap between theoretical descriptions of surface tension and observable phenomena in complex fluid systems.

1.1.4 Late Nineteenth and Early Twentieth Century: Thermodynamics and Measurement

By the late nineteenth century, the influence of thermodynamics on the study of interfaces became increasingly evident. The development of modern energy concepts, particularly the formalization of free energy and work, enabled scientists such as Dupré and Gibbs to apply thermodynamic principles directly to wetting phenomena [20–22]. Rather than viewing interfaces purely mechanically, Josiah Willard Gibbs formally defined interfacial free energy as a key thermodynamic property. This conceptual breakthrough provided the necessary framework for the quantitative analysis of contact angles and wetting..

Parallel to these theoretical advances, experimental techniques for characterizing wetting were actively refined. Sessile drop measurements became a standard method for determining contact angles, and approaches such as the Wilhelmy plate method and Zisman plot were developed to quantify wettability and critical surface tension of solids in contact with liquids. These methods allowed surface scientists to measure not only equilibrium contact angles but also apparent and dynamic values on real, complex surfaces [23].

1.1.5 Mid- to Late Twentieth Century: Recognition of Dynamic Phenomena

Although equilibrium concepts such as the Young–Laplace equation provided a robust description of static wetting, experimental studies throughout the twentieth century revealed that liquid motion on solid surfaces could not be fully understood within this static framework. In practice, the contact angle observed when a drop is advancing differs from that when it is receding, a phenomenon known as contact angle hysteresis. This dynamic behaviour, dependent on drop motion and surface heterogeneities, became widely recognised and explored experimentally, particularly in the 1950s and 1960s [11, 24].

During this period, several empirical observations linked contact line motion, hysteresis, and energy dissipation. For instance, Furmidge’s experiments [25] on drops on inclined planes related the force needed to initiate motion to the difference between advancing and receding contact angles, providing one of the earliest quantitative connections between dynamic wetting behavior and frictional resistance on surfaces.

1.1.6 Towards Dynamic Contact Line Physics

By the late twentieth century, it became clear that the motion of the contact line involves complex interactions between hydrodynamic flow, surface heterogeneity, and molecular processes at the interface. Classical hydrodynamics alone fails to fully describe the motion of a contact line without invoking microscopic length scales or additional physics. Researchers responded with two complementary theoretical frameworks: hydrodynamic models, such as those by Cox and Voinov [6], focused on how viscous dissipation alters apparent dynamic contact angles, while Molecular Kinetic Theory (MKT) descriptions [26], developed by Blake, Haynes, and others, emphasized the role of localized molecular displacements at the solid–liquid interface.

These developments established the modern view that dynamic wetting and contact line motion arise from a combination of viscous, molecular, and pinning effects. Contemporary experiments and models continue to refine this picture, investigating how surface defects, chemical heterogeneities, and flow conditions influence dynamic contact angles and frictional forces on moving drops.

1.2 Overview of thesis

This dissertation is structured to provide a multi-scale investigation into the mechanisms of drop friction and contact angle hysteresis, progressing from the fundamental physics of a single pinning event to the macroscopic behavior of sliding drops.

Chapter 1 establishes the theoretical and historical framework of the research. It reviews the development of capillarity from early 19th-century concepts to modern theories of dynamic wetting. Furthermore, the chapter introduces the fundamental physics of contact line pinning and the Joanny-de Gennes model, which serves as the basis for understanding the energetic barriers encountered by moving droplets.

Chapter 2 details the experimental methodology and technical innovations developed for this work. This includes the preparation of specialized droplet-probes on the AFM cantilever to ensure droplet stability during force measurements. The chapter also describes the characterization techniques used for the various hydrophobic surfaces investigated throughout the thesis.

Chapter 3 focuses on the interaction between picoliter droplets and individual sub-microscopic defects. Through a combination of droplet-probe Atomic Force Microscopy (AFM) and numerical simulations in Surface Evolver, the force-distance relationship of a single pinning event is quantified. These results are used to validate the point-force model and characterize the energy dissipation associated with isolated topographic and chemical heterogeneities.

Chapter 4 expands the scope to macroscopic sliding drops and natural surface defects. A novel high-speed reflection microscopy technique is introduced, capable of capturing contact

line fluctuations at 100,000 frames per second. The chapter evaluates the density and size distribution of defects across multiple surfaces. A central focus is the analysis of the "Hysteresis Gap", the discrepancy between the energy dissipated by the defects observed with microscopy and the measured macroscopic contact angle hysteresis.

Chapter 5 Integrates the implementation of high-resolution AFM friction maps, comparing with the optical approach and using both results to obtain a complete spectrum of defect and analyzes its contribution to the contact angle hysteresis. At the very end of the chapter, the findings of the preceding chapters are synthesized, providing final remarks on the role of defects in dynamic wetting. It discusses the implications of the results for current wetting models and proposes an outlook for future research, particularly regarding molecular-scale contributions to liquid-solid friction.

1.2.1 Publications associated with this thesis

- **Diego Cortés**, Michael Kappl, Pranav Sudersan, Tomás Corrales, and Hans-Jürgen Butt. "Friction Measurements with Picoliter Droplets Using Scanning Probe Microscopy." *Physical Review Letters*, 2025.
- Yaolei Xiang, Benedikt Straub, **Diego Cortés**, Hans-Jürgen Butt, and Kaloian Koynov. "When contact lines remember: Surface charge and the evolving interaction with defects." *Droplets*, 2025.
- Aranzazu Sierra-Fernández, **Diego Cortés**, Miguel A. Monclus, Kenneth J.T. Livi, Michael Kappl, Stefan A.L. Weber, D. Howard Fairbrother, and Rafael Fort. "Nacre-Inspired Composite Coatings with Hierarchical Architecture for Durable Surface Protection." *Chemistry of Materials*, 2026.
- **Diego Cortés**, Léa Delance, Yaolei Xiang, Lin Yiang, Kaloian Koynov, and Hans-Jürgen Butt. "Contribution of nanoscopic defects on drop friction and contact angle hysteresis." Submitted to *Droplets*.

1.3 Interfaces and Surface energy

An interface can be defined as the region separating two phases; likewise, a phase is a region of space in which the chemical and physical properties of a material are uniform [27]. The study of interfaces is of utmost importance for understanding a wide variety of interactions at the nanoscopic and microscopic scales. Interfaces can be investigated from different perspectives depending on the field of study, including physics, chemistry, materials science, and biology.

An interface does not necessarily involve different states of matter. Interfaces may exist between two liquids or between a solid and a liquid, among other combinations. The only

case that does not form a stable interface is that of gas–gas systems, as gases tend to mix spontaneously.

In this work, the focus is placed on partial wetting phenomena, where three phases are involved: a solid phase (the repellent surface), a liquid phase (the drop), and a gaseous phase (air). While a liquid can fully spread on a surface to form a continuous film under complete wetting conditions, partial wetting causes the liquid to remain bounded. In this regime, the three phases meet at the so called three-phase contact line, which plays a central role in the description of wetting behavior. In addition, the liquid–air and liquid–solid interfaces contribute significantly to the overall force balance and energy landscape governing wetting.

Despite extensive research, several fundamental questions related to wetting dynamics remain open. In particular, the roles of contact angle hysteresis, electrical charging effects, and friction forces at the contact line are still not fully understood. Clarifying how these factors influence drop motion and resistance on solid surfaces is essential for developing a comprehensive description of wetting and drop friction phenomena.

1.3.1 Surface Tension and Surface Energy

Surface tension and surface energy are fundamental concepts for understanding wetting phenomena and liquid–solid interactions [28]. Surface energy refers to the excess free energy associated with the presence of an interface compared to the bulk phases, and it arises from the imbalance of intermolecular forces experienced by molecules at the interface. In liquids, surface energy is directly related to surface tension, which quantifies the energetic cost of creating additional interfacial area.

Surface tension (ST) is therefore one of the key physical quantities governing wetting behavior and drop interactions. It determines the equilibrium shape of liquid interfaces, the forces acting at boundaries, and ultimately the macroscopic behavior of liquids in contact with solid surfaces. Differences in surface tension lead to variations in liquid geometry, capillary forces, and dynamic response, all of which are central to wetting phenomena.

To develop a deeper understanding of surface tension, it is useful to introduce its definition from two complementary perspectives: a mechanical approach and a thermodynamic (energetic) approach. These two viewpoints provide equivalent descriptions of surface tension, yet they emphasize different physical aspects of the same interfacial phenomenon [7].

The mechanical interpretation of surface tension considers it as a force per unit length acting tangentially along an interface. This concept can be illustrated using a simple two-dimensional liquid model, as shown in Fig. 1.1. In this representation, the blue region corresponds to a bidimensional liquid film bounded by a movable rod. When the rod is displaced by an amount Δx in the horizontal direction, the surface area of the liquid increases by $\Delta A = 2b \cdot \Delta x$, where b is the length of the rod. The force required to maintain mechanical equilibrium during this

deformation is directly related to the surface tension.

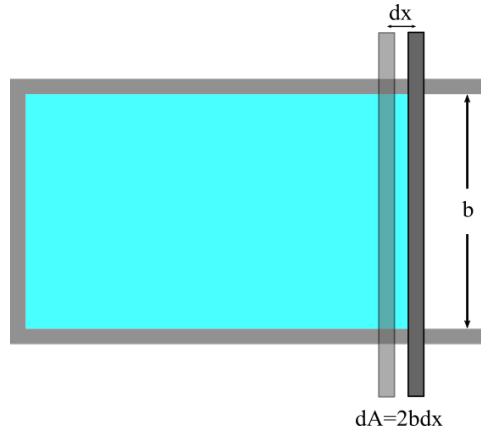


Figure 1.1: Scheme of the mechanical ST explanation, the blue colored square represent the bidimensional liquid. The rod can move in the x direction, then any change in the area is related to the rod displacement by $\Delta A = 2b \cdot \Delta x$.

1.3.2 Contact Angle

The simplest way to quantify the wetting of a liquid on a surface is to measure the contact angle (CA) [28]. When we put a drop on a surface, the shape of it will change according to the surface tension of the liquid, but also to the energy of the surface. In wetting experiments, the three phase interface between the liquid, solid and air is also called contact line, where the liquid and the surface will form an angle (figure 1.2). Depending on the wetting state of the liquid, we will call this angle contact angle (CA), in general, we will use this CA to have an idea of the wetting properties of the solid interacting with a particular liquid, since the liquid will have the same behaviour with the surface, the CA will be the same with a small dispersion and we can characterise the surface using this number.

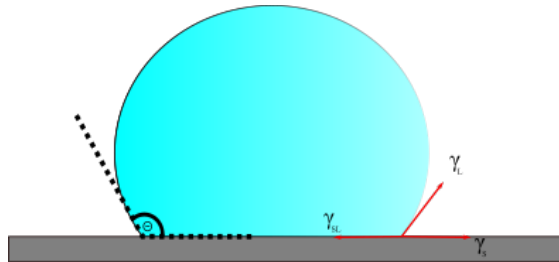


Figure 1.2: Representation of a drop lying on a surface, in the left side the contact angle (Θ) is shown, in the right side, the interface tensions that are present at the contact line.

1.3.3 Young's Equation

We know that for a liquid drop on a surface, the contact angle quantify the wetting interaction of the liquid on the solid surface. For total wetting we have $CA = 0$ then the liquid does not have a drop shape, but a puddle. In the case where $CA > 0$, the liquid have a drop shape and the contact angle will depend on the equilibrium between the spreading force between the liquid and solid and the ST contribution. To understand this equilibrium of forces, Young proposed a model where we consider the three different interfacial tensions in the contact line [29]:

The solid-vapor interface γ_S , the surface tension γ_L and the surface liquid interface γ_{SL} . Looking at figure 1.2 we can make a balance of this tensions, but for the ST we need to consider the horizontal contribution, then we get the equation 1.1 relating this interfacial tensions with the CA. When the solid-vapor interface is higher than the solid liquid interface we can notice that the term $\gamma_L \cos \Theta$ is positive, this mean that the CA is in the range $0 < \Theta < 90^\circ$. In the opposite case, the term $\gamma_L \cos \Theta$ is negative and thus the CA should be higher than 90° .

$$\gamma_L \cos \Theta = \gamma_S - \gamma_{SL} \quad (1.1)$$

Although this formula gives us a good idea of the liquid solid behavior, in practice is not accurate. This is because the surfaces are not perfect and uniform, the roughness and heterogeneity have an influence in the wetting phenomena [30].

1.3.4 Dynamic Contact Angle and Hysteresis

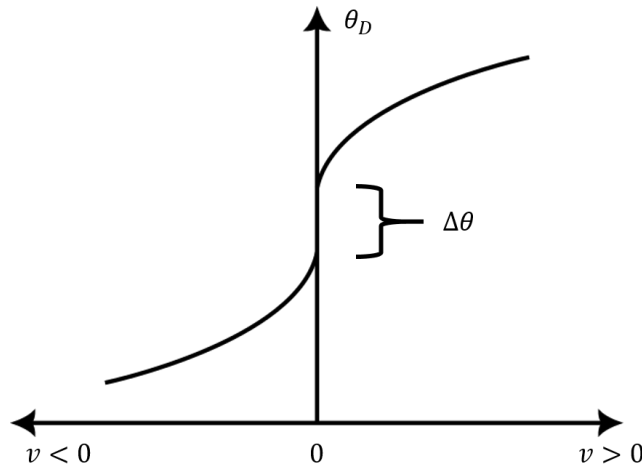


Figure 1.3: Schematic representation of contact angle hysteresis (CAH). The plot displays the contact angle (vertical axis) as a function of the moving contact line speed (horizontal axis) for both the advancing angle θ_a (left) and receding angle θ_r (right). The resulting hysteresis is quantified as $\Delta\theta = \theta_a - \theta_r$.

Despite the foundational achievements in the study of wetting phenomena, the transition

from theoretical models to real-world applications remains a significant area of inquiry. Young's equation provides a description for an ideal, chemically homogeneous, and perfectly smooth surface; however, such conditions are rarely met in experimental or industrial settings [31, 32].

As a droplet moves across a surface, its contact angles change dynamically based on the direction and speed of translation (Figure 1.3). During this motion, the system is characterized by two distinct dynamic contact angles: the advancing contact angle (θ_a) at the leading edge and the receding contact angle (θ_r) at the trailing edge. The difference between θ_a and θ_r defines the contact angle hysteresis (CAH), a key indicator of surface heterogeneity and energy dissipation during droplet motion

1.3.5 Furmidge's Equation and Lateral Force Derivation

Characterizing a surface solely through the static contact angle is insufficient for describing dynamic behavior, as static measurements often fail to capture the real nature of surfaces interacting with liquids [33]. On real surfaces, topographic roughness or chemical heterogeneities can trap the droplet in metastable states, such as the Cassie-Baxter or Wenzel regimes, contributing directly to the observed hysteresis.

To quantify the lateral force required to move a droplet, the tension along the triple-phase contact line must be integrated. By parameterizing the contact line using the azimuthal angle ϕ , the differential force contribution in the direction of motion is confined within an element $d\phi$ (Figure 1.4).

The total friction force F_f is obtained by integrating the component of the surface tension force acting parallel to the surface along the entire contact line [25]:

$$F_f = \int_0^{2\pi} \gamma \cos \theta(\phi) \cos \phi r(\phi) d\phi \quad (1.2)$$

Derivation: To arrive at a practical form of this equation, an assumption regarding the distribution of the contact angle $\theta(\phi)$ is required. A common simplification assumes that the contact angle varies such that the integral can be approximated by a characteristic width and a geometric factor k , with values between 0 and 1. For a droplet with a width w (perpendicular to the direction of motion), the integration of the horizontal force components results in the standard form of Furmidge's equation [25, 33]:

$$F_L = kw\gamma(\cos \theta_r - \cos \theta_a) \quad (1.3)$$

In this formulation, k is an experimental constant typically ranging between $1/2$ and $\pi/2$, depending on the specific shape of the contact line. Empirical evidence has consistently demonstrated that the lateral friction force is directly proportional to the contact angle hysteresis. In an ideal system where $\theta_a = \theta_r$ (zero hysteresis), the net frictional force on the droplet vanishes,

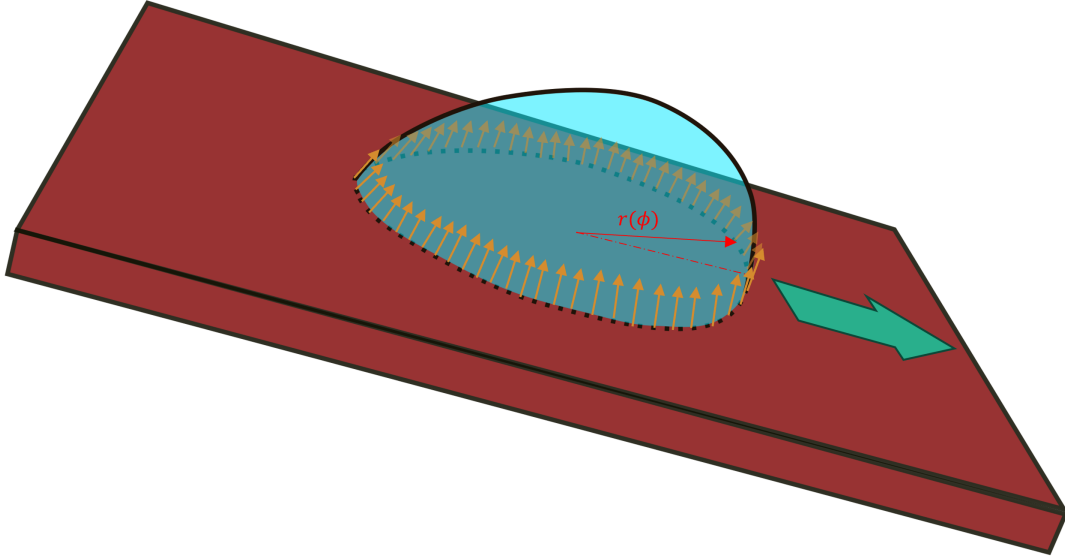


Figure 1.4: Schematic of a sliding drop of radius $r(\phi)$. The differential force contributions (orange) are defined based on the azimuthal angle ϕ and integrated to determine the total friction force.

highlighting that CAH is the fundamental origin of lateral adhesion and resistance to motion.

1.3.5.1 Roll Off Angle

Roll off angle (RA) is a straightforward procedure to quantify the adhesion of the liquid and the surface, providing a further understanding of the wetting interaction [34]. The surface rest on a leveled stage with a drop is placed on top of it, then by tilting the surface the drop will slide depending on its wetting state. We can separate the result in two kinds. When the RA is less than 90° we can have a quantitative result, associating the roll-off angle with the wetting of the surface. On the other hand, when the angle of 90° is exceeded and there is no movement of the drop we cannot obtain a RA [35]. One important step is to consider the static CA and the RA to make conclusions, for example, if the CA of a liquid is over 120° and there is no displacement, the drop is in Wenzel state.

1.3.6 Young-Laplace Equation

As the ST tends to minimize the surface, when a liquid is not in a container, we could expect to see always a planar shape in the liquid on a solid (CA zero). Nevertheless, in many cases we have a curvature and a $CA > 0$. This curvature is influenced by balance between the solid-

liquid interaction as well as the pressure inside and outside our liquid. Nevertheless the drops can have more shapes, to explain bubbles, meniscus and other geometries seen in liquids we need a further understanding of the surface behavior. For curved interfaces we can appreciate that, since the liquid is in equilibrium, there is a different pressure between the two parts of the interface, we call this the Laplace pressure. The Laplace pressure provokes a curvature that could be either positive or negative [27]. For positive or convex curvatures, the center of the curvature is inside the liquid phase, and the curvature will bend outside the liquid (e.g drops, meniscus on a hydrophobic surface). On the other hand, negative curvatures will have a concave shape, and the center of the curvature will be outside the liquid phase (bubbles, meniscus on hydrophilic system).

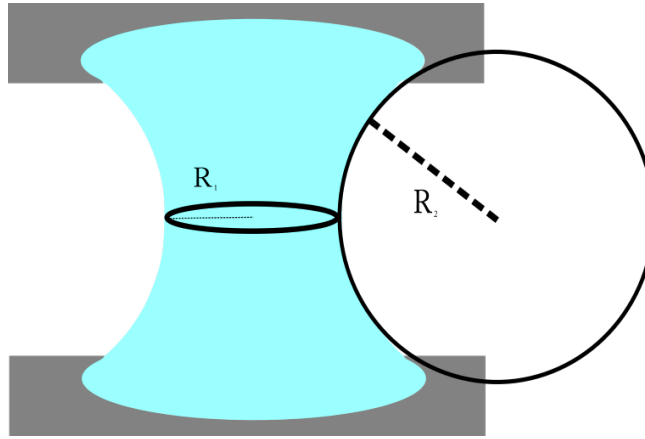


Figure 1.5: Representation of a liquid meniscus between two plates, in this example the two radius for the curvature are shown.

Equation 1.4 shows the relation between the curvature of the liquid and the Laplace pressure between the liquid and the environment when the liquid is in equilibrium. For example, for a drop we have positive curvature and thus positive pressure difference. The opposite case is for meniscus (Fig. 1.4) and liquid bubbles, where we have a negative pressure difference and thus a negative curvature [27].

$$\Delta P = \gamma \cdot \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \quad (1.4)$$

1.3.7 Curvature: Differential Approach

Most of these rules and results come directly from experiments and are empirical results and have a practical approach as well, if we want to have a further understanding and try to model, for example, contact line dynamics, is convenient to work directly with the geometrical representation of the contact line, allowing us to use differential calculus tools, as we will see in this section [36, 37].

To do so, we need to represent the interface as a parametric surface, for both the perturbed and unperturbed contact lines. Let us describe the height of the liquid–air interface by a scalar field

$$z = \zeta(u, v),$$

where u and v are two arbitrary coordinates that parametrize the surface. For example, in a simple cartesian frame, we could take $(u, v) = (x, y)$, but in general, any convenient parametrization can be chosen depending on the geometry of the problem.

The position vector of a point on the interface can be written as:

$$\vec{r}(u, v) = (u, v, \zeta(u, v)). \quad (1.5)$$

From this parametrization, the unit normal vector to the interface becomes:

$$\vec{n} = \frac{(-\partial_u \zeta, -\partial_v \zeta, 1)}{\sqrt{1 + (\partial_u \zeta)^2 + (\partial_v \zeta)^2}}. \quad (1.6)$$

Without going too deep into the mathematical formalism, the mean curvature of the interface can be expressed in compact form as:

$$-\frac{1}{2} \nabla \cdot \vec{n}, \quad (1.7)$$

where $\nabla \cdot \vec{n}$ is the divergence of the unit normal.

In the limit of small slopes, $|\partial_u \zeta|, |\partial_v \zeta| \ll 1$, this reduces to:

$$k \approx \frac{1}{2} (\partial_{uu} \zeta + \partial_{vv} \zeta) = \frac{1}{2} \nabla^2 \zeta, \quad (1.8)$$

which is the form most commonly used for linear perturbation analyses of weakly deformed interfaces.

1.4 Small Perturbation on the Contact Line

Continuing with the previous approach, let us consider a liquid with a contact angle $\theta = \pi/2$, where the contact line is perturbed along the x -axis in the form

$$u(y) = u_q \cdot \cos(qy),$$

where u_q is the amplitude of the perturbation and q is the **wavenumber**, related to the spatial wavelength λ of the perturbation by

$$q = \frac{2\pi}{\lambda}.$$

To describe how this small perturbation affects the liquid–air interface, it is convenient to parametrize its surface as:

$$\vec{r}(y, z) = \begin{pmatrix} \zeta(y, z) \\ y \\ z \end{pmatrix}, \quad (1.9)$$

where $\zeta(y, z)$ denotes the displacement of the interface along the x -direction at position (y, z) .

To find the actual form of $\zeta(y, z)$, we express the Laplace condition in terms of the (y, z) coordinates:

$$\Delta P = \gamma \left(\frac{\partial^2 \zeta}{\partial y^2} + \frac{\partial^2 \zeta}{\partial z^2} \right). \quad (1.10)$$

Due to the small deflection assumption, we set $\Delta P = 0$, which simplifies the equation to:

$$\frac{\partial^2 \zeta}{\partial y^2} + \frac{\partial^2 \zeta}{\partial z^2} = 0. \quad (1.11)$$

This is a well-known Laplace equation. On the solid substrate (at $z = 0$), the interface displacement matches the imposed perturbation:

$$\zeta(y, 0) = u_q \cdot \cos(qy), \quad (1.12)$$

and for large values of z , the perturbation must vanish:

$$\lim_{z \rightarrow \infty} \zeta(y, z) = 0. \quad (1.13)$$

As usual for differential equations of this form, we propose a separable solution

$$\zeta(y, z) = Y(y)Z(z),$$

where applying the boundary condition at $z = 0$ leads to:

$$Y(y) = \cos(qy), \quad (1.14)$$

and the decay condition as $z \rightarrow \infty$ yields:

$$Z(z) = e^{-qz}. \quad (1.15)$$

Thus, we obtain the final expression for the interface displacement:

$$\boxed{\zeta(y, z) = u_q \cos(qy) e^{-qz}}. \quad (1.16)$$

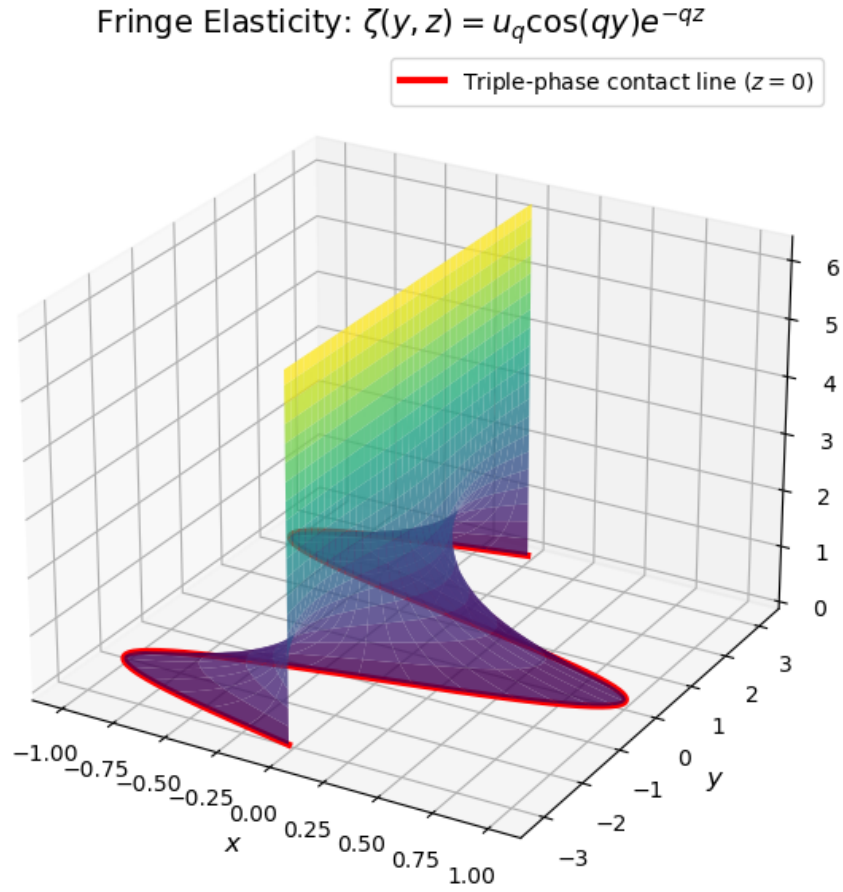


Figure 1.6: Three-dimensional representation of the solution of the liquid–air interface perturbation $\zeta(y, z) = u_q \cos(qy)e^{-qz}$. The colored surface represents the displacement of the liquid–air interface along the x -direction (ζ), while the red curve at $z = 0$ highlights the triple-phase contact line where the sinusoidal perturbation $u(y) = u_q \cos(qy)$ is imposed.

