1 Introduction

In this chapter, a concise history and overview of the subjects and definitions relevant to our study are provided, highlighting their connections to surface wettability, droplet rolling, and the droplet bouncing properties. Concepts of surface characterization, biomimetic techniques, and recent advancements in bio-inspired special wettability are also reviewed, with a particular focus on self-cleaning surfaces inspired by the lotus "lotus effect "and superhydrophobic plant surfaces. Additionally, a brief discussion on the electrowetting and magnetowetting techniques offered. At the end, the research motivation and scope of the thesis are outlined.

1.1 Background: A brief history

On February 14, 1990, the Voyager-1 space probe captured an iconic image from a distance of around six billion kilometers and it became the most amazing picture in the world [1]. This was our planet ! Our Earth ! Voyager-1 introduced us to look, we are just a blue pixel in this vast universe and showed us things that we may never see in our lifetime. This unique inherent attraction and beauty of our Earth planet is due to the presence of water on it. Water enabled the possibility of biological evolution, and its dynamic cycle spanning liquid, evaporation, condensation, and solidification has been essential for sustaining life. We can look in surrounding nature to our daily lives, when rain happen, we can glimpse the raindrop rolling down from some kinds of plant leaves while from some other kinds of plant leaves water droplet wet the leaves surface. The eyes surface is highly wettable which forms tear film, keep our eyes wet, clean and smooth, and help focus light for a clear vision [2, 3]. The wetting phenomena are abundant in nature, serving as a source of inspiration through their exceptional wetting-dewetting engineering. The field of surface wettability study has an extraordinary period of development in the last decade due to its potential applications. Nature serves as an eternal wellspring of inspiration, driving scientists to unravel its fundamental mechanism and control for technological advancement. In the pursuit of comfort and convenience, there has been a growing interest in bioinspired designs and products. Broadly speaking, nature has inspired our technological advancements in two ways: whole structural design and surface engineering. The former includes, lotus (*Nelumbo nucifera*) inspired lotus temple (India) [4], kingfisher's bird inspired Japan's bullet train nose [5], dragonfly inspired helicopter [6], etc. On the other hand, later one essentially relies on microscopic surface reconstruction aspect, like gecko feet inspired gecko tape [7, 8], shark skin inspired aircraft coating with thin film [9], lotus leaf inspired self-cleaning surface etc. [10, 11]. Similarly, other examples abound belongings to the biological surfaces which exhibit remarkable multifunctionality that captivate our fascination: the anti-fogging capability of mosquito eyes [12, 13], the impressive water-walking skill of water striders [14, 15], the directional adhesion seen in butterfly wings and rice leaves [16, 17], the anti-reflection feature of superhydrophobic cicada wings [18, 19], and the water collection mechanism of desert beetles [20, 21]. These diverse adaptations inspire awe and offer valuable insights for innovation.

One deal with the wetting and spreading phenomena under surface science, which is essentially occur at the interface of two phases (liquid-liquid, liquid-solid, and liquid-air). Wettability is defined by how a surface interacts with the boundary between a solid and a liquid, known as the interface. This interface marks the transition between two distinct states of matter. Specifically, when referring to a solid or liquid surface, we're describing the interface between two phases [22]. The wettability of a solid surface refers to how much a water droplet spreads on it. When the surface is hydrophilic (water-loving), the water spreads easily. In contrast, when the surface is hydrophobic (water-repelling), the water droplet forms a spherical cap like shape and resists spreading on surface. When a solid surface is highly repellent with low adhesion, water droplets can easily roll off, especially on an inclined surface. In contrast, water-attracting surfaces cause droplets to adhere and spread more easily. Such properties can be easily predicted by physical contact angle (CA) measurements, which is defined as the geometrical angle formed between the tangential surface tension force of two interfaces (liquid-air and solid-liquid). Conventionally, the hydrophilicity or hydrophobicity of a solid surface is assessed by the water contact angle (WCA) defined by Young's equation (1805). When the WCA is less than 90°, the surface is hydrophilic. For values between 90° and 145°, the surface is hydrophobic. When the WCA exceeds 145°, the surface is superhydrophobic [23].