1.4.1 Localized Force

For a small force localized at a single point along the contact line, the Laplace pressure condition is expressed as:

$$\gamma \left(\frac{\partial^2 \zeta}{\partial y^2} + \frac{\partial^2 \zeta}{\partial z^2} \right) = f \delta(x) \delta(y), \quad (1.17)$$

where f is the magnitude of the localized force, and δ denotes the delta Dirac function, localizing the perturbation at the origin of the (x, y) coordinates.

The solution to this equation, obtained using the two-dimensional Green's function of the Laplace operator, is:

$$\zeta(y, z) = \frac{f}{\pi\gamma} \ln \left(\frac{L}{\sqrt{y^2 + z^2}} \right), \quad (1.18)$$

where L is a macroscopic cutoff length (typically the system size or a wavelength scale) that sets the far-field reference of the deformation.

At the triple-phase contact line ($z = 0$), the displacement simplifies to:

$$u(y) = \zeta(y, 0) = \frac{f}{\pi\gamma} \ln \left(\frac{L}{|y|} \right). \quad (1.19)$$

1.4.2 Strong Pinning

For strong pinning, with elongated distortions of the contact line, it is not convenient to use cartesian coordinates, even assuming $\theta_a = 90^\circ$. We can expect the distortion to be a meniscus; the most convenient way to represent its surface is cylindrical, as a surface of revolution generated by the profile $r = r(x)$ (axis along x), as represented in figure 1.7. Using the fact that $\Delta P = 0$, leading to $k = 0$, for this system, zero curvature fulfills the condition $\nabla \cdot \vec{n} = 0$. For a surface of revolution $r = r(x)$, this gives the mean-curvature equation

$$\frac{1}{r} \frac{1}{\sqrt{1 + (r'(x))^2}} - \frac{r''(x)}{(1 + (r'(x))^2)^{3/2}} = 0 \quad (1.20)$$

which is equivalent to minimizing the surface area ($\delta A = 0$) but here is obtained directly from $\nabla \cdot \vec{n} = 0$.

A first integral follows immediately:

$$\frac{r(x)}{\sqrt{1 + (r'(x))^2}} = r_0 \quad (1.21)$$

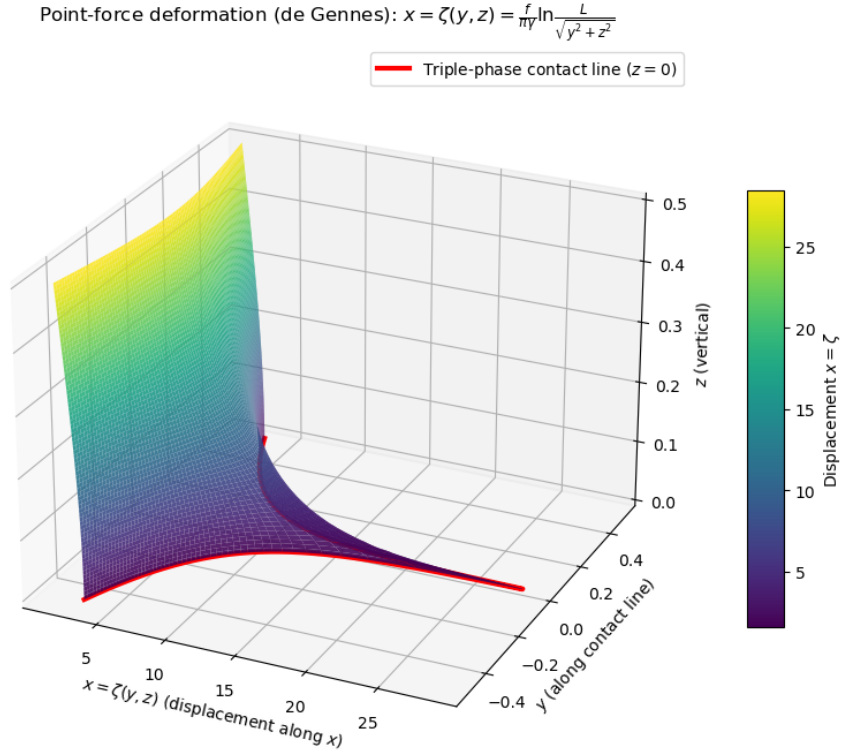


Figure 1.7: Three-dimensional representation of the liquid–air interface deformation induced by a localized point force applied at the triple-phase contact line, following the de Gennes model. The surface shows the displacement $x = \zeta(y, z) = \frac{f}{\pi\gamma} \ln \left(\frac{L}{\sqrt{y^2 + z^2}} \right)$ along the normal direction (x), with y along the contact line and z the vertical height. The red curve at $z = 0$ highlights the triple-phase line and the logarithmic displacement profile.

where r_0 is the minimum value of r (which will be $\sim$ defect size), then

$$r'(x) = \pm \sqrt{\left(\frac{r(x)}{r_0} \right)^2 - 1}. \quad (1.22)$$

Integrating, we obtain the catenary form:

$$r(x) = r_0 \cosh \left(\frac{x}{r_0} \right) \quad (1.23)$$

Which for $x \gg r_0$ we have the expression $r = \frac{1}{2} r_0 \exp(x/r_0)$, if we make the change of variables $u(y) = x$ and $y = r$, we obtain the equation:

$$u(y) = r_0 \ln \left(\frac{2y}{r_0} \right) \quad (1.24)$$

using the fact that the force exerted over the defect will be determined by the minimum radius (arc) $f = \gamma\pi r_0$, we obtain the form:

$$u(y) = \frac{f}{\pi\gamma} \ln \left(\frac{2y}{r_0} \right) \quad (1.25)$$

We can define the maximum elongation u_m in terms of $2y$ (or $2r$), noted sometimes as $L/2$, we will use this notation for consistency with the literature. If we assume that the value of $\frac{L}{r_0}$ doesn't change considerably:

$$u = \frac{f}{\pi\gamma} \ln \left(\frac{L}{r_0} \right) \approx K^{-1} f \quad (1.26)$$

We will assume that this will be the case for any pinning, in the future different configuration will lead to different values of K , for this generic case, we will have:

$$K = \frac{\pi\gamma}{\ln(L/r_0)} \quad (1.27)$$

Finally we can define the Energy when the contact line is stretched by a considerable defect to reach a maximum length u_m :

$$W = \frac{1}{2} K u_m^2 = \frac{u_m^2}{2} \frac{\pi\gamma}{\ln(L/r_0)} \quad \text{or} \quad W = \frac{1}{2} \frac{f_m^2}{K} = \frac{f_m^2 \ln L/r_0}{2\pi\gamma} \quad (1.28)$$

This framework for pinning and expression for the Energy will be useful for the next chapters.

1.5 Energy dissipation and Contact Angle

When discussing sliding drops, adhesion, and friction, numerous open questions remain regarding the fundamental mechanisms that determine the Contact Angle (CA) and Contact Angle Hysteresis (CAH). Although there is no single definitive explanation, various theoretical approaches and models have been proposed to account for the friction forces and dynamic contact angles of moving drops. It is important to emphasize that the applicability of these theories depends heavily on the sliding speed of the droplet and the specific physical and chemical characteristics of the underlying surface. While many of these models provide useful insights and have been experimentally proven under specific boundary conditions, they remain non-universal and cannot comprehensively predict droplet dynamics across all scenarios. Therefore, to clearly introduce these concepts and properly evaluate the different candidates responsible for droplet friction within the context of this research, it is crucial to separate the phenomena by their physical scale. To achieve this, we will define the relevant orders of magnitude and dimensional regimes associated with sliding drops, recognizing three distinct levels: Microscopic, Mesoscopic, and Macroscopic (Fig 1.8).

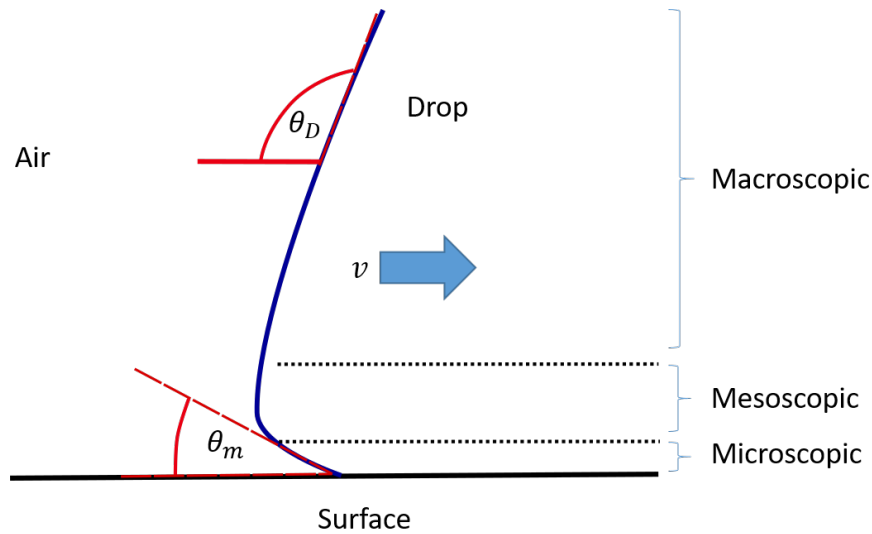


Figure 1.8: Illustration of a rear contact line of a sliding drop moving at speed v , we can recognize a "microscopic" contact angle, which will be influenced by the molecular energy barriers as the interface moves, the macroscopic in the other hand, is the one we see with naked eyes, and it's value can depend on many factors, depending on the speed and surface properties.

1. Microscale (nm–100 nm):

- Here the molecular interactions are protagonist.
- Relevant for Molecular Kinetic Theory [38].
- MKT theory uses the statistical and quantum properties of the molecules involved to define the local barriers and how they affect the CA of sliding drops.
- This is also the scale where **surface adaptation** occurs (e.g., the time-dependent reorientation of polymer chains or functional groups upon liquid contact) [39], and where the fundamental mechanisms of **drop charging** [40] originate (such as ion exchange and the formation of the electrical double layer).

2. Mesoscale (100 nm–10 μm):

- At this length scale, the contact line can be treated as a continuous string.
- Relevant for Joanny–de Gennes models of pinning (1984) and later patch models.
- The interactions of the contact line with physical patches, chemical defects, or localized charge domains will dissipate energy, causing the hysteresis.

3. Macroscale (10 μm –mm and beyond):

- Here we consider the whole drop and its geometry, introducing concepts such as viscous bending and hydrodynamic dissipation.

- Relevant for Cox–Voinov law [6], Hocking models [41], and hydrodynamic approaches (1980s–2000s).
- This scale sets advancing/receding angles under flow, oscillations, spreading, and encompasses macroscopic forces like bulk electrostatic drag resulting from drop charging.

1.5.1 Hydrodynamic Theory

As shown in Fig. 1.3, increasing the drop velocity, or equivalently the applied external force, leads to an increase in contact angle hysteresis, affecting both the advancing and receding dynamic contact angles. This observation clearly indicates that the motion of sliding drops is speed-dependent. Such a dependence is commonly characterized by the capillary number, defined as

$$\text{Ca} = \frac{\eta U}{\gamma}, \quad (1.29)$$

where η is the liquid viscosity, U is a velocity of the drop, and γ is the liquid-air surface tension. The capillary number represents the ratio between viscous forces and capillary forces and plays a central role in dynamic wetting phenomena [42].

Within the hydrodynamic theory of wetting, the observed speed dependence of the dynamic contact angles is attributed to viscous dissipation in the liquid near the moving contact line. In this framework, the microscopic contact angle at the solid surface is assumed to remain constant and equal to its equilibrium value, while the macroscopic shape of the drop and the apparent contact angles are governed by hydrodynamic flow. As the velocity increases, viscous stresses distort the liquid interface over increasingly larger length scales, leading to variations in the measured advancing and receding contact angles.

This approach provides a successful description of dynamic wetting behavior at sufficiently large scales, where hydrodynamic effects dominate. However, it does not explicitly account for molecular-scale interactions or surface heterogeneities, which may become important at small scales or low velocities.

1.5.2 MKT Theory

On the other hand, if we focus on the microscopic scale and consider the statistical properties of the molecules at the liquid-solid interface, the microscopic contact angle itself is no longer fixed but becomes velocity dependent. This is the central idea of the Molecular Kinetic Theory (MKT) of wetting [38].

In MKT, the motion of the contact line is described as a sequence of thermally activated molecular displacements between adsorption sites at the solid surface. Each displacement corresponds to a molecule jumping forward or backward over a characteristic molecular distance λ ,

with an associated activation energy that depends on the local interfacial configuration. When the contact line is at rest, forward and backward jumps occur with equal probability, resulting in no net motion and an equilibrium contact angle.

Under an applied driving force, such as an external force or a pressure gradient, the balance between forward and backward molecular jumps is broken. This asymmetry leads to a net contact line velocity U , which can be expressed as [43]:

$$U = 2\lambda k_0 \sinh\left(\frac{F\lambda}{2k_B T}\right), \quad (1.30)$$

where k_0 is the molecular jump frequency at equilibrium, F is the driving force per unit length acting on the contact line (which as we know, depends on the CAH), k_B is the Boltzmann constant, and T is the temperature.

Within this framework, the deviation of the microscopic contact angle from its equilibrium value is directly linked to the applied force and the resulting molecular kinetics. As the velocity increases, larger deviations from equilibrium are required to sustain the enhanced rate of molecular jumps, leading to changes in both advancing and receding microscopic contact angles. Consequently, contact angle hysteresis naturally emerges from the asymmetric molecular dynamics at the contact line.

Unlike hydrodynamic theory, which attributes dissipation to viscous flow in the bulk liquid, MKT localizes dissipation at the contact line itself. This makes MKT particularly relevant at low capillary numbers or in situations where molecular-scale effects, surface chemistry, or nanoscale roughness play a dominant role. In practice, dynamic wetting behavior often reflects a crossover between the MKT regime at small scales and low velocities and the hydrodynamic regime at larger scales, where viscous dissipation in the liquid becomes predominant.

1.5.3 Defect Contribution

As seen on the previous section, the interaction between a droplet and surface defects generates discrete forces and energy dissipation at the three-phase contact line. As expected, a distribution of these defects leads to successive pinning and depinning events at both the advancing and receding fronts. The summation of these micro-scale interactions results in non-uniform energy dissipation, which manifests macroscopically as Contact Angle Hysteresis (CAH). In fact, a significant body of literature [44–47] identifies these defects as the primary, if not the dominant, driver of CAH.

The existing discrepancies between theoretical approaches prompt a deeper investigation into the actual influence of surface heterogeneities. By shifting our focus toward smooth surfaces with a minimized defect density, we can more accurately isolate and quantify the specific contributions of defects to CAH and the broader friction process. This investigation requires

a specialized experimental framework to capture and analyze contact line dynamics with high precision. Consequently, the next chapter details the technical procedures, sample preparation protocols, and characterization methods utilized to ensure the acquisition of consistent and reliable data.

Chapter 2

Experimental Methods

2.1 Sample Preparation and Characterization

The selection of hydrophobic surfaces for this study was driven by the necessity to compare different mechanisms of contact angle hysteresis. Specifically, these surfaces represent a gradient of molecular architectures: from rigid, highly fluorinated monolayers (PFOTS and PFOMS) to semi-crystalline fluoropolymers (Teflon) and flexible polymer brushes (PDMS). By utilizing these distinct materials, it becomes possible to isolate the influence of topographic roughness from molecular adaptation and chain mobility, thereby addressing the "Hysteresis Gap" between nanoscopic observations and macroscopic behavior.

2.1.1 Fluorinated Silane Monolayers (PFOTS and PFOMS)

Fluorinated coatings were prepared via chemical vapor deposition (CVD) to produce low-energy surfaces with high chemical stability [48]. Indium Tin Oxide (ITO) glass slides were first cleaned in a sequence of sonic baths using acetone, toluene, and ethanol for 5 minutes each. Following the cleaning process, the substrates were dried in a vacuum oven at 60°C for 1 hour. Surface activation was achieved through exposure to 100% O₂ plasma for 10 minutes.

For PFOTS coatings, the activated slides were placed in a vacuum desiccator alongside a vial containing 1 mL of 1H, 1H, 2H, 2H-perfluorooctadecyltrichlorosilane (97%, Sigma-Aldrich). The deposition proceeded for 30 minutes at a pressure below 100 mbar. Similarly, PFOMS surfaces were prepared using 1H, 1H, 2H, 2H-perfluorooctyldimethylchlorosilane (94%, Tokyo Chemical Industry) under identical conditions. Post-deposition, all samples were rinsed thoroughly with ethanol, isopropanol, and deionized water to remove physisorbed molecules.

2.1.2 Polymer Thin Films (PS and Teflon AF)

Polystyrene (PS) and Teflon AF 1600 were selected to represent smooth, non-crystalline and semi-crystalline polymer environments, respectively [40].

The PS films, with a target thickness of 35 nm, were prepared by dip-coating at a pulling speed of $90 \text{ mm}\cdot\text{min}^{-1}$ from a 1 wt% PS solution (M_w : $192 \text{ kg}\cdot\text{mol}^{-1}$) in toluene. To ensure film stability and remove residual solvent, the samples were annealed under vacuum at 120°C for 24 hours.

Teflon films (60 nm thick) were prepared by dip-coating at a speed of $10 \text{ mm}\cdot\text{min}^{-1}$ from a 1 wt% Teflon AF 1600 solution in FC-75. These substrates underwent a specialized annealing process at 160°C under vacuum for 24 hours to promote structural uniformity and maximize hydrophobicity.

2.1.3 Polydimethylsiloxane (PDMS) Brushes

To investigate the influence of liquid-like grafting and molecular flexibility, PDMS brushes [49, 50] were prepared on sol-gel coated slides. ITO glass slides were placed in sealed environments containing $100 \mu\text{L}$ of 1,3-dichlorotetramethyldisiloxane for 8 minutes at a controlled relative humidity of 20%. After exposure, the substrates were rinsed with toluene and ethanol.

For "capped" PDMS samples—designed to eliminate the influence of hydroxyl end groups—the surfaces were further reacted with $100 \mu\text{L}$ of chlorotrimethylsilane for 2 hours. This substitution of hydroxyl groups with methyl groups allows for the study of purely dispersive interactions and minimizes hydrogen bonding at the interface, providing a crucial reference for "ideal" hydrophobic behavior with minimal hysteresis.

2.2 Atomic Force Microscopy

Atomic Force Microscope (AFM) is one of a series of scanning probe microscopes (SPM) that have been created to overcome the barrier of the optical resolution limit [51]. AFM uses a micro-sized cantilever with a probe to scan surface with nanometric, in some cases atomic, resolution and to make force measurement with different settings and probes [52].

AFM allow us to scan in 3 dimensions using Piezoelectric crystals. The cantilever, usually made of silicon, is irradiated with a laser beam to detect the deformation of the cantilever when it moves through a surface and the laser beam is deflected, this deflection is measured by a Position Sensitive Photodetector (PSD) that is able to detect the vertical and lateral deflection of the cantilever. The laser and the PSD have to be aligned as shown in figure 2.1. AFM measures changes in the height of the surface with a resolution of fractions of nanometers to Angstroms. To relate the virtual deflection(V) and the cantilever deflection(Δz) we need to

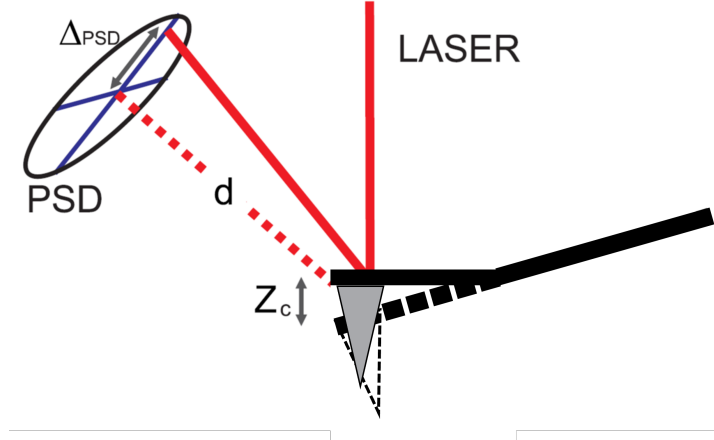


Figure 2.1: Illustration of the sensing mechanism of the AFM, the laser ideally is aligned in the center of the PSD, Z_c represent the cantilever deflection.

find the Deflection Sensitivity(S_{def}), defined by the formula:

$$\Delta z = S_{\text{def}} \Delta V. \quad (2.1)$$

By knowing the elastic properties of the cantilever, we can also calculate the force that is acting on the cantilever using its vertical deflection. For a cantilever the force is related with its deformation as shown in equation 2.4 where k is the elastic constant and Δz it's the cantilever deflection.

$$F = -k \cdot \Delta z \quad (2.2)$$

2.2.1 Operating Modes

2.2.1.1 Contact Mode Imaging

In contact mode, the cantilever tip statically scans the sample surface and its topography is recorded using the virtual deflection shifts measured on the PSD, to keep the deflection constant, the microscope changes the height of the cantilever and the system records this height. This kind of operation mode is used for surfaces that are not too rough, and low stiffness cantilevers must be used. Contact imaging can be very precise for flat surfaces, but has several problems for rough and soft surfaces, the constant contact between the surface and the tip makes the tip susceptible to damage and contamination .

2.2.1.2 Intermittent Contact Mode

Intermittent Contact Mode, or AC mode uses the natural resonance frequency of the cantilever to detect the interaction of the tip and the surface, when the tip begins to interact with the the surface the cantilever will suffer a shift in the frequency or the amplitude, the PSD detects this change, adjusting the height of the cantilever. This method is often used to measure rough or smooth surfaces, as the interaction of the tip and the sample is minimum, both remain unaffected.

2.3 Lateral Force Microscopy (LFM)

Lateral Force Microscopy (LFM) [53] extends the capabilities of standard Atomic Force Microscopy by measuring the torsional deformation of the cantilever as the probe moves across a surface. While vertical deflection is utilized to measure normal force interactions, lateral deflection captures the torsion forces resulting from friction between the surface and the probe—whether using colloidal probes, tips, or, as in this study, liquid droplets (Figure 2.2). Because the vertical and lateral deflection signals are independent, LFM allows for the simultaneous acquisition of topographical height and lateral interaction data in a single scan.

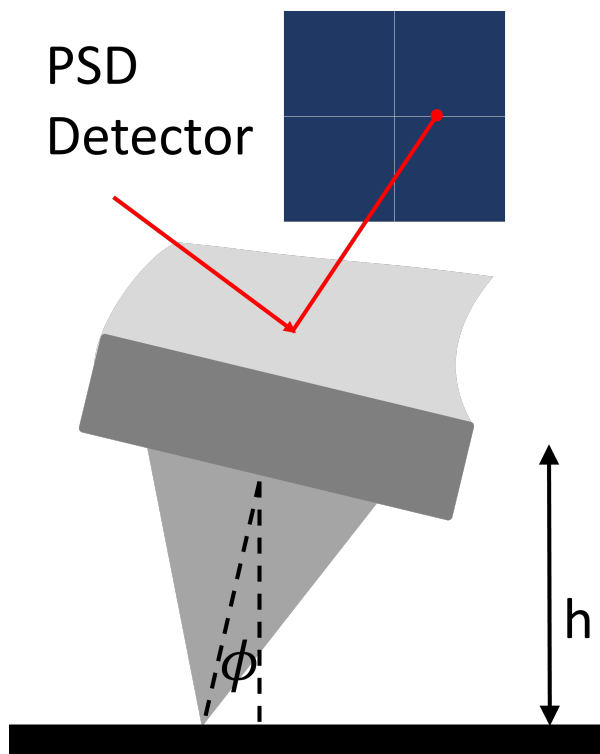


Figure 2.2: Scheme of a lateral force measurement. As the probe scans the surface, the Position Sensitive Detector (PSD) tracks the lateral deflection. Once calibrated, these signals are converted from voltage into force units (Newtons).

The primary challenge in LFM lies in the calibration of the lateral deflection sensitivity and the torsional spring constant. To achieve reliable measurements, the cantilever is first calibrated in contact mode. During this process, precise tuning of the Integral (I) and Proportional (P) gains is crucial; because a liquid droplet is significantly more sensitive to mechanical vibrations than a solid tip, optimized gain settings are essential for obtaining stable LFM data and clear confocal imagery.

In practice, it is often impossible to perfectly center the lateral deflection on the PSD. Consequently, the individual trace and retrace signals cannot be taken as absolute friction values due to the inherent lateral offset. To isolate the true friction force from these instrumental offsets, we process the data by calculating the difference between the trace and retrace channels.

While the raw trace and retrace maps remain useful for qualitative analysis, the quantitative friction values are extracted using the following relationship:

$$Friction = \frac{Trace - Retrace}{2} \quad (2.3)$$

In our workflow, the AFM data is exported as a 3D map. We utilize a custom Python script to visualize the profiles and perform this matrix subtraction, resulting in a corrected map that accurately represents the lateral forces across the scanned surface.

2.4 Droplet Probe Fabrication

The droplet probe technique involves the precise attachment of a micro-scale liquid droplet to a tipless cantilever to serve as a functionalized probe for force spectroscopy and lateral force microscopy [54]. In this study, cantilevers with nominal spring constants of approximately 0.03 N/m and 8.5 N/m were selected to accommodate different force regimes. The fabrication process is conducted using a high-resolution micro-manipulator integrated with an optical microscope to ensure accurate droplet positioning.

The attachment procedure relies on the balance of adhesive forces between the liquid phase, the cantilever substrate, and the delivery medium. Initially, microliter-sized reservoirs of the test liquid are deposited onto a glass slide. The tipless cantilever is then brought into contact with these reservoirs to facilitate droplet transfer. To achieve smaller, more controlled droplet volumes, a two-step transfer process may be employed: an uncoated, more hydrophilic cantilever is used to pre-pattern the glass slide with micro-droplets before the final probe attachment.

Surface functionalization of the delivery slide plays a critical role in the success of the transfer. It has been observed that utilizing fluorinated substrates significantly enhances the efficiency of droplet pickup. The low surface energy of the fluorinated coating reduces the work of adhesion between the droplet and the slide, favoring the wetting of the cantilever and allowing the droplet to detach from the substrate with minimal volume loss or satellite formation.

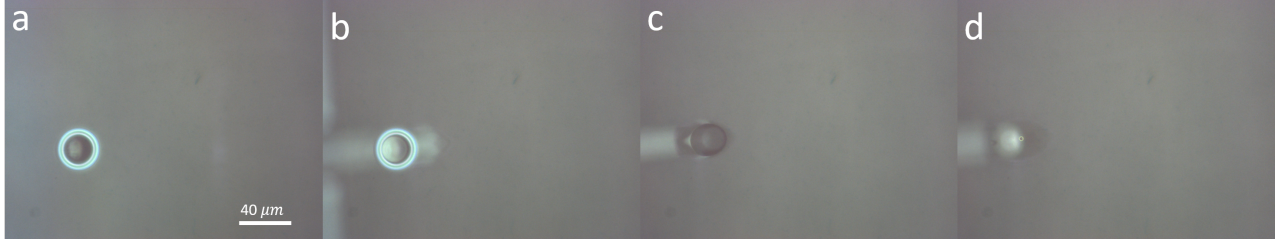


Figure 2.3: Sequence of images showing the process of attaching the droplet to a tipless cantilever. Images were taken with an inverted optical microscope. (a) and (b) show the approach to a previously micro-sized drop resting on a Teflon surface. (c) shows the cantilever making contact with the droplet. (d) As we retract the cantilever, the drop prefers to stay on the cantilever rather than the hydrophobic surface. There is a barely noticeable small droplet left on the surface.

2.4.1 Cantilever Preparation

In order to obtain droplets we need to avoid wetting on the cantilever, to achieve this, it is useful to make the cantilever hydrophobic and obtain a contact angle above 30° , the time of the fluorination depends on the droplet and the cantilever composition. In addition to this, we will form a hydrophilic area on the end of the cantilever, to tune the shape and position of the drop. This way, we make sure that the drop does not displace on the cantilever, minimizing possible artifacts, from now on, we call this area "Sticky Point".

2.4.1.1 Fluorination process

As in the case of the soot template surface, for the fluorination of the cantilevers we use CVD technique.

- Plasma Cleaner: We put the cantilevers in the plasma cleaner for 5 minutes at 100% of capacity.
- Desiccator: We put the cantilevers in the desiccator with $100\mu L$ of trichloroperfluorodecylsilane at $50[mbar]$ for 30 minutes.

2.4.2 Sticky Point

Droplet probe has been used in previous research [55], nevertheless just on superhydrophobic, mainly because of the need of an hydrophobic cantilever, if the surface energy of the probed surface is similar to the cantilever, it can and will pin in the surface and leave the cantilever, to avoid this problem we developed the sticky point, which consist in a hydrophilic in the cantilever [54], which will ensure that the drop remains attached to the cantilever. Thanks to our sticky point, we can control the radius of the drop and we can measure strong interactions, as we will see further in the thesis.

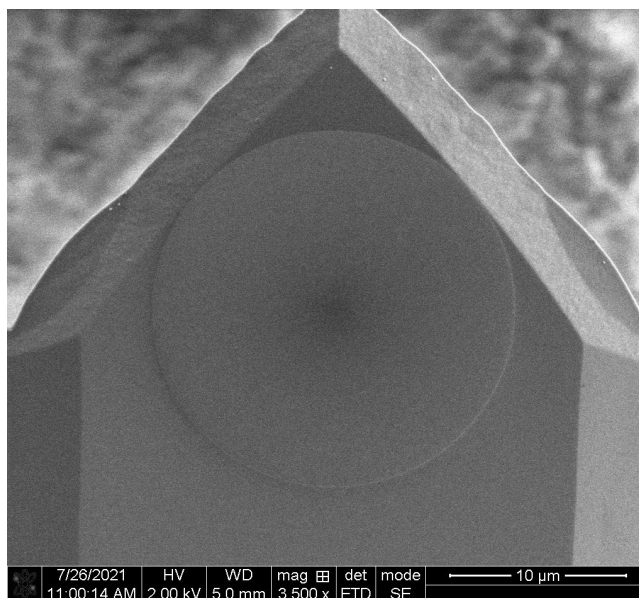


Figure 2.4: Example of a sticky point, the SEM image show the cantilever after being expose to the ion beam.

2.5 Contact Angle Goniometry and Dynamic Wetting

A standard characterization of the wetting properties of hydrophobic materials involves the measurement of the static contact angle [56], which provides fundamental insight into the thermodynamic equilibrium between the liquid and solid interfaces (Section 1.3). However, the measurement of the static contact angle alone is insufficient to fully characterize the quality and functional performance of a hydrophobic surface. While a high static angle indicates a degree of water repellency at equilibrium, it does not reveal how a droplet interacts with surface heterogeneities during movement or the magnitude of energy dissipated as the interface slides.

Consequently, it is necessary to include contact angle hysteresis (CAH) in our characterization to evaluate the dynamic mobility of the liquid on the substrate. The CAH serves as a global quantification of the energy dissipated during droplet motion, representing the cumulative energy barrier that the triple-phase contact line must overcome to transition from a pinned state to a sliding regime.

To obtain these values, we perform quasi-static inflation–deflation experiments using a sessile-drop goniometer (OCA35, DataPhysics Instruments GmbH). This procedure allows for the determination of the stability limits of the triple-phase contact line by continuously varying the droplet volume via a submerged needle. For each measurement, a droplet was formed on the surface and its volume was modulated by approximately 50 μL at a controlled rate of 0.5 $\mu\text{L/s}$.

The advancing contact angle (θ_a) is recorded during the inflation phase as the contact line begins to expand, while the receding contact angle (θ_r) is recorded during the deflation phase as the liquid is withdrawn. Ideally, as shown in Figure 2.5b, these values reach a constant plateau;

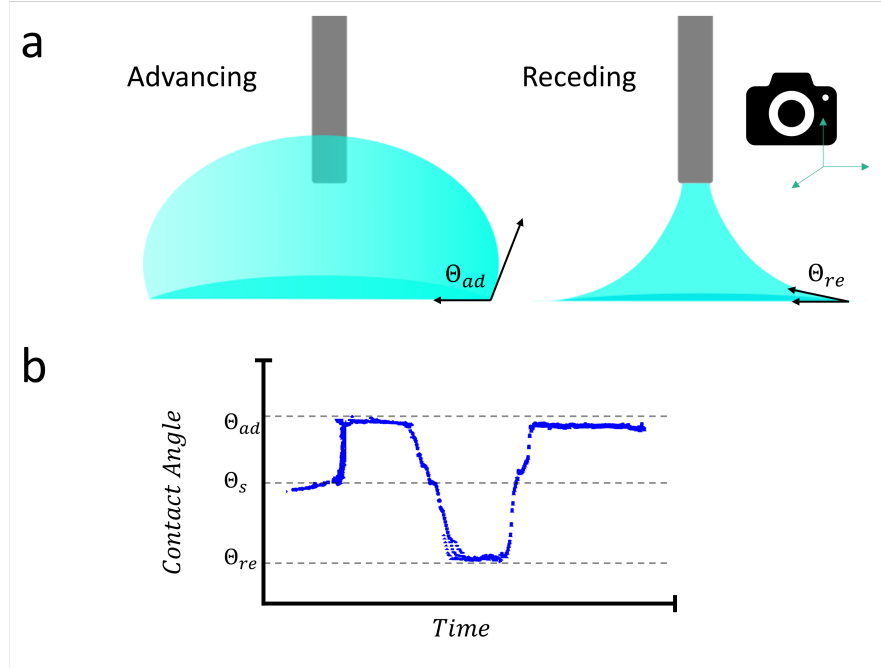


Figure 2.5: (a) Schematic representation of the experimental setup for measuring contact angle hysteresis via inflation–deflation cycles. (b) Typical evolution of the contact angle over time, used to identify the plateau values of the advancing and receding angles.

however, in practice, the angles may vary over successive cycles due to surface adaptation, water penetration, or charge deposition [57]. To ensure reproducibility and account for these effects, three complete inflation–deflation cycles were performed for each sample, with measurements collected at three different positions on every substrate. The reported values represent the average over all cycles and locations, and the total contact angle hysteresis was calculated as:

$$\Delta\theta = \theta_a - \theta_r \quad (2.4)$$

This macroscopic characterization provides the essential building blocks for the more technical chapters of this thesis. By quantifying the CAH, we define the global "energy budget" of the system, which serves as the primary reference for our microscopic force measurements. Specifically, these values are utilized in the Furmidge equation to calibrate the cantilever, allowing us to bridge the gap between the macroscopic wetting signature and the localized, nano-Newton pinning forces captured by the AFM droplet probe.

2.6 Tilted Plate Setup

2.6.1 Inverted Microscopy and Fast Camera

In order to image CL-defect interactions and fluctuations, we use a tilted plate setup, with inverted microscopy. This device, first presented and described in [58], consist of an inverted microscope (IX83, Olympus, Japan) whose optic path have been extended using an objective inverter (InverterScope®, LSM TECH, USA) which allows 360° rotation. By mounting a sample holder around the free end of the inverter, we make sure the objective is perpendicular to the sample. Finally, to make sure we are able to observe the pinning and the fluctuation using high magnification, we need to use fast microscopy to reach high frame rates and low exposure times. An ultra-high-speed camera (TMX 7510, Phantom, USA) is connected to the microscope to record the contact line dynamics. The camera can operate at 76 000 fps at full resolution (1280 x 800 pixels) and higher if we reduce reduced resolution.

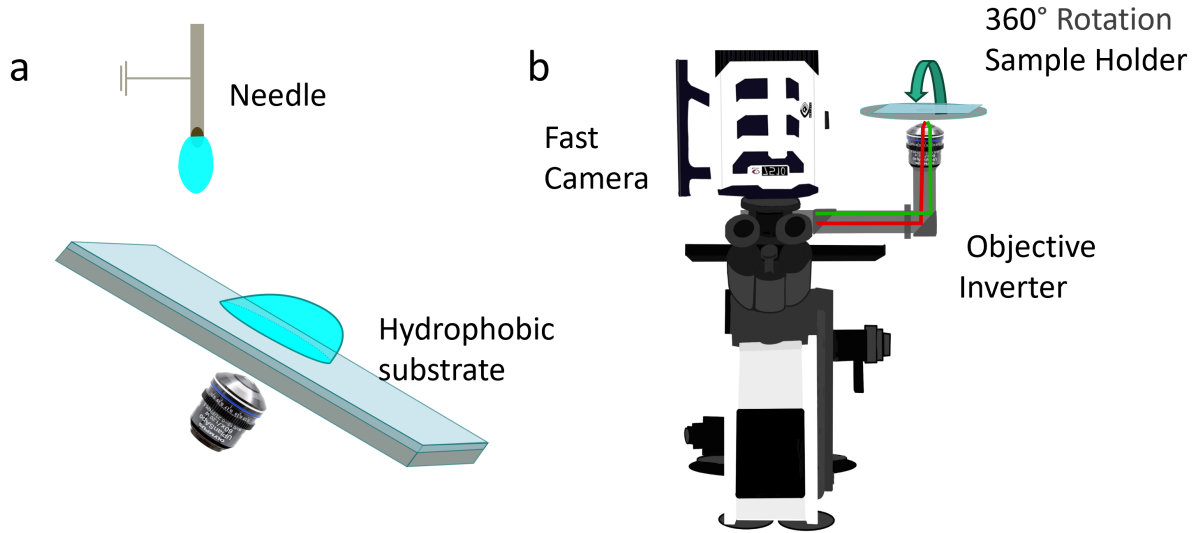


Figure 2.6: Experimental setup for high-speed reflection microscopy. (a) Schematic of the tilted-plate setup where the droplet is imaged from below. (b) Inverted microscope integrated with an objective inverter and ultra-high-speed camera to record contact line dynamics at the triple-phase boundary.

For the sliding drops experiments, we use a peristaltic pump connected to a grounded tip at distance 10-15 mm from the surface. After sliding distance 20-25 mm, the drop enters the field of view of the Microscope, triggering the Fast camera.

The sliding drop is illuminated from below through the microscope objective with parallel light. The light reflected on a solid/air or solid/water interface is collected with the same

objective and imaged with the fast camera. As the reflection on solid/air interfaces is much higher than that on solid/water interfaces, the solid/air interface appears brighter than the solid/water interface on the image of reflection mode. Thus, the contact line which is the boundary of these two parts could be clearly observed.

The illumination is done by a high-power LED. There is a rotation bayonet on the horizontal arm of the objective inverter, which enables microscopic observation of the sample stage at different tilt angles. A piezoelectric objective focus scanner (ND72Z2LAQ PIFOC®[®], Physik Instrumente) with a minimum incremental motion of 5 nm is fixed below the objective for focusing. High magnification water-immersion objective (UPlanSApo 60x 1.20 w, Olympus, Japan) was used in the experiments resulting in pixel size of 303 nm .

Chapter 3

AFM: Measuring Contact Line-Defect Interactions

Following the discussion of hydrodynamic, viscous, and molecular approaches to energy dissipation, this chapter focuses on interactions at the submicroscopic and nanoscopic scales. Specifically, we utilize a droplet probe to measure friction forces on hydrophobic surfaces. We examine three distinct types of interactions: first, the natural pinning that occurs on seemingly smooth surfaces, where we observe contact line deflections ranging from 100 to 1,000 nm; and second, the measurement of a defined defect configuration, in this case, a hemisphere, analyzed via a linear-force model inspired by the theoretical work of de Gennes [37]. Third, we aim to experimentally quantify an upper limit for the "peripheral length", which correspond to the characteristic width of the region surrounding the three-phase contact line that actively contributes to the total friction force [39, 59].

3.1 Setup

The experimental setup utilized a JPK NanoWizard IV AFM equipped with a droplet probe. Picoliter droplets, approximately 30 μm in diameter, were attached to a tipless cantilever as detailed in Section 2.4. Following attachment, the probe approached the surface, and the normal response of the cantilever was calibrated.

The AFM was operated in contact mode with a normal force setpoint of 0 nN, while the feedback parameters, specifically the I-Gain and P-Gain, were set to zero. We employed a default scan speed of 225 $\mu\text{m/s}$. Variations in the scan speed to 112 or 459 $\mu\text{m/s}$ did not result in a measurable change in the friction force, suggesting that the observed phenomena are independent of velocity within this range.

To justify ignoring viscous dissipation, we calculate the Capillary number (Ca), which rep-

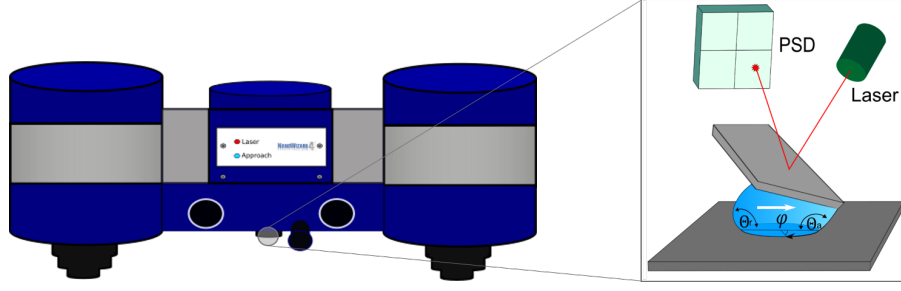


Figure 3.1: The experimental measurements were performed using a JPK NanoWizard IV equipped with a droplet probe.

resents the ratio between viscous and capillary forces:

$$Ca = \frac{\eta U}{\gamma} \quad (3.1)$$

Using the liquid viscosity $\eta \approx 1 \text{ mPa}\cdot\text{s}$, the scanning velocity $U = 225 \text{ }\mu\text{m/s}$, and the liquid-air surface tension $\gamma \approx 72 \text{ mN/m}$, we obtain:

$$Ca = \frac{(10^{-3} \text{ Pa}\cdot\text{s}) \cdot (2.25 \times 10^{-4} \text{ m/s})}{0.072 \text{ N/m}} \approx 3.1 \times 10^{-6} \quad (3.2)$$

This value is several orders of magnitude below the threshold ($Ca \approx 10^{-3}$) where hydrodynamic bending typically influences the apparent contact angle. Therefore, viscous dissipation is negligible, and the measured friction arises purely from the pinning-depinning process at the contact line.

A typical scan size was $100 \times 100 \text{ }\mu\text{m}^2$ at 512×512 pixels, which took 8.5 min to record.

3.1.0.1 Sample and Liquid Characterization

Advancing (θ_a) and receding (θ_r) contact angles were measured by placing a drop onto the Teflon surface. Three inflation-deflation cycles were performed changing the volume of the drop by $50 \text{ }\mu\text{L}$ at a rate of $0.5 \text{ }\mu\text{Ls}^{-1}$. Each sample was measured in three different areas, contact angles were determined by averaging the values of all measurements. Viscosity was measured with a rolling ball viscometer (LOVIS 2000M, Anton Paar) with $600 \text{ }\mu\text{L}$ solution at 25°C . Surface tension was measured with the Du Noüy ring method using a tensiometer (DataPhysics DCAT 11EC).

3.1.0.2 Fixing a Colloid on the Surface

To fix isolated nanospheres as defects on the surfaces, an aqueous suspension of silica particles was diluted by mixing with acetone to a volume fraction of 0.1%. Acetone was used because of its fast evaporation and low contact angle. After sonicating for 5 min, a drop of the dilute

suspension was deposited on the Teflon film. After evaporation of the liquid, samples were annealed at 160°C. The Teflon film softens and colloids sinter to the film. On such a sample we had aggregates and isolated particles. Friction measurements were carried out on isolated particles. For SEM, the samples were sputter coated with 7 nm Pt layer to minimize sample charging during imaging. The average of the measured diameter of the colloids was 440 ± 15 nm.

3.2 Data Analysis

After performing our friction force experiments, we obtain a map with the drop surface interaction, every line will correspond to a sliding process, and we will be able to recognize the friction regime of a sliding drop [60]. (i)static regime(ii) quasi static (iii) dynamic. As we can see in figure 3.2, which represent a raw line scan force, the friction force increase until it reach a plateau value. This will be the case for both smooth surface and sintered sphere.

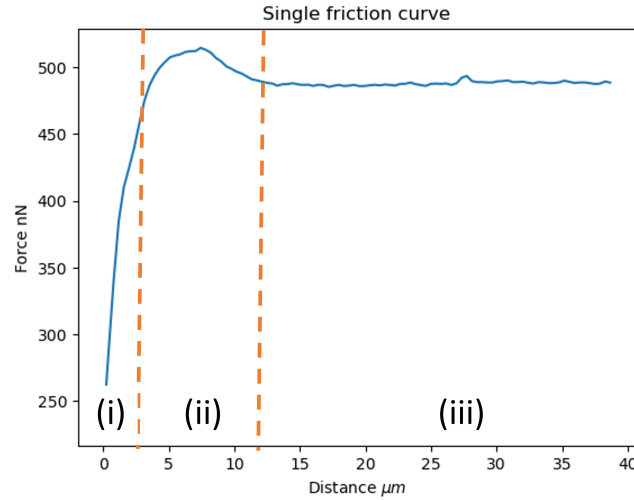


Figure 3.2: Single line Scan, as we can see the regimes involved in drop friction are clear to distinguish. (i) In the static regime the force increases almost linearly, there is not drop motion involved but a rearrangement of the contact line. (ii) Here we reach a maximum of force we need to start moving the drop, part of the contact line is moving. (iii) Once the drop becomes a moving object, the friction force reach a constant value, this because the CAH has also reach a steady value. The force has been calibrated using the dynamic friction value.

3.2.1 Force Calibration

To quantify the pinning forces observed in our microscopic scans, the cantilever must be accurately calibrated. We leverage the consistency between our local contact line measurements and the macroscopic wetting behavior to perform this calibration. Specifically, by measuring the

surface area of the "printed ring" left on the substrate, we can reliably estimate the dimensions of the contact zone.

Using the Furmidge equation, we determine the steady-state (plateau) dynamic friction force acting on the drop. This macroscopic force serves as a reference standard; by comparing the known capillary force to the voltage output of our sensor, we can derive the calibration constant for the cantilever. The high degree of consistency between the measured force and the theoretical expectations further validates our experimental assumptions regarding the system's energy dissipation.

The calibration factor, C_{cal} , is derived from the relationship between the measured voltage ΔV and the Furmidge-derived retention force:

$$C_{cal} = \frac{\Delta V}{w\gamma(\cos \theta_r - \cos \theta_a)} \quad (3.3)$$

where w is the width of the drop (or the characteristic length L), γ is the surface tension, and θ_a and θ_r are the advancing and receding contact angles, respectively.

3.2.2 Background Extraction

The measured lateral force maps contain slowly varying background contributions that are not associated with contact line pinning. These contributions arise from effects such as gradual evaporation of the droplet, slow adaptation of the liquid–solid interface, and mechanical drift of the cantilever during scanning. In order to isolate the localized pinning–depinning signal at the contact line, a background extraction procedure is applied.

Background subtraction is performed following standard friction force atomic force microscopy (AFM) methodologies. The procedure is applied independently to each scan line and for a single scan direction. For each force–position line, a low-order polynomial is fitted to the measured signal to capture the slowly varying background component. This fitted polynomial is then subtracted from the original data.

After subtraction, each corrected scan line is shifted such that its mean value is zero. This step removes residual offsets and eliminates large-scale tilts in both the fast-scan (x) and slow-scan (y) directions. The resulting force map therefore emphasizes localized variations in the lateral force, which are attributed to contact line pinning and depinning events.

Trace and retrace scans were treated equivalently and exhibited identical behavior after background subtraction, confirming the robustness of the procedure.

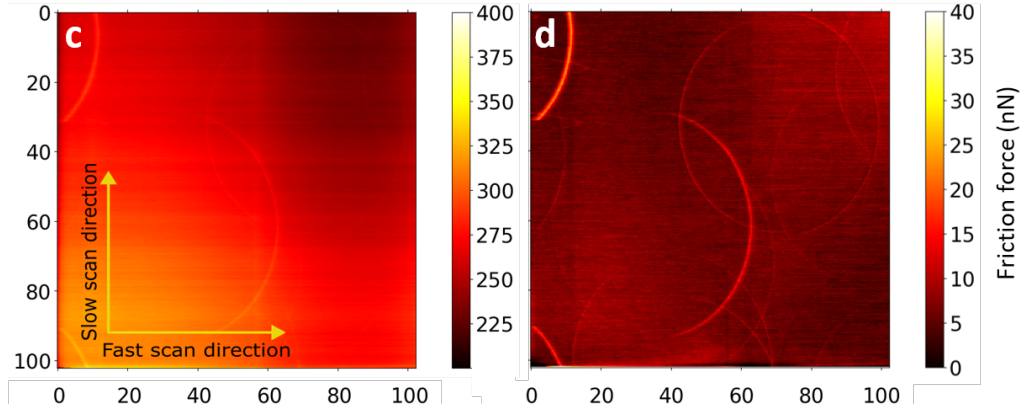


Figure 3.3: Friction Map before and after background extraction.

3.3 Results for Smooth Surface

3.3.1 Peripheral Thickness and Contact Line Deflection

Topographic imaging of the Teflon-coated glass surfaces reveals an rms roughness of the order of half a nanometer, with isolated defects typically in the nanometer height range. While such heterogeneities are ubiquitous, not all of them are expected to interact strongly with a moving contact line. In particular, only defects that induce a sufficiently large deformation of the three-phase contact line lead to detectable pinning events.

This distinction becomes evident in the friction maps obtained with picoliter droplets. After background subtraction, the friction signal reveals a series of well-defined ring-like features (Fig. 3.3). Each ring corresponds to a localized pinning event occurring when the contact line passes over an individual defect. All rings share the same diameter, equal to the width of the droplet contact area, while their intensity and width vary from ring to ring.

The thickness of each ring reflects the lateral distance over which the cantilever experiences an additional force during the pinning-depinning process. This distance corresponds to the maximal deflection of the contact line caused by the defect, by which we can estimate an upper bound for the **peripheral thickness** [39, 59] (also referred as peripheral length). By analyzing individual line profiles across the rings, a maximum value for the peripheral length δ can be defined as the distance between the onset of the force perturbation and the point at which the force relaxes back to the background level.

Experimentally, the smallest resolvable peripheral thickness is found to be approximately

$$\delta_{\min} \approx 200 \text{ nm} \quad (3.4)$$

as determined from friction maps acquired over a scan area of 520×520 pixels². This value is set by the lateral resolution of the measurement and the signal-to-noise ratio of the lateral force signal; thinner regions of interaction cannot be reliably distinguished from background

fluctuations.

This minimum detectable deflection provides an experimental upper limit for the peripheral thickness, defined as the spatial region around the contact line that actively contributes to friction and dissipation. Since only defects intersecting this peripheral region generate a measurable response, the observed ring thickness implies that dissipation is localized within a zone of width

$$\xi \lesssim 200 \text{ nm}$$

around the three-phase contact line.

The fact that all rings have identical diameters demonstrates that individual pinning events are spatially localized and independent of one another. Defects inside the droplet footprint but outside the peripheral length do not contribute to the friction signal, confirming that contact line dissipation is confined to a narrow, high-interaction zone at the triple-phase boundary.

3.4 Sphere Results

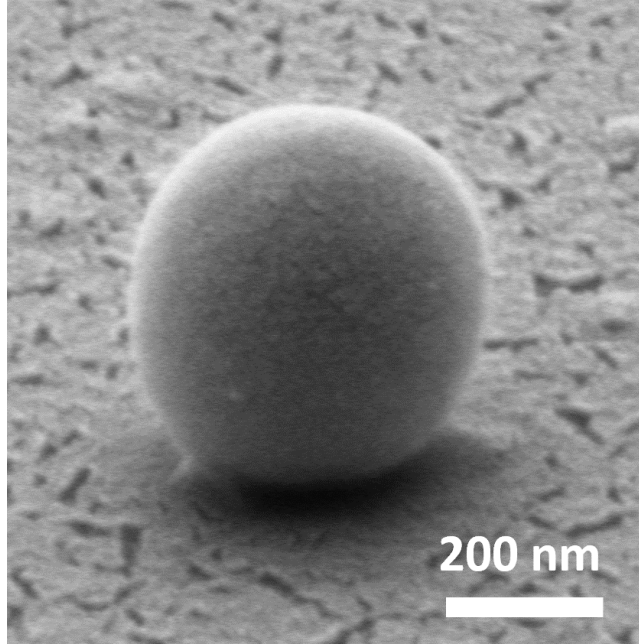


Figure 3.4: SEM image of an isolated colloid attached to the surface, from the image we can contrast the colloid radius with its nominal value, and estimate the level of sintering in the surface.

To gain a deeper understanding of the defect-drop interaction and the resulting energy dissipation, we conducted control experiments using spherical colloidal defects. This approach allows for a precise corroboration and expansion of the theoretical models by controlling the sphere radius ($R = 220 \text{ nm}$) and utilizing materials with well-characterized surface energies.

The friction maps for these spherical defects reveal a distinct ring-like dissipation pattern, which is significantly more pronounced than those observed on natural heterogeneities. Notably, the background friction force—representing the intrinsic resistance of the smooth surrounding substrate—remained constant at approximately 350 nN, identical to the values obtained for defect-free surfaces. This consistency confirms that our force calibration remains valid across different samples. Once this background is subtracted, the localized interaction force can be isolated, as shown in Figure 3.6.

3.4.1 Azimuthal Dependence

One of the primary advantages of utilizing friction maps is the ability to observe the drop-defect interaction at every point along the three-phase contact line. As the defect enters and subsequently leaves the liquid phase, a specific friction profile is generated. To visualize this process systematically, we record the friction values in relation to the azimuthal angle ϕ .

As shown in Figure 3.5, the domain is defined from -90° to $+90^\circ$, where 0° corresponds to the central axis of the drop's motion. This mapping is essential to understand how the projection of the capillary force changes depending on the relative orientation of the contact line and the defect trajectory.

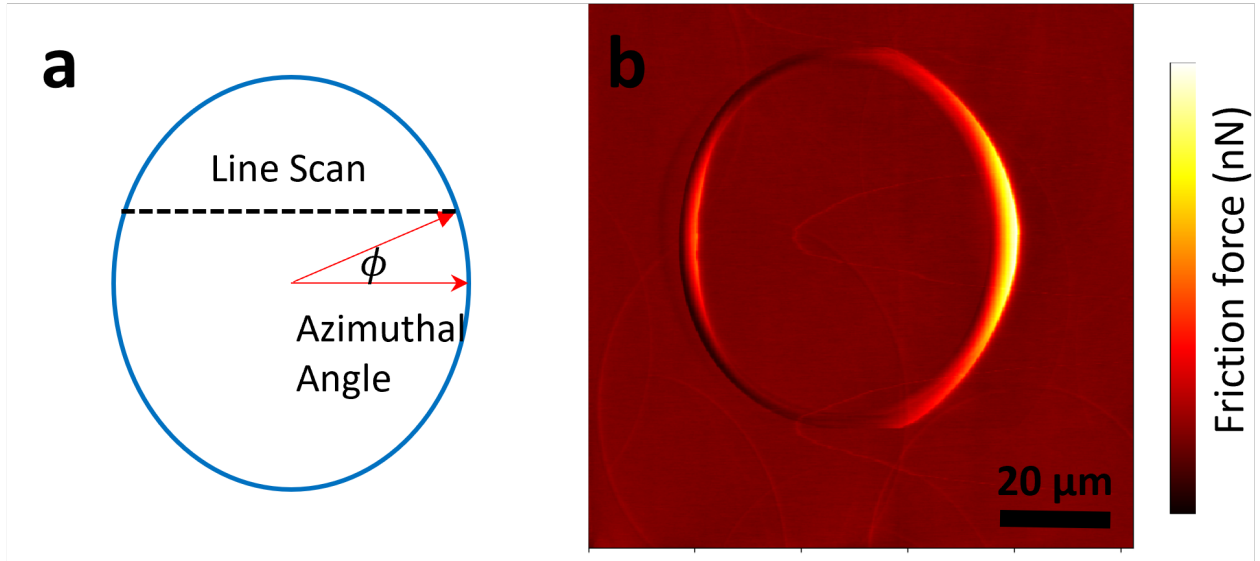


Figure 3.5: a) Scheme showing how the azimuthal angle is extracted; the dashed lines correspond to the horizontal line scans cutting the contact line, represented by the ellipsoidal ring in blue. b) Friction map obtained from the drop-colloid interaction.

3.4.2 Linear Behavior and azimuthal dependence results

Figure 3.6 illustrates the experimental force profiles for scan lines where the azimuthal angle is close to 0° . After subtracting the background friction, the interaction forces are found to be in the order of tens of nanonewtons. The interaction follows a distinct and consistent sequence: an initial "snap-in" (meniscus formation pulling the drop), followed by a linear increase in force as the contact line is stretched, and finally a rapid "snap-out" or depinning event as the force reaches its maximum and returns to the background level.

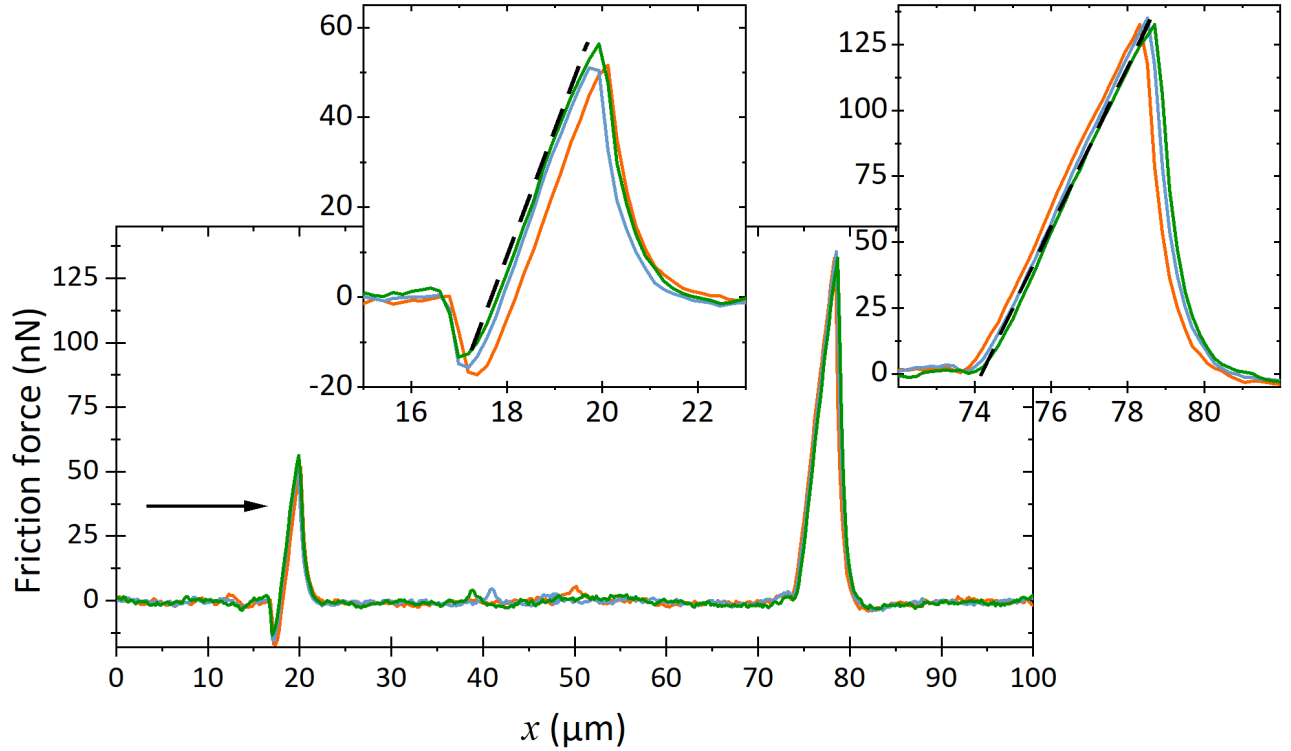


Figure 3.6: Drop-sphere interaction curves. Near the center ($\phi \approx 0^\circ$), the curves overlap significantly, exhibiting a clear snap-in, a linear force increase, and a final snap-out.

Quantitative analysis of these profiles shows that the maximum receding force ($F_r \approx 125$ nN) is significantly greater than the maximum advancing force ($F_a \approx 50$ nN). To process the large volume of data and analyze the azimuthal dependence, we utilized custom Python software to fit an ellipse to the friction maps. This procedure allowed us to automatically isolate the advancing and receding segments and extract the peak forces, the effective spring constant (k), and the lateral work (W_x) for thousands of individual interaction points.

The results of this analysis, plotted in Figure 3.7, characterize the experimental dependence of these parameters on the azimuthal angle ϕ . Both the peak force and the slope k vary significantly, showing a clear decrease as the interaction occurs further from the drop's central axis toward its edges. Similarly, the experimental lateral work W_x , calculated by integrating the area under the force-distance peaks, shows a consistent value for small angles but exhibits a

significant decrease for $|\phi| \geq 20^\circ$. As indicated by the dotted lines in the plots, this experimental decrease in both force and work was notably steeper than the expected theoretical fit.

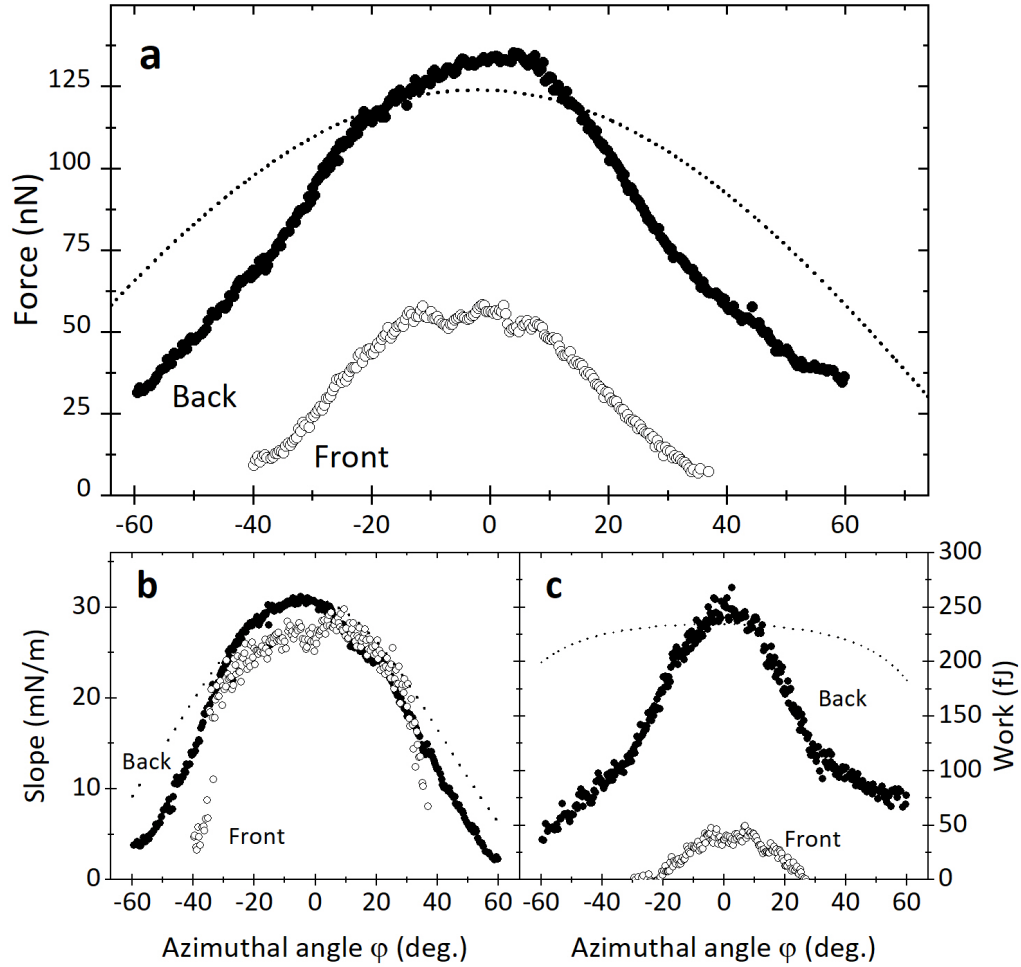


Figure 3.7: (a) Peak force, (b) slope, and (c) work of the contact line when overcoming the defect, plotted versus the azimuthal angle ϕ for both the advancing and receding edges.

3.5 Defect-Drop Interaction Model

To theoretically characterize the mechanical interaction between a picoliter droplet and a sub-microscopic defect, a model is established based on the energetic and geometric considerations of the three-phase contact line. This framework allows for the quantification of localized pinning forces and the resulting energy dissipation as the droplet moves across a surface heterogeneity. To ensure the physical and mathematical tractability of the system, the following assumptions are derived from the experimental and numerical findings:

- **Geometric Idealization:** The defect is modeled as a single hemispherical particle of radius $R = 220$ nm, where the equatorial plane resides on the substrate. The degree

of sintering or immersion is defined by the opening angle β , which is 90° for a perfect hemisphere.

- **Scale Separation:** The defect radius is assumed to be several orders of magnitude smaller than both the macroscopic droplet footprint and the capillary length, $\kappa = \sqrt{\gamma/\rho g}$.
- **Local Interface Planarity:** Due to the significant scale separation, the liquid-air interface is assumed to be locally planar in the immediate vicinity of the defect.
- **Quasi-Static Approximation:** Droplet motion is assumed to be sufficiently slow such that the system exists in a state of thermodynamic equilibrium at any given position.
- **Linear Elastic Response:** Following the Joanny and de Gennes formalism [37], the pinning force is assumed to increase linearly with the extension of the meniscus. This allows the contact line to be modeled as an effective spring with constants k_a and k_r for the advancing and receding edges.
- **Concentrated Dissipation:** Energy dissipation is assumed to be localized within a peripheral zone of approximately 200 nm around the contact line.

3.5.1 Meniscus Formed by a Sphere

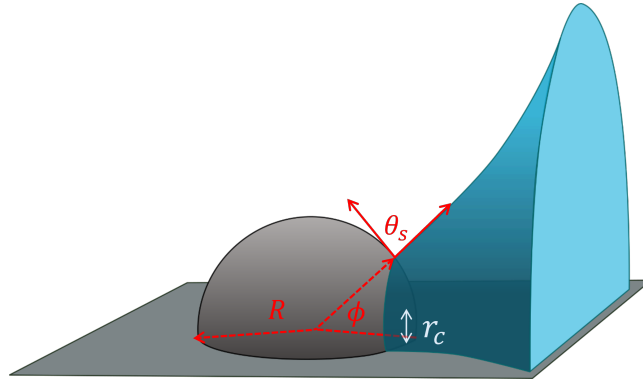


Figure 3.8: Schematic profile of the meniscus formed on the semi-spherical defect ($\beta = 90$), illustrating the sphere radius R , the contact line radius r_c , the central angle ϕ , and the contact angle of the sphere θ_{defect} .

A crucial part of modeling this interaction is finding the correct values for k and the maximum forces involved in the droplet-defect interaction. To achieve this, we consider the case of a meniscus formed by a droplet on a sphere of radius R . If the sphere has a contact angle θ_{defect} , the central angle ϕ describing the contact line radius r_c , as we can see in figure 3.8, r_c can be express as:

$$r_c = R \sin \phi \quad (3.5)$$

The total capillary force is expressed as $f = 2\gamma\pi r_c = 2\gamma\pi R \sin \phi$. For our model, the horizontal component f_x is the primary quantity of interest as it leads to the maximum pinning force [61]. As shown in Figure 3.9, the horizontal force generated by the contact line tension is:

$$f_x = 2\gamma\pi R \sin \phi \sin(\theta_{defect} - \phi) \quad (3.6)$$

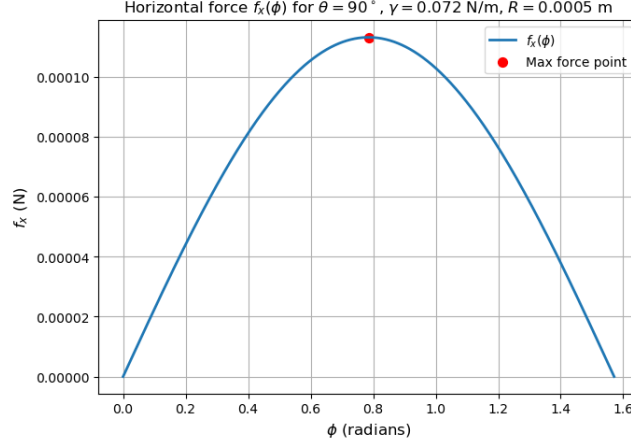


Figure 3.9: Force expressed in terms of ϕ . For such a function, it is straightforward to calculate the maximum.

To express the maximum force in terms of θ_{defect} , we find the extremum of f_x with respect to ϕ :

$$\frac{\partial f_x}{\partial \phi} = 2\gamma\pi R (\cos(\theta_{defect} - \phi) \sin \phi - \cos \phi \sin(\theta_{defect} - \phi)) = 0 \quad (3.7)$$

By dividing by the constants and the term $\cos \phi \cos(\theta_{defect} - \phi)$, the expression simplifies to:

$$\tan \phi - \tan(\theta_{defect} - \phi) = 0, \quad \text{therefore} \quad \phi = \theta_{defect}/2 \quad (3.8)$$

Finally, adjusting for a partially sintered spherical cap where the contact length is modified by the opening angle β , we obtain the expression for the maximum force when pulling a sphere:

$$F_{\max} = 2(\pi - \beta)R\gamma \sin^2 \left(\frac{\theta_{defect}}{2} \right) \quad (3.9)$$

Knowing the maximum force of our sphere is crucial to develop our model, we can continue with the calculation of the effective spring constant k , which characterizes the restorative force of the contact line as it pins to the defect. Following the formalism of Joanny and de Gennes, this spring constant is determined by the surface tension and the logarithmic ratio between the

droplet width L and the defect diameter D :

$$k_{a/r} = \frac{\pi\gamma \sin^2 \theta_{a/r}}{\ln(L/D)} \quad (3.10)$$

Using the experimental parameters ($\gamma = 69.7$ mN/m, $L = 66$ μm , $D = 440$ nm), we obtain theoretical values of $k_a = 0.036$ N/m and $k_r = 0.039$ N/m. These values show excellent agreement with our measured slopes of 0.027 N/m and 0.031 N/m. Furthermore, applying Eq. 3.9 with $\theta_{\text{defect}} \approx 70^\circ$, $R = 220$ nm, and $\beta = 35^\circ$ yields $F_a = 26$ nN and $F_r = 52$ nN, aligning well with the experimental peak forces recorded in our friction maps.

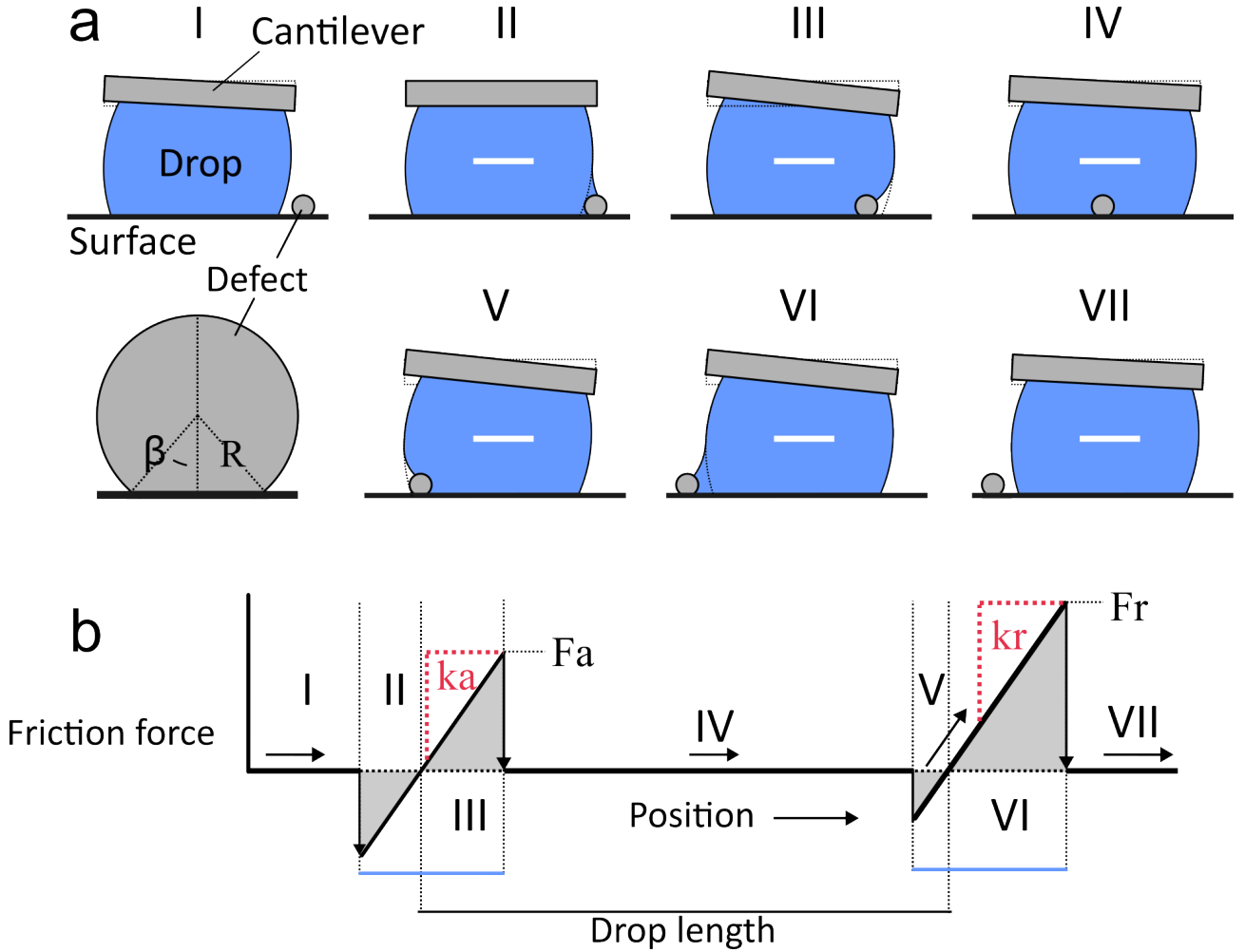


Figure 3.10: (a) Schematic front view of the sequence of events when the drop passes a spherical defect. (b) Capillary friction force acting on the drop according to the linear spring model. Blue arrows indicate the width which was used as an upper limit for the peripheral thickness.

As the droplet probe scans the hydrophobic surface, the interaction with localized defects manifests as a sequence of distinct mechanical stages, as illustrated in Figure 3.10.

Initially, as the drop approaches the defect, a precursor meniscus is established, pulling the

droplet forward in a characteristic "snap-in" event (Phase II). As the displacement increases, this meniscus diminishes until the net capillary force vanishes. Continued motion results in the formation of a resistive meniscus that acts against the direction of scanning (Phase III). The advancing contact line remains pinned until the lateral force reaches the critical threshold, F_a , triggering a depinning event.

Once the defect is fully engulfed (Phase IV), it resides within the bulk liquid and exerts no further force on the droplet. A reciprocal process occurs as the receding contact line encounters the defect: the liquid front jumps forward to partially dewet the particle (Phase V), followed by the development of a rear meniscus (Phase VI). The interaction concludes only when the resistive force exceeds the threshold F_r , allowing the droplet to be released from the pinning site (Phase VII).

3.6 Analysis of Experimental Results

The experimental force profiles in figure 3.6 reveal a characteristic sequence starting with a "snap-in" region where the meniscus pulls the droplet forward. The force crosses the zero-equilibrium at a displacement of $\approx 0.2 \mu\text{m}$, which marks the onset of the resisting pinning force encountered by the contact line.

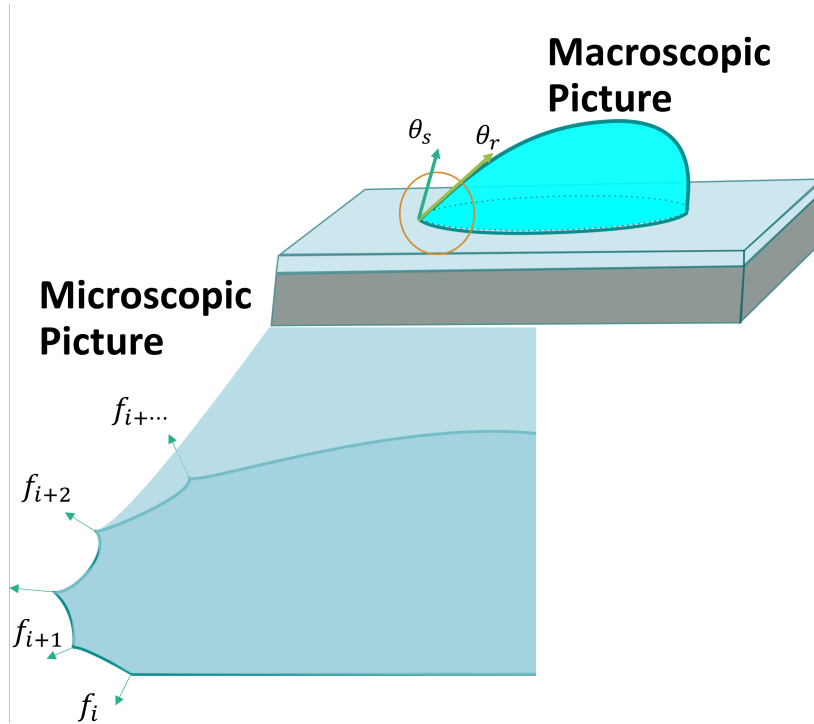


Figure 3.11: Schematic of a sliding drop and the contribution of small localized pinning on the contact line. What is the contribution of small pinning (f_i) in the microscopic scale to the overall macroscopic CAH?

Through the systematic measurement of these interactions, we can extend the framework to calculate the macroscopic contribution of a surface with a defect density n . We begin by considering a droplet on a surface with a static contact angle θ_s , where the horizontal component of the surface tension is $\gamma \cos \theta_s$. The presence of defects introduces localized energy barriers that must be overcome for the contact line to move (Figure 3.11).

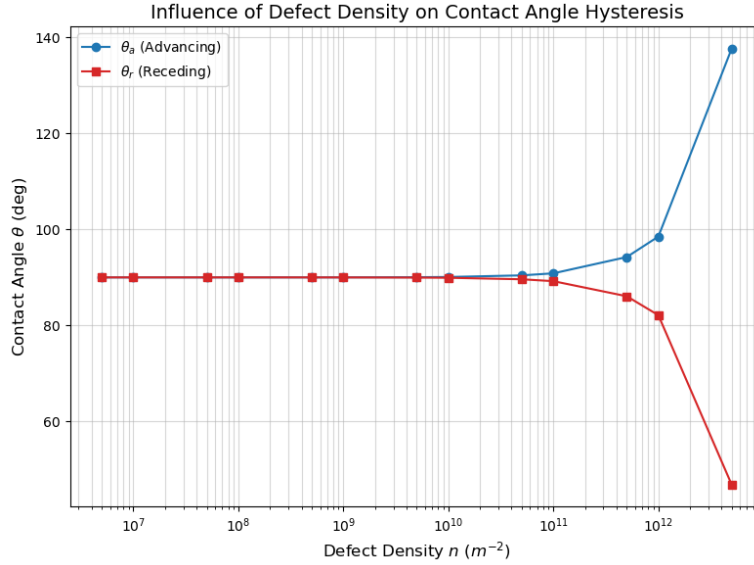


Figure 3.12: Plot showing the calculated dependency of CAH versus the density of hemispherical defects due to energy dissipation ($R = 220$ nm, $\theta_s = 90^\circ$). The data reveals that for densities below $10^8 m^{-2}$, the impact on CAH is negligible, whereas higher densities lead to significant deviations from the equilibrium angle.

Following an energy balance approach, the work performed by the macroscopic lateral force F_L over a displacement Δx accounts for the dissipation at the three-phase boundary. By defining the energy dissipation of a single defect at the advancing line as W_{ad} and at the receding line as W_{re} , we describe the shift from static equilibrium as follows:

For the advancing contact line, the work done per unit area to push the line forward against the defects is:

$$\gamma(\cos \theta_s - \cos \theta_a) = nW_{ad} \quad (3.11)$$

Conversely, for the receding contact line, the work required to pull the line away from the pinning sites is:

$$\gamma(\cos \theta_r - \cos \theta_s) = nW_{re} \quad (3.12)$$

By summing these two contributions, we recover the relationship for the total hysteresis in terms of the energy dissipated by a density n of defects:

$$\gamma(\cos \theta_r - \cos \theta_a) = n(W_{ad} + W_{re}) \quad (3.13)$$

Utilizing the experimental parameters for the hemispherical defect geometry ($R = 220$ nm), we can predict the evolution of θ_a and θ_r relative to the equilibrium angle as a function of n :

Based on the values observed in our dataset (Fig. 3.12), the relationship follows an inverse cosine dependence where the shift in $\cos \theta$ scales linearly with the density of pinning sites:

$$\theta_a = \arccos \left(\cos(90^\circ) - \frac{W_{ad}}{\gamma} \cdot n \right) \cdot \frac{180}{\pi} \quad (3.14)$$

$$\theta_r = \arccos \left(\cos(90^\circ) + \frac{W_{re}}{\gamma} \cdot n \right) \cdot \frac{180}{\pi} \quad (3.15)$$

In these expressions, W_{ad} and W_{re} represent the characteristic work of the pinning events extracted from our experimental friction maps, providing a physical basis for the observed shifts in contact angles.

3.7 Numerical Simulations

To complement our experimental observations and validate the localized force models, we performed numerical simulations using the Surface Evolver [62] software package. The primary objective was to characterize the mechanical energy landscape and the lateral force-distance relationship as a picoliter drop's receding contact line interacts with a single hemispherical defect.

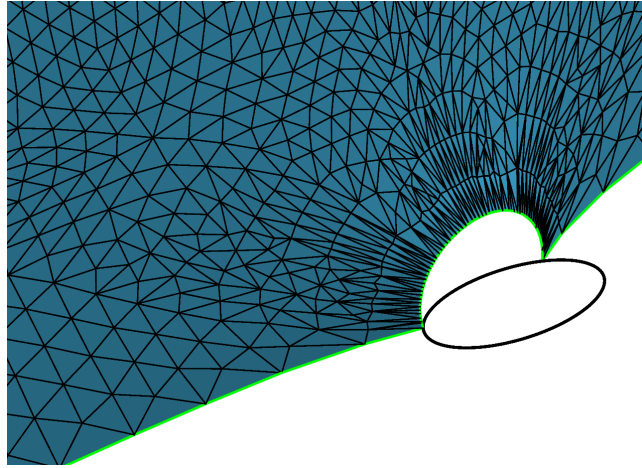


Figure 3.13: Visual representation of the Surface Evolver Simulation procedure, the mesh correspond to the liquid air interface.

3.7.1 Simulation Methodology and Boundary Conditions

The simulation environment was constructed by defining the liquid-air, liquid-solid, and liquid-defect interfaces through a refined mesh of triangles, as shown in figure 3.13. The total energy

of the system was minimized by seeking a state that satisfies the Laplace condition ($\Delta P = 0$) while adhering to several key physical constraints:

1. **Thermodynamic Equilibrium:** Interfacial energies were indirectly defined using Young's equation, setting the term $\gamma_{SL} - \gamma_S$ equal to $-\gamma \cos \theta$ for both the substrate and the defect.
2. **Volume Conservation:** The total liquid volume was held constant at $V = 64$ pL throughout the displacement process.
3. **Cantilever Pinning (The Sticky Point):** A critical feature of our experimental design is the "sticky point" on the cantilever, which prevents the drop from sliding off the probe during high-force interactions. In the simulation, this is modeled by pinning the top contact line to a fixed circular boundary with a diameter of $35 \mu\text{m}$, mimicking the physical anchoring provided by the hydrophilic spot.

Simulations were conducted using non-dimensional parameters normalized relative to the characteristic length $R_0 = (3V/4\pi)^{1/3}$.

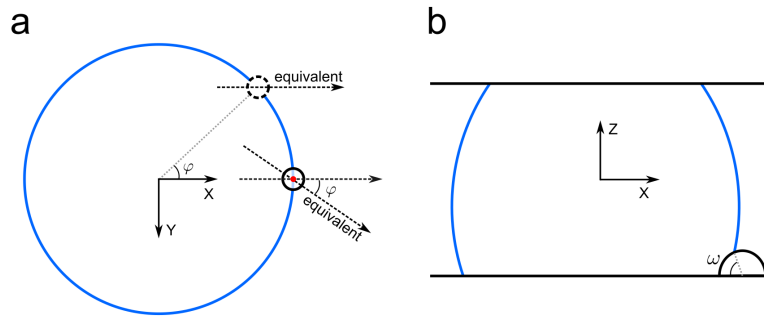


Figure 3.14: (a) Schematic representation of the contact line on the substrate. The defect position is readjusted relative to the reference point (red). (b) Side view illustrating the position angle ω on the hemispherical defect.

3.8 Conclusions and Discussion

Despite the open questions regarding the azimuthal angle dependence, this work demonstrates through a combination of experiments and numerical simulations that the pinning models described by de Gennes are valid at this sub-microscopic length scale. This is a significant finding, as these interactions occur at scales approaching the limits of thermal fluctuation energy barriers.

Experiments on nominally smooth surfaces show that natural topographic and chemical heterogeneities lead to discrete pinning events, which manifest as well-defined ring-like features in the friction maps. These features reveal that dissipation is not a uniform process but is

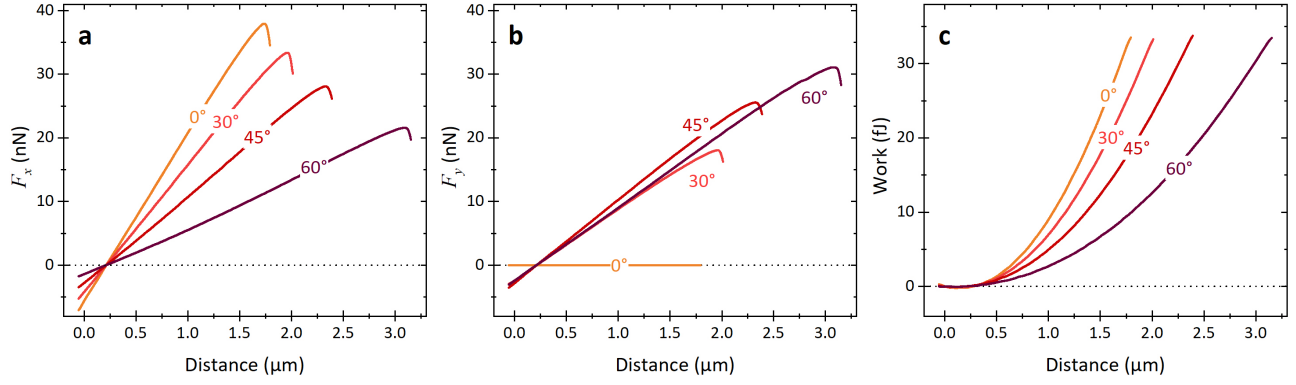


Figure 3.15: Surface Evolver results for $R = 220$ nm and $\theta_{sub} = 114^\circ$. (a) Lateral force F_x vs. displacement for various angles φ . (b) Perpendicular force F_y . (c) Calculated work W performed during meniscus stretching.

localized within a peripheral zone of approximately 200 nm around the three-phase contact line.

We can highlight the fact that the use of FFM with a droplet probe is a sensitive and powerful tool to image the local wetting landscape and resolve the discrete energy dissipation events at the triple-phase boundary with nanometric precision. The ability to quantify the force-distance relationship and the work terms W_{ad} and W_{re} for a single defect provides a fundamental "building block" for understanding macroscopic friction.

The analytical derivation relating microscopic work to macroscopic angles reveals a critical threshold for surface influence. Observing the obtained results, we see that a huge density of defects, exceeding 10^{11} m^{-2} , is required to change the CAH by more than a few degrees. In contrast, for the low densities typically measured on smooth hydrophobic surfaces ($\sim 10^8 \text{ m}^{-2}$), the calculated contribution of these discrete defects to the contact angle shift is nearly negligible.

This finding motivates the next chapter, which investigates the influence of these defects over the overall CAH and friction. We will expand our model to different defect configurations, such as rectangular patches and pillars, to investigate how the density and distribution of these microscopic interactions govern the overall energy dissipation and contact angle hysteresis on a larger scale.

Chapter 4

Reflection Microscopy: Imaging Contact Line Dynamics

Having validated the force profiles of a droplet interacting with isolated defects through both experimental picoliter measurements and Surface Evolver simulations, it is now necessary to expand this framework to more general and complex surface configurations. While Atomic Force Microscopy (AFM) has proven to be an exceptional tool for visualizing and quantifying contact line interactions with nanometric precision, the technique presents inherent limitations for large-scale surface analysis.

In cases involving strong pinning sites or high defect densities, the magnitude of localized events can obscure the background friction signal, leading to a loss of information regarding the intrinsic surface properties. Furthermore, characterizing larger topographical features is challenging with a droplet probe, as the shape and strength of the defect significantly influence the overall contact line dynamics in ways that exceed the typical AFM scan area.

Another critical constraint is the trade-off between temporal and spatial resolution. Acquisition of a high-quality AFM friction map requires significant time, often exceeding 8 minutes per scan, and because acquisition time scales quadratically with resolution, achieving higher detail is often impractical for dynamic studies.

To address these limitations, we have implemented a faster, more practical method to study contact line dynamics using the inverted microscope and high-speed camera device discussed in Section 2.2. This approach allows for real-time measurements at high velocities, though it introduces new challenges regarding data processing and image analysis, which will be detailed in this chapter.

4.1 Optical Measurements

4.1.1 Experiment

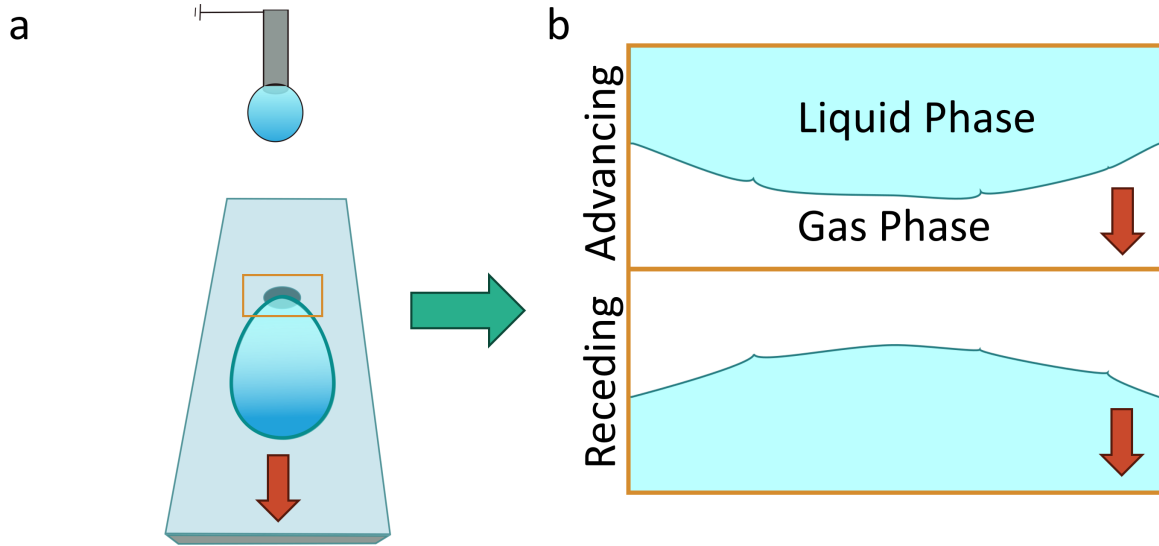


Figure 4.1: a) Top view of the experiment, the drops lands on the surface and slide. when the drops goes through the field of view marked in orange, the camera is triggered. b) field of view, representation of the three phases meeting forming the contact line. The red arrow indicates the direction of motion

To characterize the dynamics of the contact line over larger surface areas and at higher velocities than those attainable via AFM, we utilized a custom-built optical setup. The experiments involved placing a droplet (typically 5–10 μL for macroscopic studies) on the target substrate, which was positioned above an inverted microscope objective (Section 2.6).

The fluid delivery was controlled by a peristaltic pump connected to a grounded needle positioned 10–15 mm above the surface, which allowed for a constant and reproducible drop flow. After traveling approximately 20–25 mm down the tilted substrate, the droplet entered the microscope field of view, triggering image acquisition, the tilt was set between 30° to 45° . This setup enabled the recording of the three-phase contact line from below at frame rates up to 100000 fps, providing a clear visualization of the contact area footprint and the local distortions caused by surface heterogeneities.

4.1.2 Sample Characterization

Expanding upon the investigation of Teflon surfaces presented in the previous chapter, the scope of this research is broadened to include a diverse set of smooth hydrophobic substrates in table 4.1. This selection comprises a polystyrene (PS) film prepared via dip-coating, two

	RMS Roughness	Advancing Contact Angle	Receding Contact Angle	CAH (°, ±2°)	$\frac{1}{A} \sum W_i$ (mN/m)	$\Delta\Theta_r$ (°)
PS	0.4 nm	100°	84°	16°	0.14	0.10
Teflon	0.6 nm	125°	112°	13°	0.043	0.04
PFOTS	0.5 nm	117°	97°	20°	0.128	0.10
PFOMS	0.3 nm	106°	93°	13°	0.379	0.30
PDMS	0.3 nm	108°	105°	3°	0.018	0.01

Table 4.1: Characterization of the hydrophobic surfaces and estimated reduction in receding contact angle due to defects. RMS is the root-mean-square roughness as measured by AFM. Contact angles were measured with water using a sessile drop. CAH is the contact angle hysteresis. The defect energy density for the receding contact line, $\frac{1}{A} \sum W_i$, was calculated with measured deflections according to eq. (3). The resulting decrease in the receding contact angle, $\Delta\Theta_r$, was also calculated with eq. (3).

surfaces synthesized through Chemical Vapor Deposition (CVD), and a surface functionalized with polydimethylsiloxane (PDMS) brushes. These specific materials were selected to provide a range of characteristic contact angles and varying molecular architectures, from rigid bulk polymers to highly mobile, surface-grafted chains. By characterizing these five distinct surfaces, we aim to determine if a universal relationship exists between localized surface defects and macroscopic wetting behavior across different chemical environments.

To correlate the macroscopic wetting behavior with the surface topography, the series of hydrophobic surfaces were characterized (Table 4.1). Topographic profiles and surface roughness parameters were determined via Atomic Force Microscopy (AFM) operated in tapping mode over $5 \times 5 \mu\text{m}^2$ scan areas. The characterized values for the surfaces investigated are summarized in Table 4.1. These metrics provide the baseline for determining the "background" hysteresis and the threshold at which discrete defect interactions begin to dominate the macroscopic energy dissipation.

4.2 Image Processing and Data Visualization

When we image contact line deflections, we need to use high frame rate to observe the contact line without distortions, however, with such a short time, in average $4 \mu\text{s}$ of exposure time, we can't obtain well define images, and the brightness of the pixels is not homogeneous. Another important fact is that we are using a water immersion objective, where there is a liquid meniscus between the slide and the objective, in a completely horizontal case the image is homogeneous, but the gravity affects the meniscus causing aberration throughout the image. As a result, we can see in both fig 4.2 a and b, the contact line lost sharpness in the edges. Thus we have to perform very careful image processing to obtain trustful and reproducible data.

The image processing workflow [63] is summarized in Figure 4.3. To transform raw video

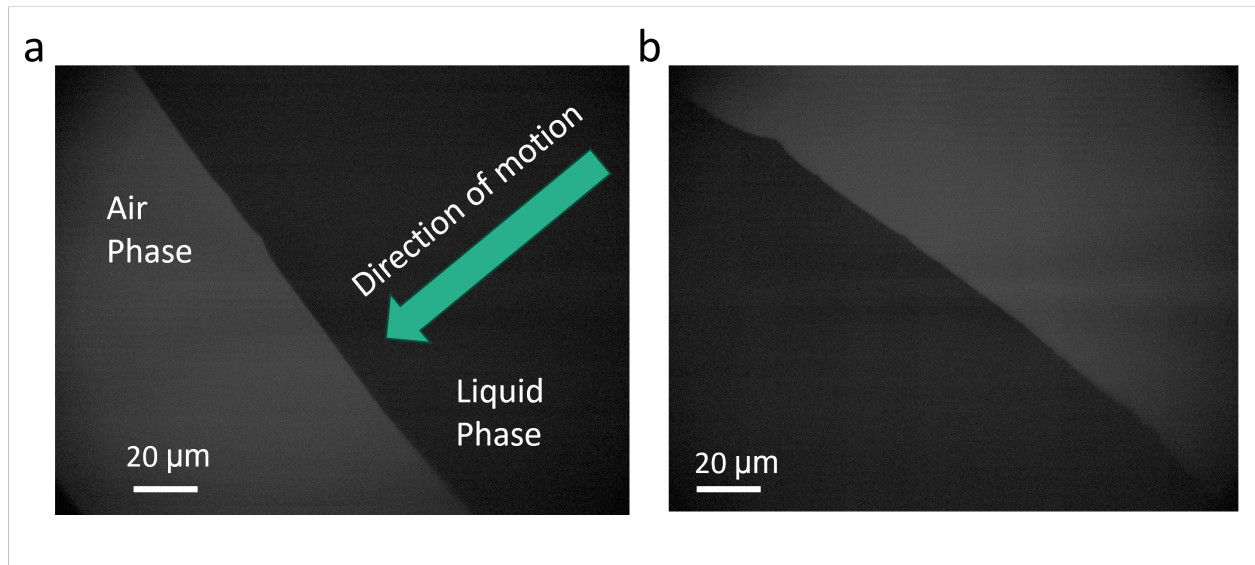


Figure 4.2: a) Example of a Front Contact line frame, of a water drop sliding on a PFOMS surface, b) Rear contact line, we can appreciate the contact line and its interactions.

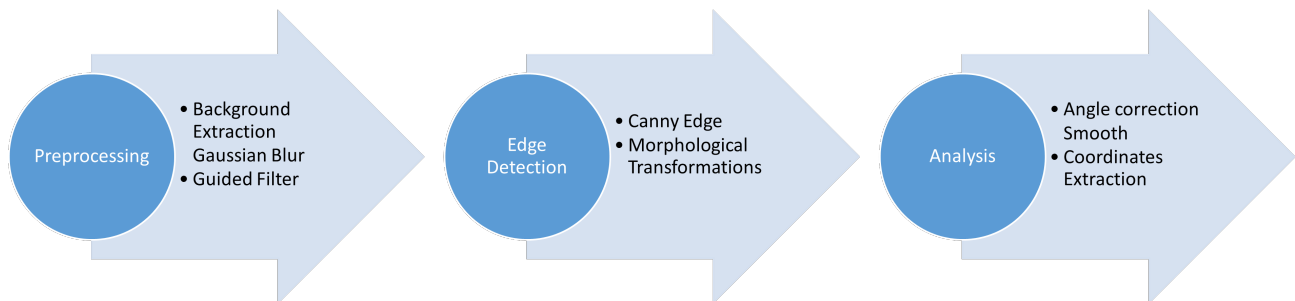


Figure 4.3: Workflow for image analysis and defect quantification, detailing the preprocessing, edge detection, and coordinate analysis stages.

frames into quantifiable data, we follow a three-stage pipeline.

4.2.1 Preprocessing

4.2.1.1 Metadata Extraction and Signal Normalization

The initial phase of the data analysis pipeline involves the extraction of critical metadata from the raw `.cine` video containers. Parameters including the bit-depth (*bpp*) and exposure settings are retrieved to ensure physical consistency across the dataset. Given that raw sensor data is

typically captured at high dynamic ranges (e.g., 12-bit or 16-bit), the images are first normalized and mapped to a standard 8-bit unsigned integer space (*uint8*) using the relation [64]:

$$I_{8bit} = \lfloor \frac{I_{raw}}{2^{bpp} - 1} \times 255 \rfloor \quad (4.1)$$

Subsequently, a gamma correction is applied to account for the non-linear response of the optical system, linearizing the intensity values via a pre-computed Look-Up Table (LUT) based on the specific setup parameters.

4.2.1.2 Background Subtraction and Contrast Optimization

To isolate the dynamic features of interest from static optical noise and non-uniformities in the illumination field, a background subtraction method is implemented. A background model is estimated by applying a wide-aperture Gaussian blur (51×51 kernel) to the gamma-corrected frame, effectively capturing the low-frequency spatial variance of the light source. By subtracting this model from the original signal, we obtain a corrected image with a flattened baseline:

$$I_{corrected} = I_{\gamma} - G_{\sigma=51}(I_{\gamma}) \quad (4.2)$$

Following subtraction, Global Histogram Equalization is performed [65]. This step redistributes the intensity frequencies to follow a uniform distribution, maximizing the contrast of the interface and ensuring that the gradient-based operators in the subsequent stages receive a high-contrast input.

4.2.1.3 Iterative Edge-Preserving Denoising

A central challenge in isolating the contact line is the presence of high frequency stochastic noise which can lead to over segmentation. To resolve this, we employ an iterative filtering architecture. This involves a sequence of N cycles, where N is adapted to the specific noise characteristics of each video, alternating between Gaussian smoothing and Guided Filtering.

4.2.1.4 Gaussian smoothing

Gaussian smoothing applies a 'blur' effect to an image to reduce noise and eliminate high intensity peaks or artifacts. In two dimensions, the operation is defined by the continuous function [66]:

$$G(x, y) = \frac{1}{2\pi\sigma^2} e^{-\frac{x^2+y^2}{2\sigma^2}} \quad (4.3)$$

Since digital image processing relies on discrete pixel data, this continuous function is implemented using an approximated discrete kernel.

4.2.1.5 Guided Filtering

The Guided Filter [67] serves as an edge-preserving smoothing operator that utilizes a local linear model. For a window ω_k centered at pixel k , the output q is defined as:

$$q_i = a_k I_i + b_k, \quad \forall i \in \omega_k \quad (4.4)$$

where I is the guidance image. In our implementation, the image acts as its own guide (self-guidance), allowing the filter to suppress noise within homogenous regions while preventing the "blurring out" of sharp intensity gradients. By repeating this process through N iterations, the internal textures of the droplet are suppressed, yielding a simplified manifold optimized for the Canny edge detection algorithm.

4.2.2 Edge Detection

We utilize the Canny edge algorithm to identify the interface coordinates. Morphological transformations (such as closing operations) are then applied to bridge gaps and remove isolated artifacts, ensuring a continuous and clean contact line (CL) [68,69].

a) Low-Frequency Edges b) High-Frequency Edges c) Intersected Edges

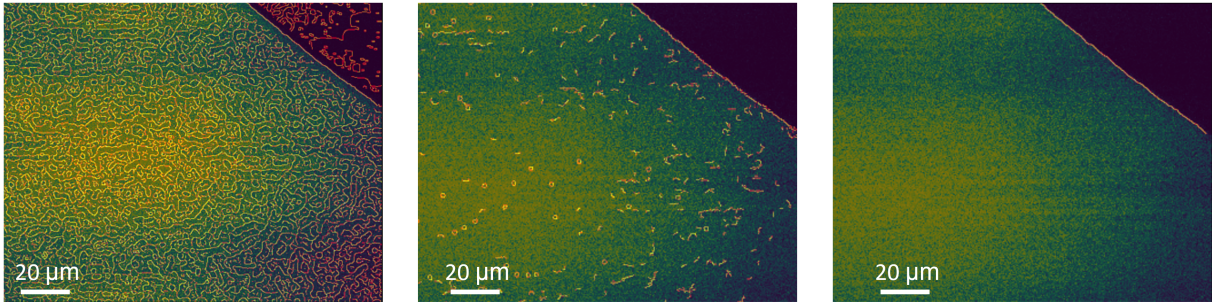


Figure 4.4: Representation of the two approaches for edge extraction, we notice that both intersect on the contact line, and we take advantage of this to calculate the final edges. The image correspond to a water drop sliding on a PFOTS surface.

4.2.2.1 Morphological Feature Extraction

The final segmentation is performed using a multi-scale Canny operator to capture the full spectral range of the image gradients. In this hierarchical approach, a **low-frequency edge map** (Figure 4.4a) is first generated with a larger 7×7 aperture; this coarser scale is more sensitive to broader intensity transitions and ensures the connectivity of the global boundary. Simultaneously, a **high frequency edge map** (Figure 4.4b) is produced using a standard 3×3 aperture to define the primary topological structure with high spatial precision. These

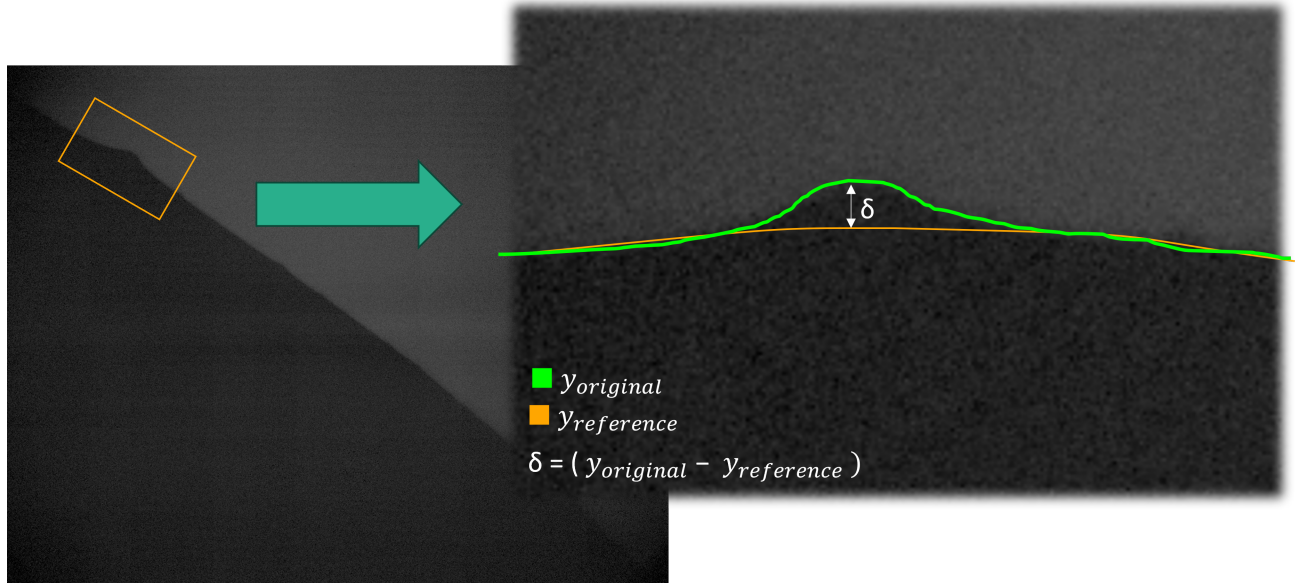


Figure 4.5: Visual representation of how the coordinates are extracted, and the deflection values are obtained.

high frequency edges are subsequently dilated using a 5×5 structuring element to bridge infinitesimal gaps and ensure contour closure. To obtain the final interface coordinates, the high and low frequency edge maps are intersected (4.4c). This logical intersection allows for the robust extraction of the largest continuous contour, effectively isolating the primary physical phenomenon from the background noise by retaining only the most consistent features across both scales.

4.2.3 Analysis and coordinates extraction

The final stage involves coordinate extraction and spatial correction. To ensure consistency across different experiments, we apply an angle correction by rotating the dataset so that the time-averaged CL is aligned horizontally.

Once we have a well defined contact line for every frame, it is necessary to analyze the propagation and pinning process. The field of view captured by the objective is very small relative to the drop ($\sim 1/100$ of the drop width), meaning local variations can significantly impact observations. By rotating the data to a horizontal mean, we can more accurately compare different experimental runs.

To quantify defects and pinning events, we define an "unperturbed" reference CL for each frame by fitting a third-degree polynomial to the detected coordinates as shown in figure 4.5. This reference represents the ideal contact line shape. To prevent localized pinning or jump events from biasing the fit, the reference is refined iteratively: points deviating from the fit by more than 5 pixels ($\approx 1.5 \mu\text{m}$) are excluded as outliers, and the polynomial is re-calculated.

The magnitude of pinning is then defined by the **Deviation** (δ):

$$\delta = (y_{raw} - y_{fit}) \quad (4.5)$$

A pinning site is identified and counted when this deviation exceeds a predefined threshold, signaling a departure of the physical CL from its ideal curvature due to a surface defect.

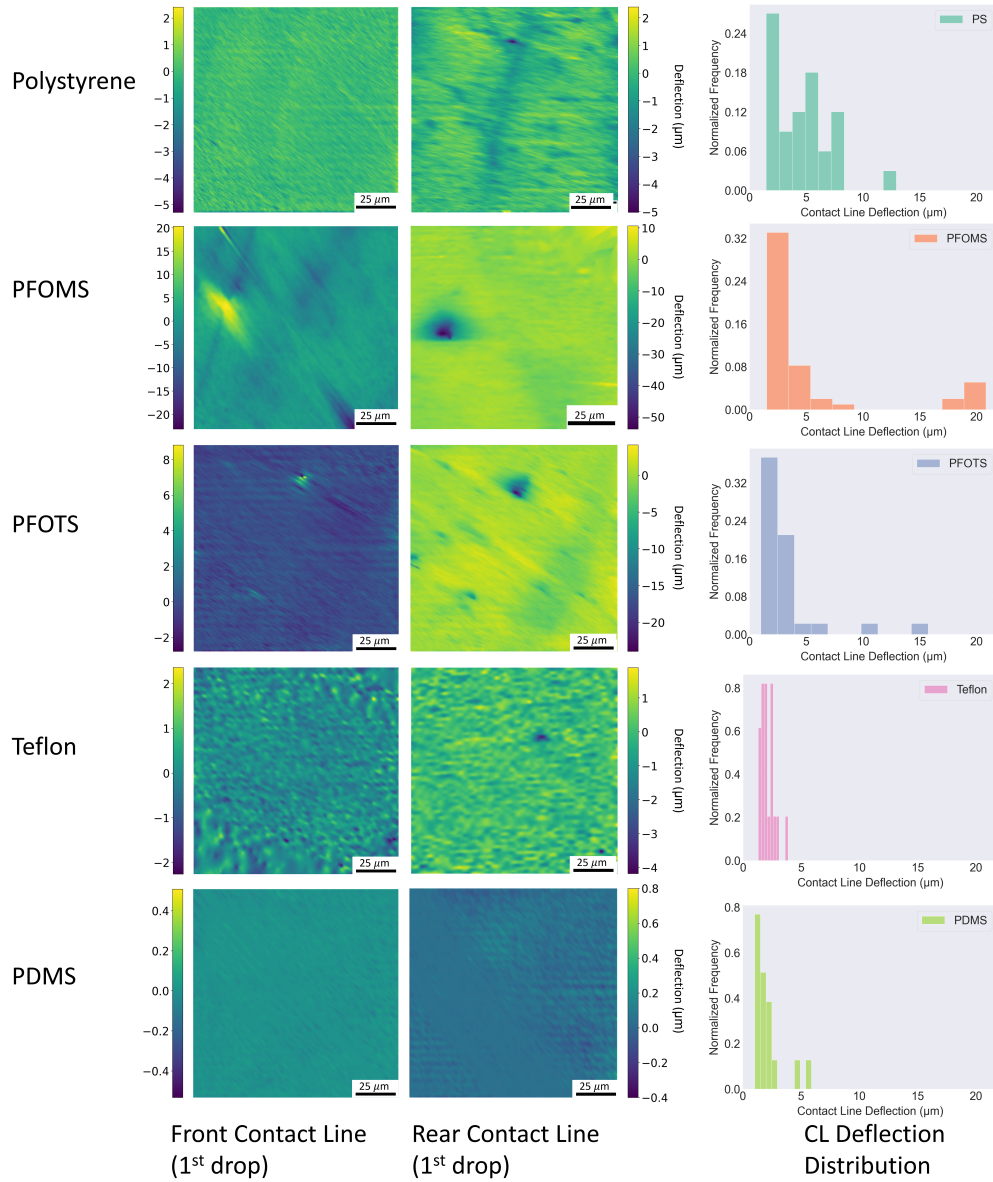


Figure 4.6: Deflection maps and defect size distributions for (a) PS, (b) PFOMS, (c) PFOTS, and (d) Teflon. The color scale indicates the magnitude of contact line deformation, where yellow represents positive pinning and blue represents negative jumps.

4.2.3.1 Quantifying the deflection

We propose 2 approaches to quantify the perturbation of the contact line as a drop slides on a hydrophobic surface:

Defect Density: A robust way to quantify the quality of a hydrophobic surface is to count the distribution of defects over a certain Area ($150 \times 150 \mu\text{m}^2$), as shown in figure 4.7.

1. We make a binary image out of the defect map and apply a conservative amplitude threshold to minimize false positives from localization noise.
2. We apply Dilation and erosion to connect deflection points that are close and erase isolated noise.
3. After filtering smaller groups and recognizing the defect events as one, we can count and characterize them.

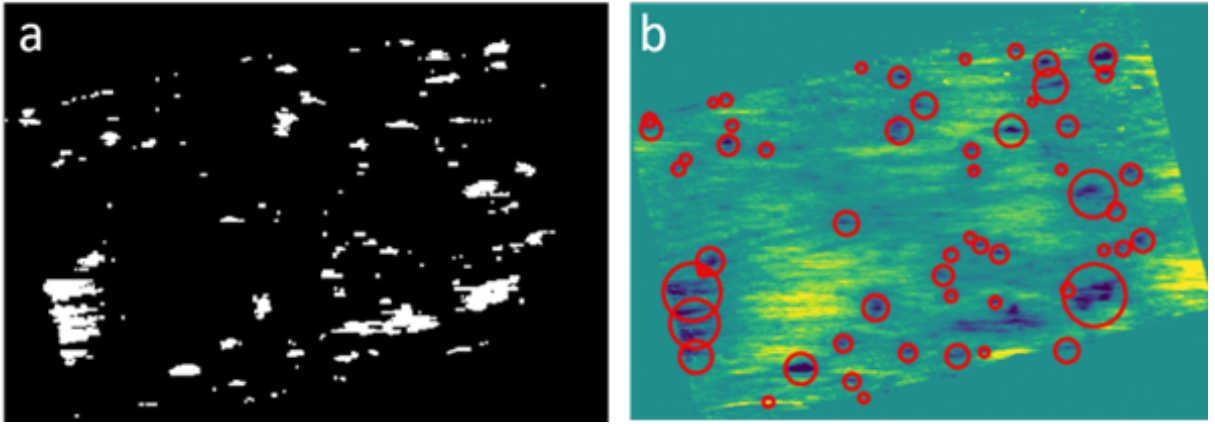


Figure 4.7: a) We make a binary image out of the deflection values in a matrix. We apply Dilation and erode to connect the deflection points that are too close and erase the isolated ones. b) After Filtering smaller groups and recognizing the defect events as one, we can count them and characterize them, storing the data.

CL roughness: A common practice to analyze topography maps or three-dimensional arrays is to define the roughness of the defects in “Z” respect to the plane. We calculate two magnitudes: the average and the root mean square (RMS) roughness. The average $\bar{z}$ is the sum of the deviation values z_n divided by the number of elements N . To get the RMS roughness, we define the central moment μ_i :

$$\mu_i = \frac{1}{N} \sum_{n=1}^N (z_n - \bar{z})^i \quad (4.6)$$

Where N is the number of elements. For $i = 2$, we obtain the square RMS roughness (variance), $\sigma = \sqrt{\mu_2}$. The average represents the overall deflection of the contact line in each

direction (positive and negative) relative to the original line. The RMS roughness accounts for the absolute value of the deflection, representing the total amount of deformation without considering the direction. Points with an absolute deflection smaller than one pixel are excluded to avoid background noise.

4.3 Results

4.3.1 Deflection Maps and Defect Density Distribution

Once the background extraction and normalization procedures are complete, the contact line deflection can be calculated following the methodology referred in figure 4.7.

The resulting deflection maps (Figure 4.6) reveal a clear asymmetry in the wetting dynamics: the advancing contact line typically exhibits weaker and less frequent deflections compared to the receding edge. This suggests that the energy barrier for the liquid front to advance over a defect is significantly lower than the force required for the rear to depinn, confirming that pinning is more pronounced on the receding side. Consequently, our quantitative density analysis is based primarily on receding contact line behavior.

By applying a threshold to these maps to filter out pixel-level noise, we determined the density of optically resolvable defects (Figure 4.8):

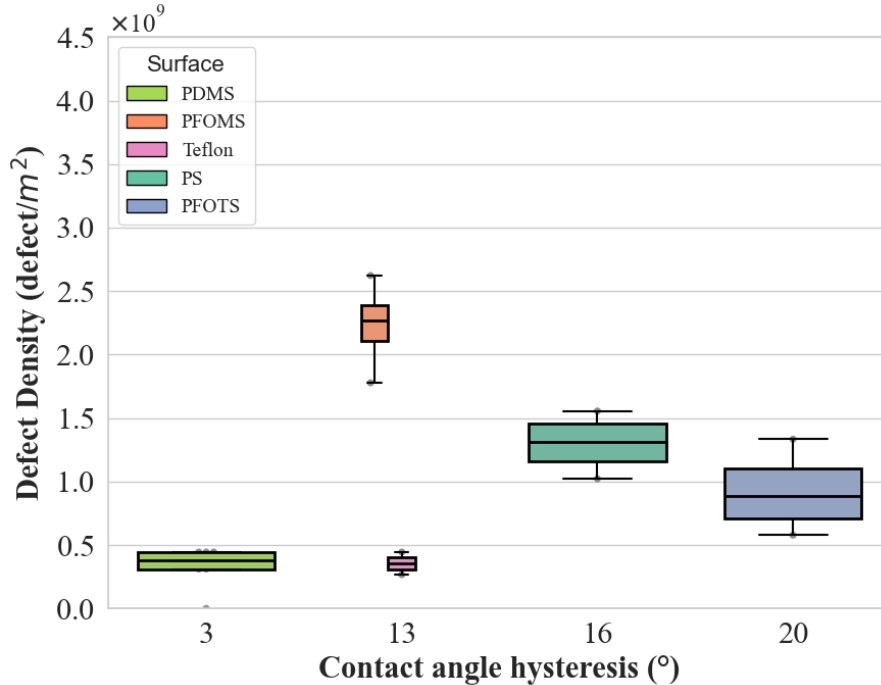


Figure 4.8: Calculated density of optically resolvable defects across the characterized substrates.

Interestingly, no direct correlation is observed between the observable defect density and the measured contact angle hysteresis (CAH). For example, PFOMS and Teflon exhibit nearly

identical defect densities (approximately 1.3×10^{-2} defects/ μm^2) yet show a discrepancy in CAH of nearly 10° . Still, we can not argue that defects do not play a role on CAH if we don't consider smaller defects, for this we will save the conversation for the next chapter, where we will resolve even smaller defects and their density.

4.3.2 Average Deflection and Contact Line Roughness

In contrast to AFM-based friction measurements, high-speed inverted microscopy enables the simultaneous characterization of the mean contact line position and its intrinsic roughness (also referred to as the standard deviation). This roughness represents the local "oscillations" or stochastic spatial noise of the contact line as it traverses a surface. As shown in Figure 4.9, we observe roughness values approaching $1 \mu\text{m}$. These values differ substantially from discrete defect counts; because these deformations are not localized to single spots but are distributed randomly along the contact line, they represent a collective response to the surface topography.

We observe from the plots that the average motion increases as the CAH increases. However, we cannot directly attribute the macroscopic CAH to this deflection, as the deflection itself may simply be a kinematic consequence of the friction. To illustrate the real influence of this "wobbling," we calculate the energy using the Joanny and de Gennes approximation for small perturbations of the contact line, as discussed in Section 3.5.

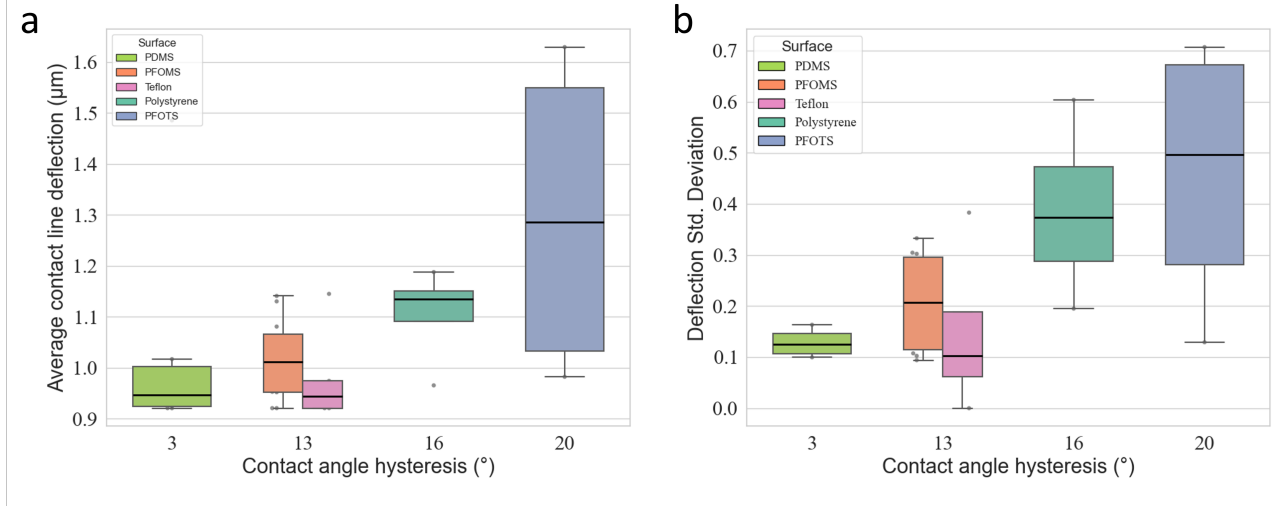


Figure 4.9: Results for the average contact line deflection (a) and roughness (b). A slight correlation is visible between the mechanical motion of the contact line and the macroscopic contact angle hysteresis.

By treating our obtained experimental data, $z_{\text{dev}}(x)$, as an arbitrary periodic function for the contact line position $\eta(x)$, we define:

$$\eta(x) = z_{\text{dev}}(x) \quad (4.7)$$

Assuming the contact angle θ is close to 90° to simplify the boundary conditions, we describe the distortion of the liquid-air interface $u(x, y)$ in the plane of the surface. Following the Fourier decomposition of the contact line profile, where η_q are the Fourier components of the experimental $z_{\text{dev}}(x)$, the overall interface profile is given by:

$$u(x, y) = \sum_q \eta_q e^{iqx} e^{-|q|y} \quad (4.8)$$

Similarly to the approach in the first chapter using well-defined periodic functions, we can plot the liquid-air interface as shown in Figure 4.10. Here, we use the experimental contact line profile as an arbitrary function to derive the associated energy. This mathematical framework allows us to translate the observed "wobbling" into a stored elastic energy term. The total energy per unit length associated with these distortions is proportional to the sum of the squares of the Fourier coefficients $|\eta_q|^2$ weighted by their respective wavenumbers $|q|$:

$$E_{el} = \frac{\gamma}{4} \sum_q |q| |\eta_q|^2 \quad (4.9)$$

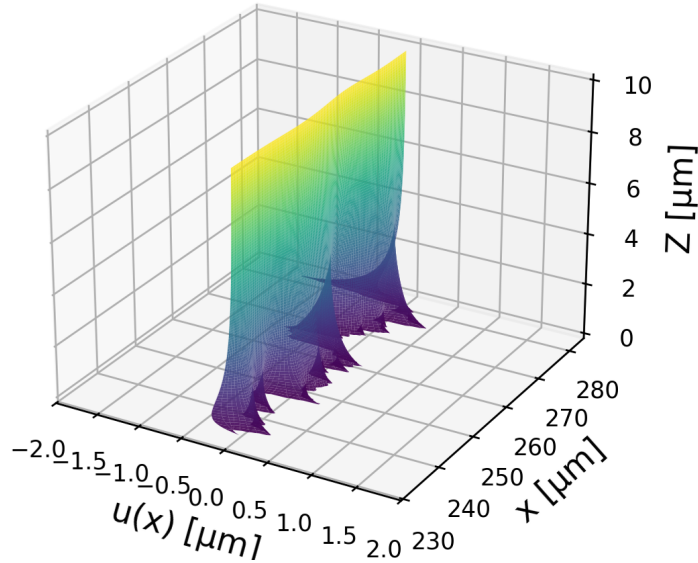


Figure 4.10: Surface plot of the interface perturbation caused by small contact line deflections ($< 1 \mu\text{m}$) on PS. The macroscopic contact angle was set to 90 degrees for simplicity.

From the results of this calculation, we can evaluate the energy stored in contact line fluctuations across the different surfaces to obtain a linear energy density. We deliberately restrict our analysis to fluctuations smaller than $1 \mu\text{m}$; as Joanny and de Gennes established, larger contact line displacements enter the "strong pinning" regime where irreversible jumps—and consequently, true hysteresis occur. Figure 4.10a shows the resulting perturbation of the liquid-air interface induced by the deformation of the three-phase contact line. In Figure 4.11b, we

observe how this linear energy density evolves over time as the drop slides.

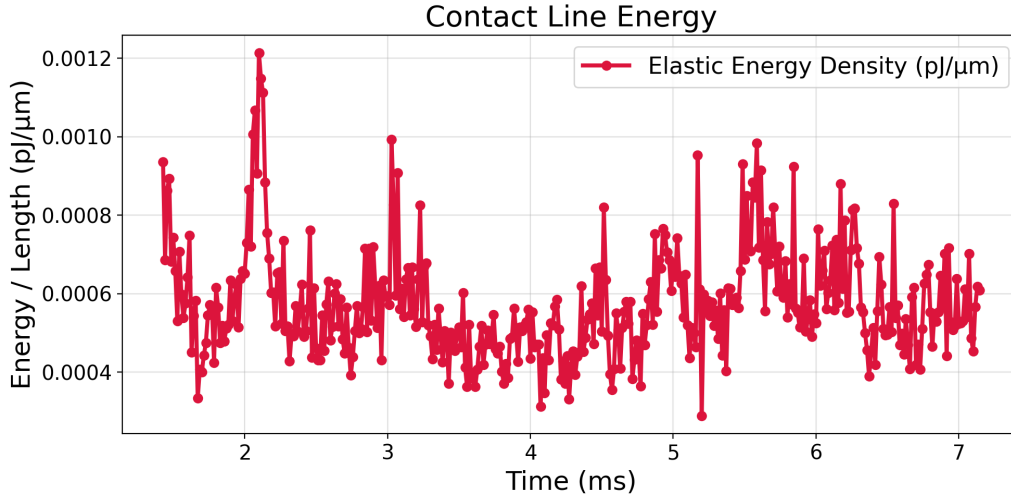


Figure 4.11: Time evolution of the energy density for the receding contact line of a drop sliding on PS. The values remain relatively constant, indicating a steady-state elastic deformation.

Contact Line Energy Density and the Reversibility Argument: By evaluating the length of the contact line over which the energy was calculated, we can extrapolate an average elastic energy density for the receding edge. The critical question is whether these persistent, small-scale fluctuations influence the macroscopic Contact Angle Hysteresis (CAH).

To answer this rigorously, we can construct a limiting-case scenario. Let us momentarily assume that all of this stored elastic energy (E_{el}) is entirely dissipated (lost as heat) as the line advances. To equate this linear energy density to the macroscopic work of adhesion hysteresis (which has units of energy per unit area, represented by γ), we must distribute E_{el} over the characteristic interaction length scale of the advance, Δx :

$$\gamma(\cos \theta_r - \cos \theta_s) \approx \frac{E_{el}}{\Delta x} \quad (4.10)$$

It is crucial to note that Δx is not an arbitrary sliding distance, but rather the correlation length of the surface features—the microscopic spatial scale over which the contact line deforms before relaxing back to its equilibrium state (in our case, $\Delta x \approx 1 \mu\text{m}$).

Using the experimental data from Figure 4.11 for a drop on PS, the receding contact line maintains a relatively constant elastic energy density of $E_{el} \approx 0.0005 \text{ pJ}/\mu\text{m}$. Assuming a nominal liquid surface tension for water of $\gamma \approx 72 \text{ pJ}/\mu\text{m}^2$ and our characteristic defect correlation length of $\Delta x \approx 1 \mu\text{m}$, substituting these values yields a theoretical maximum shift in $\cos \theta$ of roughly 6.9×10^{-6} . For a baseline contact angle near 90° , this corresponds to a macroscopic angle change of merely $\sim 0.0004^\circ$.

This quantitative result serves as a definitive physical proof of the theoretical assertion by Joanny and de Gennes: weak heterogeneities that merely cause the line to "wiggle" do not

generate meaningful hysteresis [37]. Our data demonstrates this via two distinct arguments:

- **Quantitatively:** The sheer magnitude of the stored elastic energy is vanishingly small compared to the macroscopic capillary forces.
- **Qualitatively:** These sub-micron fluctuations operate in a purely reversible regime. Because the line smoothly traverses these weak defects without undergoing abrupt, irreversible "pinning-and-snapping" events, the net energy dissipated over a macroscopic cycle is effectively zero.

Therefore, the macroscopic "wobbling" observed in high-speed microscopy cannot be the physical origin of the measured CAH. The observed 10° hysteresis must be governed by a different mechanism, pointing us directly toward the role of smaller, denser, strong-pinning defects, which we will resolve and examine in the next chapter.

Chapter 5

Influence of all Size Defects in Friction Forces

Now that we have presented two different ways of measuring and imaging contact line deflections, together with the characterization of the different surfaces involved in this research, we have a clearer picture of how defects influence contact angle hysteresis. This complements the results of Chapter 3, which explored the force profile and energy contribution of submicroscopic defects, showing that their individual energy contribution is very limited and that a large number of defects might be necessary to significantly influence the dynamic contact angle.

The aim of Chapter 4 was to explore exactly how smooth these so-called smooth surfaces are, and whether there is a contrast between the AFM topographic profile images and the observable pinning. By looking directly at the contact line dynamics, we quantified the number and strength of these defects, realizing that the surfaces, when properly cleaned, are indeed very smooth and do not present a relevant amount of topographical defects. The tilted plate experiment is useful for imaging larger fluctuations and offers many advantages over AFM experiments, such as speed, but it is ultimately limited by optical resolution.

If we want to be certain about the influence of localized defects on contact angle hysteresis, we need to corroborate the existence of pinning events below our optical limit of ~ 300 nm. By complementing these optical experiments with improved-quality droplet-probe friction measurements, where the resolution was increased to resolve features at the 50 nm scale, we provide a dual-scale analysis of wetting. Using these two complementary approaches, we calculate and demonstrate the quantitative influence of defect density and distribution on macroscopic contact angle hysteresis.

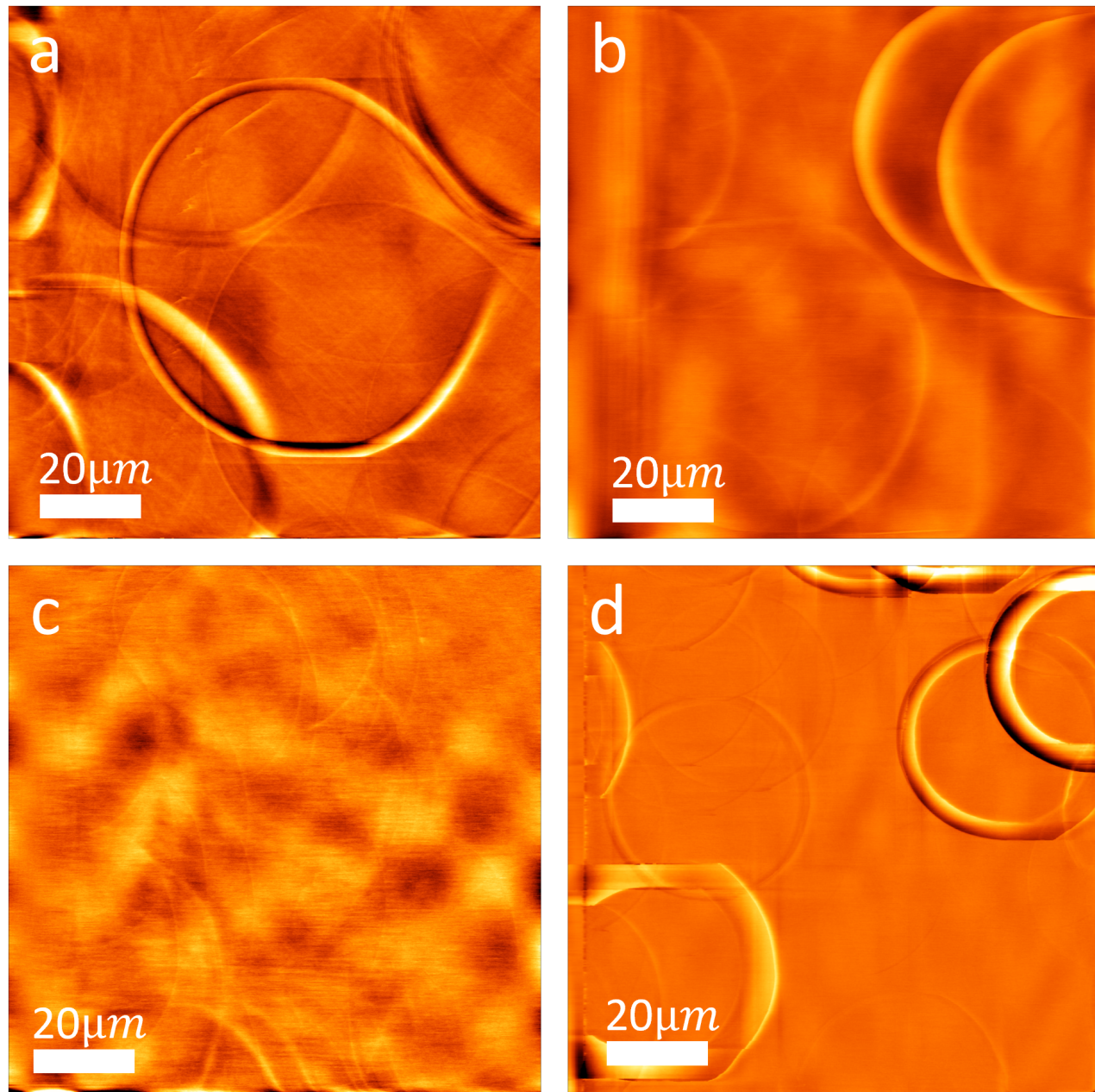


Figure 5.1: Friction Force Maps of the smooth surfaces. a) Polystyrene b) PFOTS c) PFOMS d) Teflon.

5.1 Defect Density with AFM Friction Force

One important finding from Chapter 3 is the realization that, even in the presence of many defects, we can isolate them as individual events. The existence of distinct rings in our friction maps shows that defects do not influence each other's depinning processes, at least at these scales and densities. Thus, by counting the number of rings in the AFM friction map, we can count the number of defects. This inspired us to use AFM to measure defect interactions on a smaller scale, similar to the tilted plate experiments.

As seen in the previous chapter, AFM allows us to achieve high-resolution imaging. For this step, we pushed the limits of the AFM to reach 50 nm per pixel for the same scan size by increasing the pixel density to 2040×2040 (Figure 5.1). In doing so, we detected contact line deflections very close to the thermal excitation limit, ensuring that any smaller pinning events would contribute negligibly to overall energy dissipation. To characterize the interaction strength, we define the deflection as the spatial distance between the equilibrium (zero-force) position and the maximum extension achieved immediately prior to detachment (Figure 5.2).

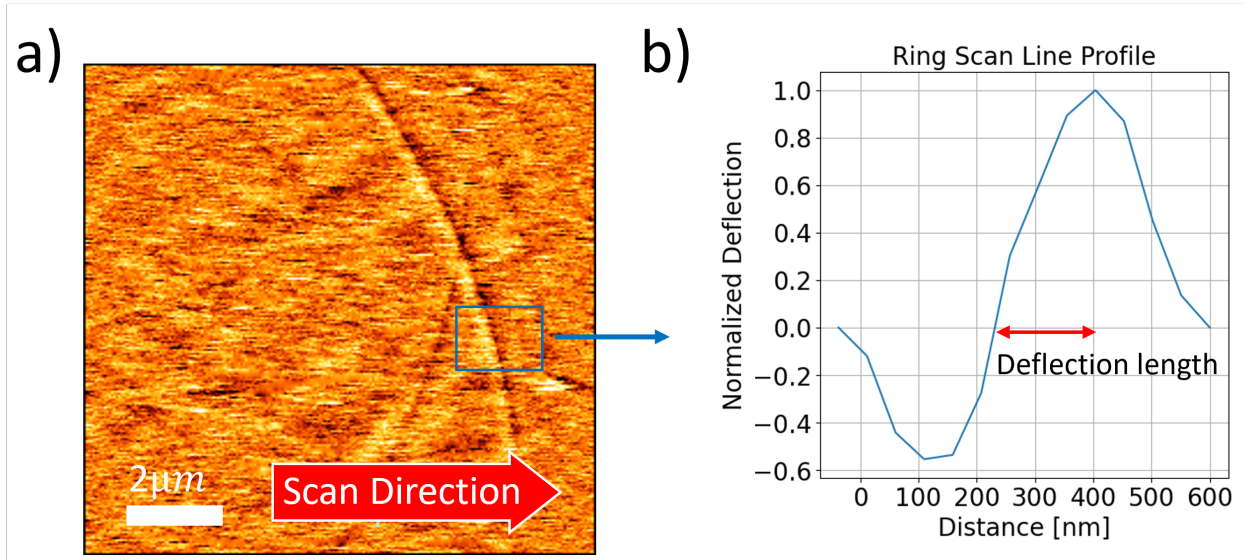


Figure 5.2: Droplet-probe AFM results. (a) Friction map of a PFOMS surface showing characteristic ring structures. (b) Single line scan profile across a natural defect, showing a depinning length of approximately 200 nm.

5.1.1 Natural Defects

In Figure 5.2, we see examples of the results for our surfaces. We leave PDMS aside due to its "brush-like" nature; we do not obtain a clear friction profile, and we lose the capacity to distinguish natural defects from background noise. For the other surfaces, reproducible ring-like force patterns emerge, representing the interaction of the picoliter drop's contact line with

individual nanoscopic defects.

5.1.2 Special Case: PDMS Brushes

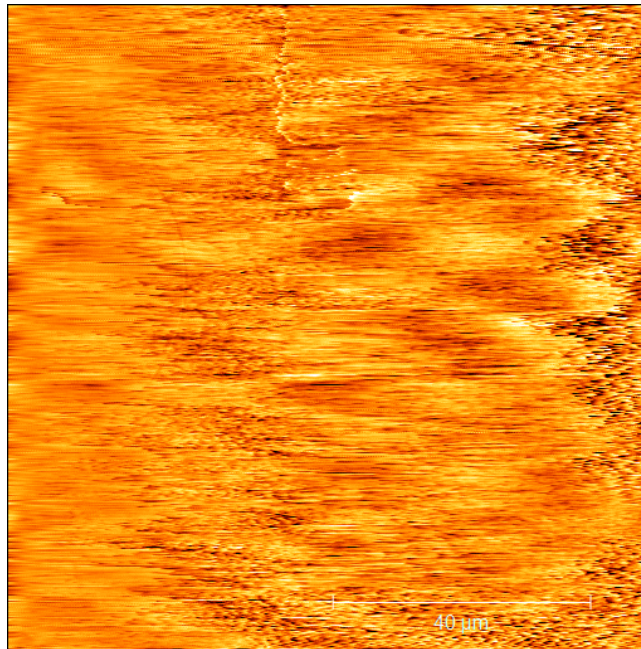


Figure 5.3: Friction force map of a drop scanning PDMS brushes; the 'forest' of pinning provoked by the brush-drop interaction is clearly visible.

Among the studied surfaces, PDMS brushes are quite unique [70]. It is well known that their low contact angle hysteresis is due to the liquid-like nature of their composition. By optimizing the length of these chains, as well as the homogeneity of the grafting density, exceptionally low hysteresis, 3° .

Despite these excellent repellent properties, PDMS brushes behave differently than standard smooth hydrophobic surfaces or coatings. Their mechanical properties differ considerably, and their interaction with liquids involves continuous deformation of the polymer layer. When attempting to incorporate AFM friction measurements onto our PDMS brushes, we observe that there is no "clean" background or a standard dynamic regime. This is due to the collective contribution of pinning and depinning events of the brushes; while these are negligible for macroscopic drops, the effect is dominant for picoliter volumes.

As seen in Figure 5.3, the friction profile is densely populated with pinning events separated by a distances ranging from hundreds of nanometers to a micrometer, and we do not observe the ring structures present in other samples. Consequently, for the following section, we will exclude PDMS from the comparative analysis and, when calculating energies, we will rely exclusively on the optical results.

5.1.3 Comparison of AFM and Optical Results

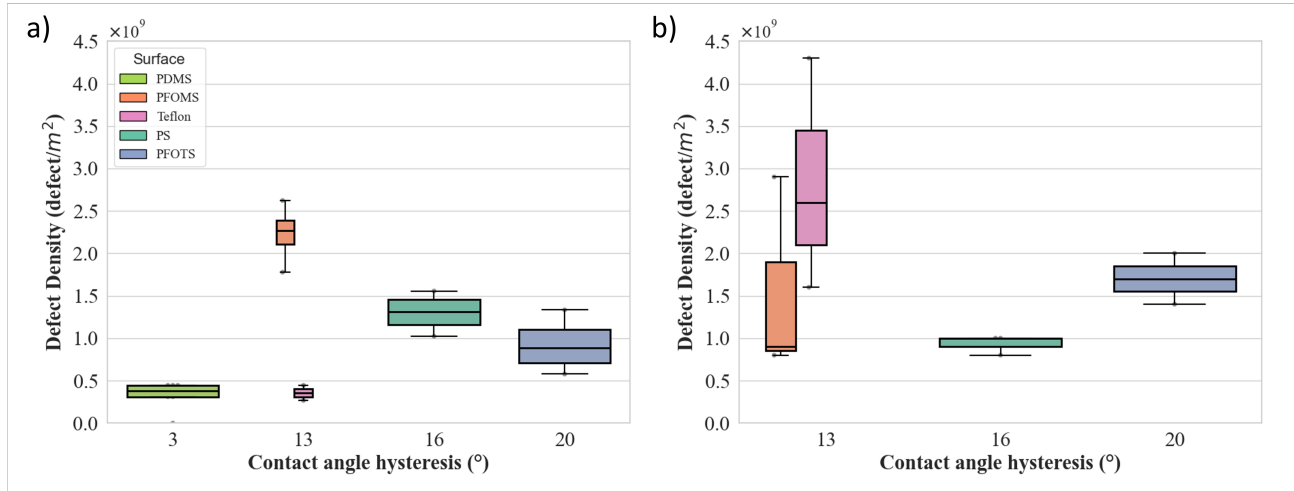


Figure 5.4: Defect density for both the AFM and optical methods. (a) shows the values for the inverted microscope (b) AFM results, we capture more defects measuring with AFM than with optical imaging.

Following the extraction of the background from the friction maps and subsequent contrast enhancement, natural defects on the nominally smooth surfaces become clearly visible. By quantifying and averaging these features, a comparison can be made between the data obtained via reflection microscopy and the AFM-based friction maps presented in Figure 5.4. It can be observed that, although discrepancies exist—particularly in the case of Teflon—the values remain within the same order of magnitude and are comparable across both experimental methodologies. Furthermore, as demonstrated by the distribution of values in Figure 5.5, the AFM-derived defect size distribution complements the optical results to provide a comprehensive multi-scale analysis of pinning. While the AFM identifies a higher density of defects, these features are predominantly smaller than 300 nm. This size regime falls below the resolution limit of the reflection microscopy setup, explaining why such defects are not optically resolvable.

The defect density in the AFM experiments is comparable to, and in some cases higher than, those obtained in optical measurements. For Teflon, AFM reveals a density of approximately 30 defects per $100 \times 100 \mu m^2$, which is significantly higher than the ~ 10 defects identified optically. Even with this higher sensitivity, the defect density does not exceed 10^{-3} defects/ μm^2 in any case, and the distribution remains narrow. These results reinforce the conclusion that even when accounting for sub-diffraction defects, the total energy dissipated remains insufficient to explain the macroscopic CAH.

We performed the same calculations as in the previous chapter to compute the density, including both the AFM and optical approaches, as shown in Figure 5.9. As observed, the energy density contribution from these additional defects is exceedingly small due to their size. This demonstrates that such small defects barely contribute to overall energy dissipation, and

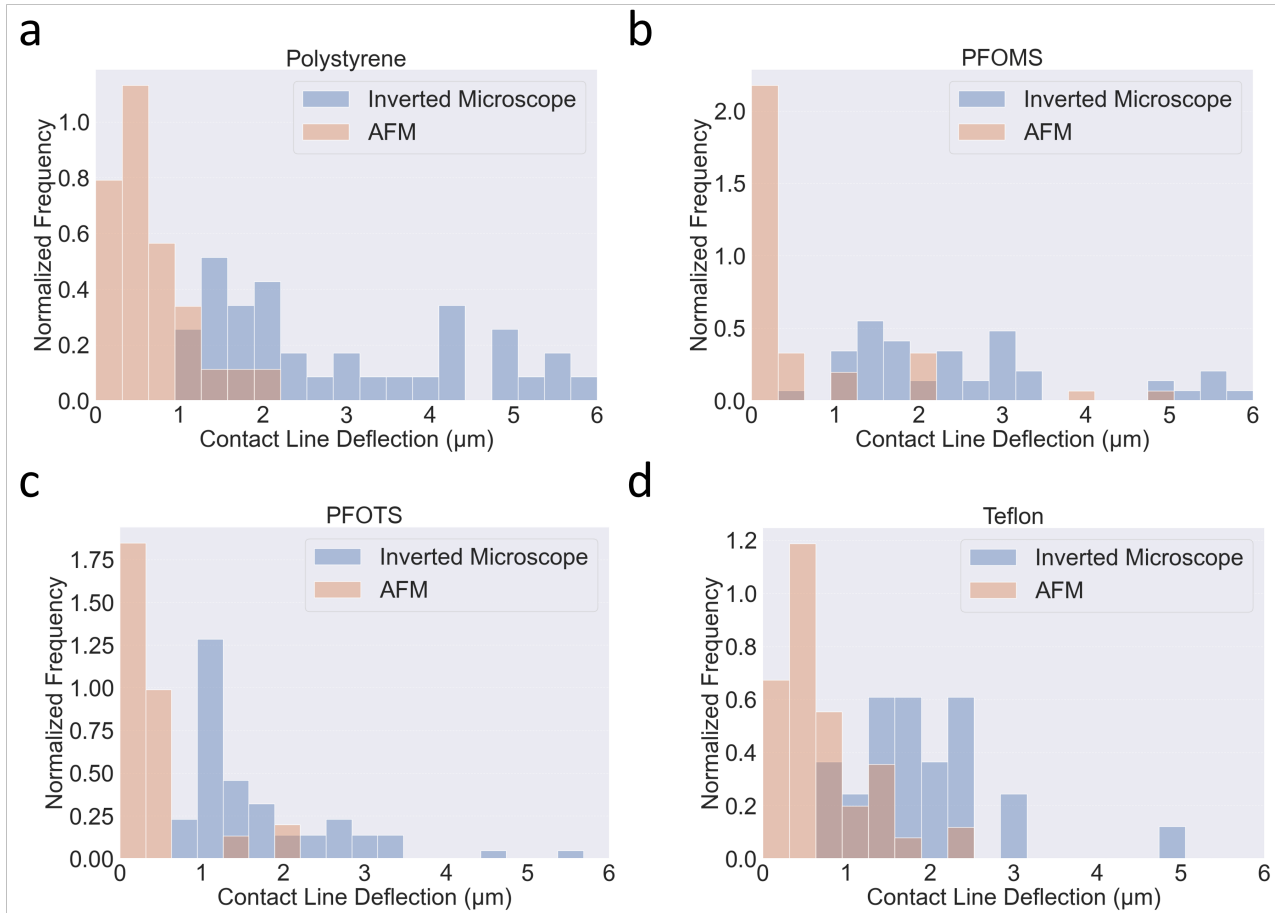


Figure 5.5: Comparison of contact line deflections measured by reflection microscopy (blue) and AFM (orange) for (a) PS, (b) PFOMS, (c) PFOTS, and (d) Teflon.

as they approach the thermal limit, they become essentially negligible. In the next section, we justify this physically by calculating the minimum defect size required to pin the contact line.

5.1.4 Thermal Activation and Minimum Interaction

To understand the full range of contact line interactions, it is crucial to know how large a defect must be to actually cause a macroscopic change in the contact line and the drop. As the defect size decreases, molecular interactions become increasingly important. Eventually, the mere thermal fluctuations of the molecules provide sufficient energy for the contact line to overcome the energy barrier represented by the defect itself. We refer to this as the thermal activation of the contact line. In this regime, the defect is so small that the contact line does not require a macroscopic external force to depin [37, 71].

Considering the Boltzmann factor for the system as $\exp(-W/kT)$ and recalling Equation 1.28, the activation energy W depends on the maximum displacement u_m , or equivalently, the maximum pinning force f_m . Assuming a very small defect, we can approximate the volumetric surface S_{Vol} to be equivalent to the planar surface S . For a defect of radius r_0 , we can define the capillary force as half the perimeter (πr_0 for a circular defect) multiplied by the balance of the interfacial energies:

$$f_m(r_0) = [(\gamma_{SL} - \gamma_{SG})_{\text{Defect}} - (\gamma_{SL} - \gamma_{SG})_{\text{Surface}}] \cdot \pi r_0 \quad (5.1)$$

Let us define the expression in brackets from Equation 5.1 as $\Delta\gamma$. We can then express this force as $f_m = \Delta\gamma \cdot \pi r_0$. It is convenient to express the work solely in terms of r_0 :

$$W = \frac{1}{2} \frac{f_m^2}{K} = \frac{1}{2} \frac{\pi^2 r_0^2 \Delta\gamma^2}{K} = \frac{\pi \Delta\gamma^2}{\gamma} r_0^2 \ln(L/r_0) \quad (5.2)$$

For the contact line to jump the barrier due to thermal activation energy, the condition $W \lesssim 20kT$ must be fulfilled [37]. This leads to:

$$\frac{\pi \Delta\gamma^2}{\gamma} r_0^2 \ln(L/r_0) < 20kT \quad (5.3)$$

To solve this condition, we assume L to be at least six orders of magnitude larger than r_0 . Because this scale difference makes the logarithmic term a slowly varying function, the critical boundary radius can be efficiently calculated using the fixed-point iteration numerical method. This method involves rearranging the equation into a recursive relation where an initial estimate of r_n is used to compute a more accurate successor:

$$r_{n+1} = \sqrt{\frac{20kT}{\frac{\pi \Delta\gamma^2}{\gamma} \ln(L/r_n)}} \quad (5.4)$$

Due to the stability of the logarithm in this regime, the sequence converges to the critical

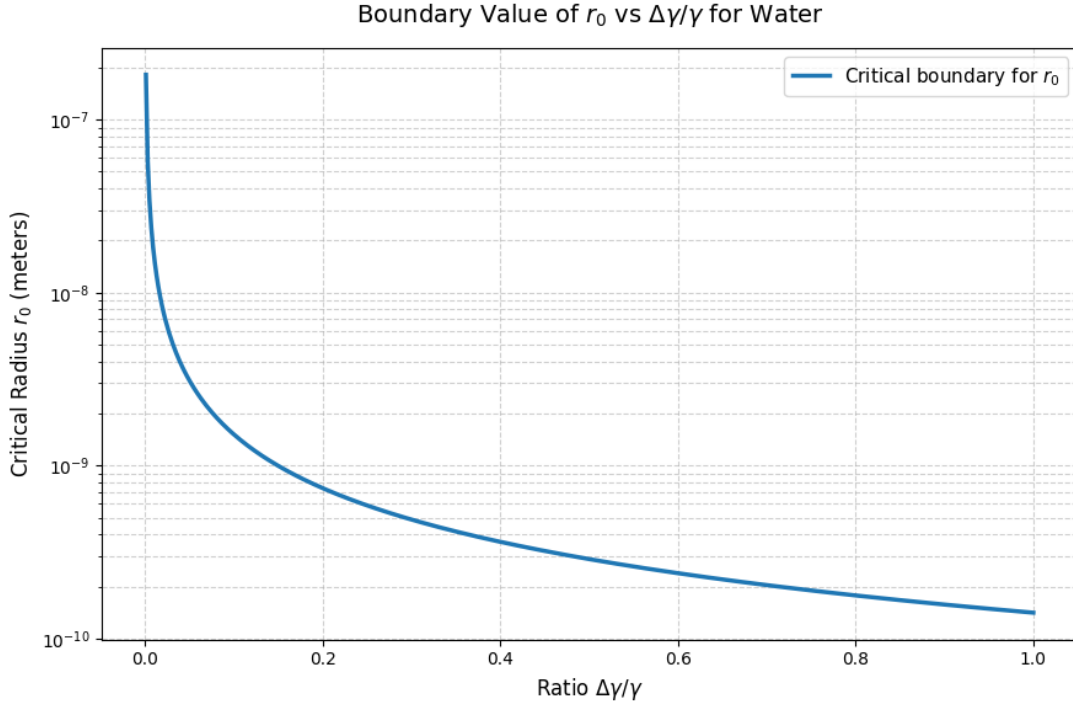


Figure 5.6: Critical boundary radius r_0 as a function of the surface tension ratio $\Delta\gamma/\gamma$ for water. The area below the curve represents the regime where thermal activation provides sufficient energy to overcome the defect's energy barrier.

radius extremely rapidly. To analyze the system's behavior, this iterative process is performed for each step in a grid of surface energy ratios, and the resulting critical values of r_0 are plotted for $\Delta\gamma/\gamma$ ranging from 0.001 to 1, as shown in Figure 5.6. As demonstrated, the more similar the defect is to the bulk surface, the smaller the minimum size required for the defect to be overcome. For highly homogeneous surfaces, we might expect critical defect sizes ranging from 10 to 100 nm.

5.2 Chemical Defects

Having explained the meniscus formation when a drop slides over a spherical defect, and having tested this model with experimental results and simulations, it is now time to expand to different defect configurations. If we want to understand the role of defects on the overall contact angle hysteresis, we must consider which defect morphologies are most prevalent. While our previous model considered spheres with different surface energies, a more common case is to find completely flat defects with varying chemical natures. Based on the obtained AFM images and the lack of visible defects in our optical images, we can claim that this type of flat, chemical defect is much more representative of smooth, transparent surfaces.

5.2.1 Rectangular Patch

We define a patch as an area on our substrate that has a particular surface energy, expressed by its contact angle (θ_p), which differs from the surrounding smooth surface with contact angle (θ_s). For a rectangular patch of width b and length l , we can describe it as a hydrophobic ($\theta_p > \theta_s$) or hydrophilic ($\theta_p < \theta_s$) patch depending on its contact angle.

It is convenient to recall the surface energy heterogeneity, or **Defect Potential**, which depends on the difference in interfacial tensions between the defect and the unperturbed surface. As defined in the previous section (Equation 5.1), we refer to this potential as $\Delta\gamma$:

$$\Delta\gamma = [\gamma_{SL} - \gamma_{SG}]_{\text{defect}} - [\gamma_{SL} - \gamma_{SG}]_{\text{surface}} \quad (5.5)$$

To detach the contact line from the patch, the drop must overcome the adhesion energy, which consists of the interfacial tension over the pinned area. When the patch is fully pinned, this energy is:

$$U_{\text{ad}} = \Delta\gamma \cdot A_{\text{pinned}} = \Delta\gamma \cdot bl \quad (5.6)$$

The opposing energy component is the meniscus elastic energy. From previous chapters, we know that the elastic energy of a meniscus stretched by a distance y is:

$$U_d = \frac{1}{2}Ky^2 = \frac{\pi\gamma \sin^2 \theta_s}{\ln(L/b)}y^2 \quad (5.7)$$

The elastic energy depends on y . This is also true for the adhesion energy if we consider a "partially wetted" patch. In this state, the pinned area is $b(y - y_0)$, where y_0 is the distance between the unperturbed contact line and the start of the patch. By identifying the different stages from Figure 5.7, we can separate the interaction into three distinct cases and find the energy minimum for each.

- **(i) Complete wetting on patch ($y > y_0 + l$):**

$$U = U_d - U_{\text{ad}} = \frac{1}{2}Ky^2 - \Delta\gamma bl \quad (5.8)$$

Minimizing the energy:

$$\frac{\partial U}{\partial y} = Ky = 0 \quad \Rightarrow \quad y_{\text{eq}} = 0 \quad (5.9)$$

Since y is constrained, $y_{\text{eq}} = y_0 + l$. Additionally, before the contact line fully interacts and stretches across the defect, there is no deflection, thus $F = 0$.

- **(ii) Partial wetting on patch ($y_0 \leq y \leq y_0 + l$):**

$$U = U_d - U_{\text{ad}} = \frac{1}{2}Ky^2 - \Delta\gamma b(y - y_0) \quad (5.10)$$

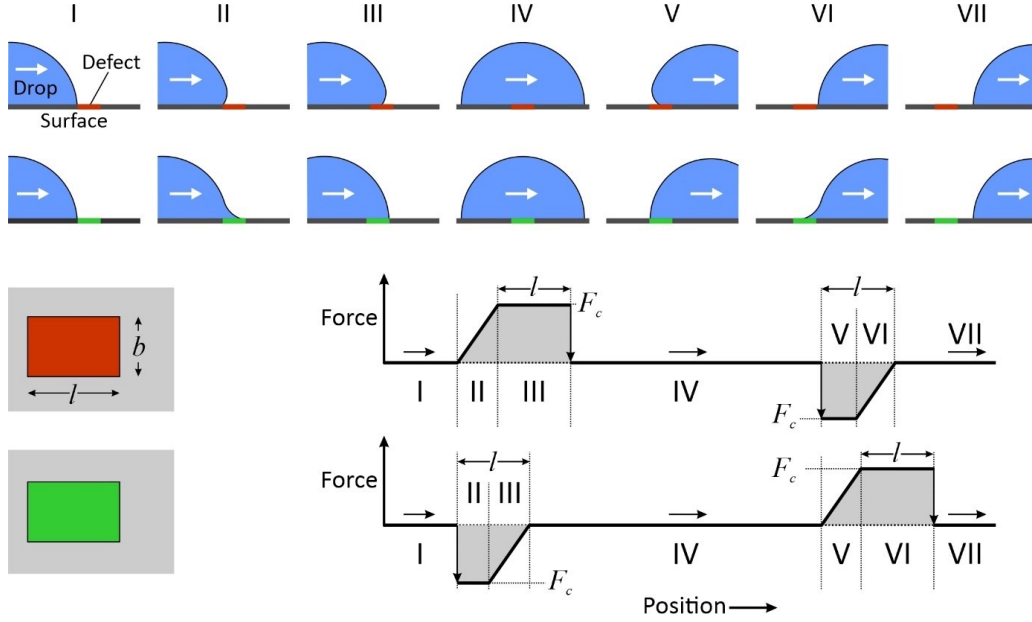


Figure 5.7: Schematic of a drop moving over a hydrophobic (red) and hydrophilic (green) patch. The smooth patch has a length l and width b . For a hydrophobic patch, the force required to move the front contact line over the patch is positive, while the receding contact line of the drop moves spontaneously over the defect. For a hydrophilic patch, the opposite is true.

Minimizing the energy:

$$\frac{\partial U}{\partial y} = Ky - \Delta\gamma b = 0 \quad \Rightarrow \quad y_{\text{eq}} = \frac{\Delta\gamma b}{K} \quad (5.11)$$

This equilibrium point acts as a limit for the stretching of the contact line. Once we reach the equilibrium point $y_{\text{eq}} = \frac{\Delta\gamma b}{K}$, as the contact line keeps sliding, the energy becomes:

$$U = \frac{1}{2}K \left(\frac{\Delta\gamma b}{K} \right)^2 - \Delta\gamma b(y - y_0) \quad (5.12)$$

The drop will feel a constant force $F_c = \Delta\gamma b$, which mirrors the capillary force produced by the contact line.

- (iii) **Before attaching** ($y < y_0$):

$$U = U_d - U_{\text{ad}} = \frac{1}{2}Ky^2 \quad (5.13)$$

Minimizing the energy:

$$\frac{\partial U}{\partial y} = Ky = 0 \quad \Rightarrow \quad y_{\text{eq}} = 0 \quad (5.14)$$

Finally, the moment before detachment depends on the defect size. If $l < \Delta\gamma b/K$, the contact line will detach immediately. In the case where $l > \Delta\gamma b/K$, the drop will remain

pinned until $y = y_{\text{eq}} = \Delta\gamma b/K$.

5.3 Interpreting the Results

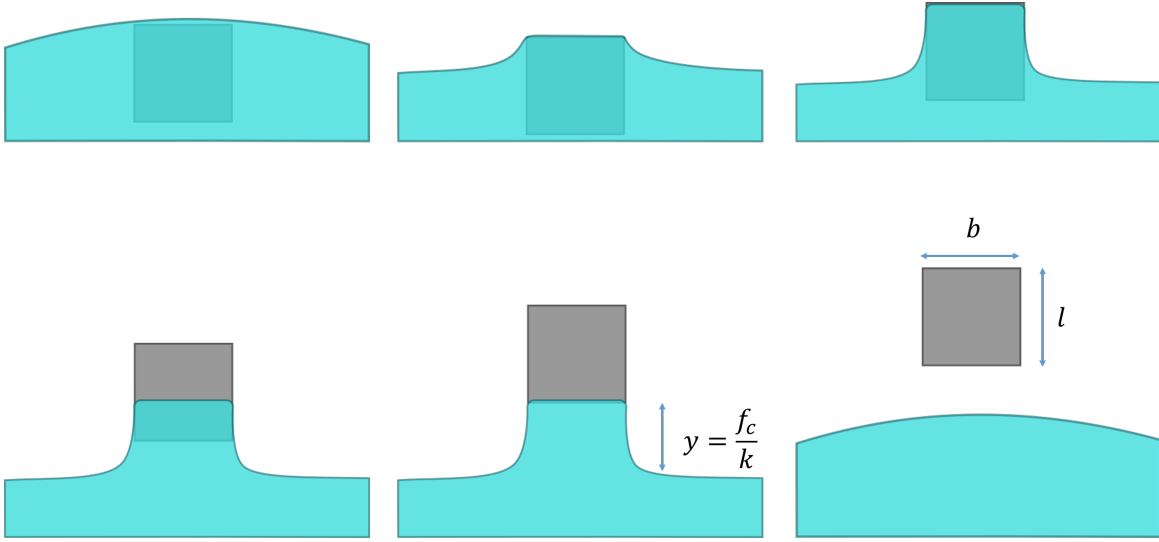


Figure 5.8: Timeline of the patch pinning; as the drop detaches, the elongation energy is well defined by the capillary force f_c .

Given that the AFM scans revealed highly smooth surfaces—rarely exhibiting defects larger than a nanometer—we will only use the chemical defect model presented in the previous section to calculate the influence of these contact line interactions, similar to our approach at the end of Chapter 3. Recalling Equation 3.12 for the receding angle, if we are confined to an area A , we can express nW_{re} in terms of the energy density:

$$\gamma(\cos \theta_r - \cos \theta_s) = \frac{1}{A} \sum W_i \quad (5.15)$$

where A is the analyzed area, and $\frac{1}{A} \sum W_i$ represents the energy density. We use the distribution of values shown in Figure 4.6 and define $A = 150 \times 150 \mu\text{m}^2$. We know from the previous section that the shape of our patches influences the work done by the contact line to overcome them. For simplicity, we assume our patches are square, meaning $b = l$ (Figure 5.8).

If we recall the force profile of a drop overcoming a defect, the total work is determined by the energy dissipated at the rear and front contact lines. For small values of b , we can neglect the jump; consistent with the observed deflection of the advancing contact line, the elastic component of the energy cancels out. Remembering the relation from Equation 5.11, where $yK = \Delta\gamma b$, we can define the total energy dissipated W_d as:

$$W_d \approx y_{\text{eq}} \Delta\gamma b = Ky_{\text{max}}^2 \quad (5.16)$$

Using this relation, we can evaluate the energy density of each surface, as shown in Figure 5.9. Here, we incorporated the energy densities derived from both optical and AFM results, weighting them appropriately to compensate for their differing areas. As observed, tracking the energy contribution yields no clear correlation between the defect energy density and the CAH. Furthermore, the energies related to these discrete interactions cannot provoke a contact angle change larger than 0.5 degrees. As established in the previous chapter, energy dissipations orders of magnitude larger would be required to account for a considerable macroscopic change, such as the contact angles reported for our studied surfaces.

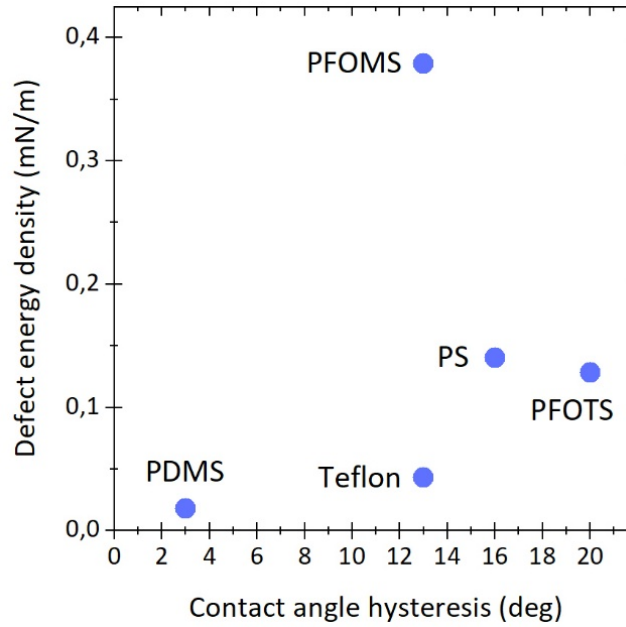


Figure 5.9: Defect energy density of the five samples studied versus the contact angle hysteresis; on this occasion, the AFM results were included. The shifts in the energy density are barely noticeable.

Chapter 6

Conclusions and Outlook

In this doctoral research, we investigated the sub-microscopic mechanisms of drop friction and contact angle hysteresis (CAH) on nominally smooth, homogeneous, hydrophobic surfaces. By combining droplet-probe Atomic Force Microscopy (AFM) with high-speed reflection microscopy, we established a comprehensive framework to probe liquid-solid interactions from the 50 nm scale up to the few micrometers of the drop footprint.

The main results of this work are summarized as follows:

- **Single-Defect Interaction:** We demonstrated that the interaction between a moving contact line and individual sub-microscopic defects follows a linear-force model. AFM force profiles and Surface Evolver simulations confirmed that pinning forces scale with defect geometry and surface energy, proving that the point-force approximation is valid at these scales.
- **High-Speed Visualization:** The development of a high-speed reflection microscope operating at 100,000 fps allowed for the direct observation of contact line fluctuations. We showed that pinning is significantly stronger and more frequent on the receding contact line than on the advancing side, confirming that detaching from a defect is the primary energy barrier.
- **Permanent Defects:** Through sliding dozens of droplets, we observed that, while the intensity of the deflection might change, which can be explained by CA fluctuations and speed due to charging, the spatial distribution of the deflection itself does not change considerably.
- **The Hysteresis Gap:** A central finding of this thesis is that while nanoscopic defects are ubiquitous on all investigated surfaces, they are not the dominant origin of CAH on seemingly smooth substrates.

- **Lack of Correlation:** Statistical analysis of several hydrophobic coatings (PFOTS, PFOMS, Teflon, PS, and PDMS) showed no direct correlation between the density or strength of resolvable defects and macroscopic hysteresis. Surfaces with nearly identical defect densities exhibited CAH values differing by as much as 10° .

6.1 Final Remarks on Energy Dissipation

Analytical calculations parameterized by our experimental defect statistics revealed that the energy dissipated by individual pinning events is far smaller than the total energy associated with macroscopic drop friction. This leads to the conclusion that even when accounting for sub-diffraction defects down to the 50 nm limit, the majority of the energy dissipated during drop motion on smooth surfaces remains unaccounted for by topographic or chemical heterogeneities. This implies that "seemingly smooth" hydrophobic surfaces possess a layer of complexity, beyond pinning interaction, this might be drop charge, surface adaptation or hydrodynamics. Most likely, the sum of these effects will govern the CAH, and we have to consider all of them if we want to fully understand the friction process.

6.2 Outlook and Future Directions

The discovery that individual nanoscopic defects cannot fully account for CAH suggests that other mechanisms must be investigated. Future research should focus on:

1. **Molecular Adaptation:** Exploring the role of surface chain mobility and molecular adaptation, where the surface structure changes in response to the liquid phase.
2. **Electrostatic Effects:** Just as a solid becomes charged through friction, droplets can deposit charge onto surfaces while becoming charged themselves. This charge separation process has significant implications for droplet friction. In this research, all charging effects were suppressed by using Indium Tin Oxide (ITO) glass to screen the charges and minimize electrostatic forces. Nevertheless, to understand the full process it's necessary as well to comprehend how the charge separates and what is the actual influence on drop friction.
3. **Dynamic Interfaces:** Investigating the role of "liquid-like" layers, such as those found in PDMS brushes, which demonstrated the lowest CAH and defect density in this work.

Bibliography

- [1] Jaroslaw Drelich, Emil Chibowski, Dennis Desheng Meng, and Konrad Terpilowski. Hydrophilic and superhydrophilic surfaces and materials. *Soft Matter*, 7(21):9804–9828, 2011.
- [2] Tejaswi Josyula, Laxman Kumar Malla, Tibin M Thomas, Srinivasa Sagar Kalichetty, Pallab Sinha Mahapatra, and Arvind Pattamatta. Fundamentals and applications of surface wetting. *Langmuir*, 40(16):8293–8326, 2024.
- [3] Ming Li, Chang Li, Bamber RK Blackman, and Saiz Eduardo. Mimicking nature to control bio-material surface wetting and adhesion. *International Materials Reviews*, 67(6):658–681, 2022.
- [4] Wilhelm Barthlott and Christoph Neinhuis. Purity of the sacred lotus. *Planta*, 202:1–8, 1997.
- [5] Indrani Banerjee, Ravindra C Pangule, and Ravi S Kane. Antifouling coatings: recent developments in the design of surfaces that prevent fouling by proteins, bacteria, and marine organisms. *Advanced materials*, 23(6):690–718, 2011.
- [6] Howard W Cox and Christopher W Macosko. Viscous dissipation in die flows. *AIChE J.*, 20:785–795, 1974.
- [7] Rossen Sedev. The molecular-kinetic approach to wetting dynamics: Achievements and limitations. *Advances in Colloid and Interface Science*, 222:661–669, 2015.
- [8] Pierre-Gilles De Gennes. Wetting: statics and dynamics. *Reviews of modern physics*, 57(3):827, 1985.
- [9] Ivan Marusic and Susan Broomhall. Leonardo da Vinci and fluid mechanics. *Annual Review of Fluid Mechanics*, 53(1):1–25, 2021.
- [10] Edward Yu. Bormashenko. Physics of Wetting. <https://www.asau.ru/files/pdf/1595345.pdf>, 2017.
- [11] Marie Boas. Hero’s Pneumatica: a study of its transmission and influence. *Isis*, 40(1):38–48, 1949.

- [12] Hero of Alexandria. Hero of Alexandria fluid devices. *EOHT*, 2026.
- [13] Pliny the Elder. Natural History: Descriptions of fluid phenomena. *Attalus*, 2026.
- [14] Francis Hauksbee. II. Several experiments touching the seeming spontaneous ascent of water. *Philosophical Transactions of the Royal Society of London*, 26(319):258–266, 1709.
- [15] Yves Pomeau and Emmanuel Villerraux. Two Hundred Years of Capillarity Research. *Physics Today*, 59:42–47, 2006.
- [16] Miguel Ángel Rodríguez-Valverde and Maria Tirado Miranda. Derivation of Jurin’s law revisited. *European journal of physics*, 32(1):49–54, 2011.
- [17] Leiv Magne Siqueland and Svein Magne Skjæveland. Derivations of the Young–Laplace Equation. *Capillarity*, 4:23–30, 2021.
- [18] Yves Pomeau and Emmanuel Villerraux. Two Hundred Years of Capillarity Research. *Phys. Today*, 59(3):42–47, 2006. Review of the development of capillarity from Young and Laplace onward.
- [19] Joseph Plateau. Statique expérimentale et théorique des liquides soumis aux seules forces moléculaires. *Gauthier-Villars*, 1873.
- [20] Marc Durand. Mechanical approach to surface tension and capillary phenomena. *American Journal of Physics*, 89(3):261–266, 2021.
- [21] BV Toshev. Gibbs’ thermodynamics of wetting. *International Journal of Mechanical Engineering Education*, 34(3):256–262, 2006.
- [22] R Denoyel, I Beurroies, and B Lefevre. Thermodynamics of wetting: information brought by microcalorimetry. *Journal of Petroleum Science and Engineering*, 45(3-4):203–212, 2004.
- [23] W Adu Zisman. Relation of the equilibrium contact angle to liquid and solid constitution. *ACS Publications*, 1964.
- [24] J.W. Drelich. Contact angles: history of over 200 years of open questions. *J. Surf. Investig.*, 2019.
- [25] CGL Furmidge. Studies at phase interfaces. I. The sliding of liquid drops on solid surfaces. *J. Colloid Sci.*, 17:309–324, 1962.
- [26] Robert A Hayes and John Ralston. The molecular-kinetic theory of wetting. *Langmuir*, 10:340–342, 1994.

- [27] Hans-Jürgen Butt, Karlheinz Graf, and Michael Kappl. *Physics and chemistry of interfaces*. John Wiley & Sons, 2013.
- [28] Rafael Tadmor. Approaches in wetting phenomena. *Soft Matter*, 7:1577–1580, 2011.
- [29] Thomas Young. III. An essay on the cohesion of fluids. *Philos. Trans. R. Soc. London*, pages 65–87, 1805.
- [30] Husseyin B Eral, DJCM 't Mannetje, and Jung Min Oh. Contact angle hysteresis review. *Colloid Polym. Sci.*, 291:247–260, 2013.
- [31] H Yildirim Erbil. Practical applications of superhydrophobic materials and coatings: problems and perspectives. *Langmuir*, 36(10):2493–2509, 2020.
- [32] Md Mahamud Hasan Tusher, Alisan Imam, and Md Shahidul Islam Shuvo. Future and challenges of coating materials. *Springer*, pages 229–251, 2023.
- [33] Xiaomei Li, Francisco Bodziony, Mariana Yin, Holger Marschall, Rüdiger Berger, and Hans-Jürgen Butt. Kinetic drop friction. *Nat. Commun.*, 14:4571, 2023.
- [34] G Macdougall and C Ockrent. Surface energy relations in liquid/solid systems I. *Proc. R. Soc. London A*, 180:151–173, 1942.
- [35] Boris Krasovitski and Abraham Marmur. Drops down the hill: theoretical study of limiting contact angles. *Langmuir*, 21:3881–3885, 2005.
- [36] Paul C Matthews. *Vector calculus*. Springer Science & Business Media, 2012.
- [37] Pierre-Gilles Gennes, Françoise Brochard-Wyart, and David Quéré. Capillarity and wetting phenomena: drops, bubbles, pearls, waves. *Springer*, 2004.
- [38] Terence D Blake and John M Haynes. Kinetics of liquid-liquid displacement. *J. Colloid Interface Sci.*, 30:421–423, 1969.
- [39] Hans-Jürgen Butt, Rüdiger Berger, Werner Steffen, Doris Vollmer, and Stefan AL Weber. Adaptive wetting—adaptation in wetting. *Langmuir*, 34:11292–11304, 2018.
- [40] Xiaomei Li, Pravash Bista, Amy Z Stetten, Henning Bonart, Maximilian T Schür, Steffen Hardt, Francisco Bodziony, Holger Marschall, Alexander Saal, Xu Deng, et al. Spontaneous charging affects the motion of sliding drops. *Nature Physics*, 18(6):713–719, 2022.
- [41] G Hocking and M Straškraba. An analysis of the effect of an upstream reservoir by means of a mathematical model of reservoir hydrodynamics. *Water Science and Technology*, 30(2):91, 1994.

- [42] Oleg V Voinov. Hydrodynamics of wetting. *Fluid Dyn.*, 11:714–721, 1976.
- [43] Terence D Blake. The physics of moving wetting lines. *Journal of colloid and interface science*, 299(1):1–13, 2006.
- [44] GD Nadkarni and S Garoff. An investigation of microscopic aspects of contact angle hysteresis: Pinning of the contact line on a single defect. *EPL (Europhysics Letters)*, 20(6):523–528, 1992.
- [45] S Moulinet, C Guthmann, and E Rolley. Roughness and dynamics of a contact line of a viscous fluid on a disordered substrate. *The European Physical Journal E*, 8(4):437–443, 2002.
- [46] Solomon S Melides, Dominic Vella, and Marco Ramaioli. Effect of Macroscopic Surface Heterogeneities on an Advancing Contact Line. *Langmuir*, 38(44):13358–13369, 2022.
- [47] T Cubaud and M Fermigier. Advancing contact lines on chemically patterned surfaces. *Journal of colloid and interface science*, 269(1):171–177, 2004.
- [48] Lin Wu, Lu Cai, Anqi Liu, Wei Wang, Yanhua Yuan, and Zhanxiong Li. Self-assembled monolayers of perfluoroalkylsilane. *Appl. Surf. Sci.*, 349:683–694, 2015.
- [49] Hannu Teisala, Philipp Baumli, Stefan AL Weber, Doris Vollmer, and Hans-Jürgen Butt. Grafting silicone at room temperature. *Langmuir*, 36:4416–4431, 2020.
- [50] Isaac J Gresham and Chiara Neto. Advances and challenges in slippery covalently-attached liquid surfaces. *Advances in Colloid and Interface Science*, 315:102906, 2023.
- [51] Gerd Binnig, Calvin F Quate, and Ch Gerber. Atomic force microscope. *Phys. Rev. Lett.*, 56:930, 1986.
- [52] Werner A Hofer, Adam S Foster, and Alexander L Shluger. Theories of scanning probe microscopes. *Rev. Mod. Phys.*, 75:1287, 2003.
- [53] UD Schwarz, P Köster, and R Wiesendanger. Quantitative analysis of lateral force microscopy. *Rev. Sci. Instrum.*, 67:2560–2567, 1996.
- [54] Diego Cortés, Michael Kappl, Hans-Jürgen Butt, Pranav Sudersan, and Tomas P Corrales. Friction Measurements with Picoliter Droplets. *Phys. Rev. Lett.*, 135:048203, 2025.
- [55] Dan Daniel, Chee Leng Lay, Anqi Sng, Coryl Jing Jun Lee, Darren Chi Neo, Xing Yi Ling, and Nikodem Tomczak. Mapping micrometer-scale wetting properties. *Proc. Natl. Acad. Sci. U. S. A.*, 116:25008–25012, 2019.

- [56] Maja Vuckovac, Mika Latikka, Kai Liu, Tommi Huhtamäki, and Robin HA Ras. Uncertainties in contact angle goniometry. *Soft Matter*, 15(35):7089–7096, 2019.
- [57] Xiaomei Li, Pravash Bista, Amy Z Stetten, Henning Bonart, Maximilian T Schür, Steffen Hardt, Francisco Bodziony, Holger Marschall, Alexander Saal, Xu Deng, et al. Spontaneous charging affects the motion of sliding drops. *Nat. Phys.*, 18:1–7, 2022.
- [58] Yaolei Xiang, Benedikt Straub, Diego Cortes, Hans-Jürgen Butt, and Kaloian Koynov. When contact lines remember: Surface charge and defects. *Droplet*, 5:e70039, 2026.
- [59] Robert S Hansen and Mirella Miotto. Relaxation phenomena and contact angle hysteresis. *J. Am. Chem. Soc.*, 79:1765, 1957.
- [60] Nan Gao, Florian Geyer, Dominik W Pilat, Sanghyuk Wooh, Doris Vollmer, Hans-Jürgen Butt, and Rüdiger Berger. How drops start sliding over solid surfaces. *Nat. Phys.*, 14:191–196, 2018.
- [61] AD Scheludko and D Nikolov. Measurement of surface tension. *Colloid Polym. Sci.*, 253:396–403, 1975.
- [62] Kenneth A Brakke. The surface evolver. *Exp. Math.*, 1:141–165, 1992.
- [63] Diego Cortes. Edge-Detection_SlidingDrops. https://github.com/Diego200000/Edge-Detection_SlidingDrops, 2026. Accessed: 2026-05-04.
- [64] Shiguang Shan, Wen Gao, Bo Cao, and Debin Zhao. Illumination normalization for robust face recognition against varying lighting conditions. In *2003 IEEE International SOI Conference. Proceedings (Cat. No. 03CH37443)*, pages 157–164. IEEE, 2003.
- [65] MA Yousuf and MRH Rakib. An effective image contrast enhancement method using global histogram equalization. *Journal of scientific research*, 3(1):43–43, 2011.
- [66] Zhou Wang and Alan C Bovik. A universal image quality index. *IEEE signal processing letters*, 9(3):81–84, 2002.
- [67] Kaiming He, Jian Sun, and Xiaoou Tang. Guided image filtering. *IEEE transactions on pattern analysis and machine intelligence*, 35(6):1397–1409, 2012.
- [68] Petros Maragos. Tutorial on advances in morphological image processing and analysis. *Optical engineering*, 26(7):623–632, 1987.
- [69] Pierre Soille et al. Morphological image analysis: principles and applications. *Springer*, 2(3), 1999.

-
- [70] Isaac J Gresham and Chiara Neto. Advances and challenges in slippery covalently-attached liquid surfaces. *Advances in Colloid and Interface Science*, 315:102906, 2023.
- [71] Kristina Davitt, Michael S Pettersen, and Etienne Rolley. Thermally activated wetting dynamics in the presence of surface roughness. *Langmuir*, 29(23):6884–6894, 2013.

Appendix A

“Use of AI tools”

This appendix outlines the utilization of artificial intelligence tools throughout the development of this thesis.

AI tool	Used for	Reason	When/where
Gemini	Coding	Implement more complex algorithms in less time and more efficiently	Chapter 3, 4 and 5
	Spelling and Grammar Correction	Improve grammar and avoiding constant iteration between reviews for feedback.	Throughout the entire work
	Latex optimization	Thesis was done in Latex, the whole latex structure was revised and constructed together with Gemini	Throughout the entire work

Diego Cortés

Doctor of Physics



30 January 1998



Mainz, Germany



+49 17635353762



linkedin.com/in/diego-cortés-506363156



di.cortesg98@gmail.com

About me

Doctor of Physics in Materials Science with core expertise in droplet-probe AFM, high-speed optical imaging, and interfacial friction mechanics.

Experienced in investigating contact angle hysteresis, defect-induced contact line pinning, and surface energetics across polymer films, monolayers, and dynamic interfaces. Skilled in advanced data analysis, image processing, and custom instrumentation maintenance.

Skills

- AFM instrumentation
- Nanomechanical characterization
- Laboratory techniques (sample preparation and characterization)
- Troubleshooting & hardware optimization
- Photolithography and photomask design
- Surface & interface analysis
- Calibration & maintenance
- Coding (Python, PyTorch & agentic architectures)
- Technical reporting & CRM

Experience

- 2023–Pres. PhD Researcher (Systems & Instrumentation Focus) MPIP, Mainz
AFM: Operation and hardware maintenance of AFM systems, including imaging, force spectroscopy, nanomechanical characterization, cell adhesion force measurements, and work with customized systems. Optical Instrumentation: Hands-on experience with customized optical and optomechanical solutions, high-speed imaging, fluorescence and confocal microscopy, including experimental setup, alignment, and data acquisition.
- 2021–2022 Research Internship (System Integration) MPIP, Mainz
Qualified a specialized droplet-probe AFM setup with confocal integration. Developed best practices for sub-component interconnection and instrument protocols.
- 2018 Research Assistant (Nanobiomaterials Lab) UTFSM
Carbon nanotube synthesis and documentation. Provided technical reporting on experimental outcomes and laboratory instrumentation upkeep.

Education

- 2022–2026 Ph.D. in Physics JGU, Mainz
Focus: Wetting, Interfacial Friction, and AFM Instrumentation. Graduated: August 2026. Successfully defended doctoral dissertation on interfacial friction forces and specialized force spectroscopy.
- 2020–2022 M.Sc. Physics Chile–Germany
Specialization in Surface Analysis, Wetting Dynamics, and Friction at Interfaces.
- 2016–2020 B.Sc. Physics Valparaíso, Chile
Core training in Mechanics, Electronics, Optics, and Laboratory Methods.

Technical Projects & Publications

- 2025 Cortés, D., et al. *Phys. Rev. Lett.* 135, 048203. First-author publication on high-precision instrument qualification.
- 2026 Xiang, Y., Straub, B., Cortés, D., Butt, H. J., & Koynov, K. *Droplet* 5(1), e70039. “When contact lines remember: Surface charge and the evolving interaction with defects.”
- 2026 Sierra-Fernández, A., Cortés, D., Monclus, M. A., Livi, K. J., Kappl, M., Weber, S. A., et al. *Chemistry of Materials*. “Nacre-Inspired Composite Coatings with Hierarchical Architecture for Durable Surface Protection.”

Languages

- 2025 English (TOEFL iBT)
99/120 (CEFR C1). Professional fluency.
- Spanish
Native speaker.