In 1907, superhydrophobicity was first observed by Ollivier [24]. In 1997, Barthlott and Neinhuis explained self-cleaning mechanism of lotus leaves [25], later known as "lotus effect", which made dynamic significant interest of researchers in both academic and industrial . It was believed that the superhydrophobicity is responsible for self-cleaning action, i.e., superhydrophobicity with low adhesion. However, Lei Jiang (2008) broken the myth by reporting rose petal which shown superhydrophobicity with high adhesion without favouring droplet roll-off [26]. This characteristic termed as "rose petal effect". The Young's law of wettability was limited to smooth solid surface. Later, Wenzel (1936) and Cassie (1944) proposed two individual models to explain wetting of textured surfaces. However, these two models were limited to the single level surface textures. It was clear now, the wetting characterization is not a single level, can occur several modes, including the Wenzel, Cassie, lotus and petal [24]. After that, the other mixed single to multilevel surface texture models have been proposed, e.g., Wenzel-Wenzel, Cassie-Wenzel, Wenzel-Cassie, and Cassie-Cassie models [27]. It should be noted that the micro, sub-micro, nano and hierarchical structures coexist in natural systems which offer complexity of the surface texture. Nature-inspired engineering extends beyond mimicking the surface structures of lotus leaves and rose petals; it also involves examining various other surfaces designed by nature with both low and high adhesion properties. When dealing with water as the liquid, the wetting on solid surface characteristics can be classified into four main categories: superhydrophilic, hydrophilic, hydrophobic, and superhydrophobic [23]. The wetting behavior may vary from isotropic to anisotropic depending on surface texture. Further, the surfaces can be classified on the basis of surface energy, surface texture, contact angle, or adhesion features [28]. Based on water contact angle (WCA) and dynamical interaction of droplet and solid, surfaces can be divided as follows (Fig. 1.1).

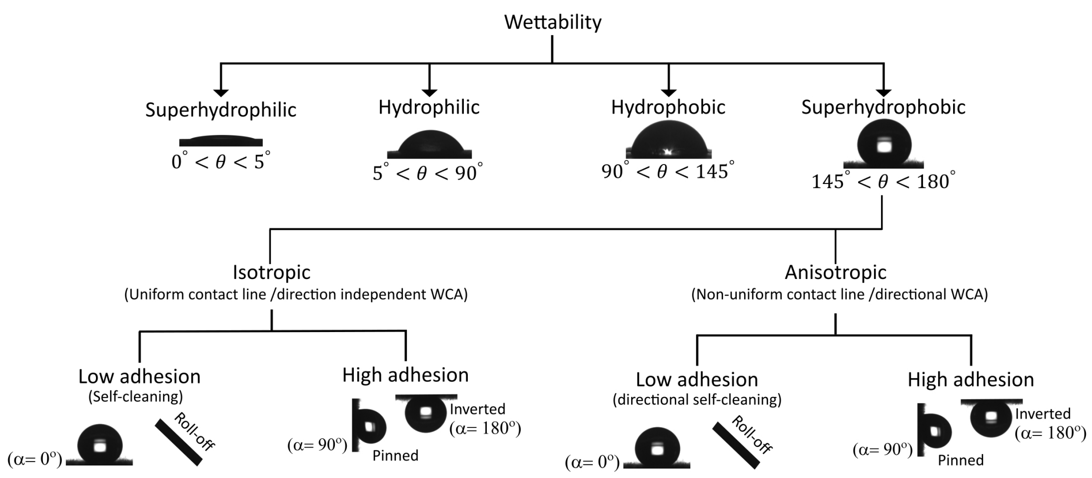

Figure 1.1: Schematic illustration of wetting of liquid on solid surface.

This thesis endeavors to delve into the exceptional wetting characteristics of biological plant leave surfaces. Our research predominantly emphasizes studying the surface texture of plant leaves, special wetting features and biomimicking for advancement of the soft-matter technology. The mimicked artificial surface wetting characteristics can be manipulated by altering surface texture, surface chemical composition, or applying any external forces. The driving forces can be either electric field [29], magnetic field [30], or temperature and pressure depending on liquid and solid surface [31]. To alter the droplet wetting state, we have used electric field assisted phenomena termed as electrowetting [32].

1.2 Special wettability in plant leaves

With the discovery of various functional assets of biological surfaces, the wetting is being revisited as a unique phenomenon that occurs at interfaces of two phases. There are several verities of the biological systems, including aquatic, avian, and plants. In nature, wettability is associated with the animal kingdom, e.g., gecko feet, cicada wings, shelduck wing feather, desert beetle, and shark skin, etc. [28, 33]. These surfaces have different wetting features from superwetting to self-cleaning. Similarly, after the amazing observation of lotus leaf and rose petal effects, researchers keep a close watch on numerous plant surfaces which possess self-cleaning and adhesion features. Superhydrophobicity in plant leaves is both robust and readily available across various plant types, including aquatic, terrestrial, lithophytic, and epiphytic species [34, 35]. The development of water-repellent or superhydrophobic surfaces relies on the interaction of three interfaces: liquid, solid, and air. Such surfaces are typically not observed in aquatic plants. Furthermore, superhydrophobic plant surfaces invariably possess a cuticle. Hence, the cuticle stands out as a pivotal innovation, serving as a fundamental requirement for the evolution of superhydrophobic self-cleaning surfaces in plants.

It should be mentioned here that the water-repellent capabilities of the leaves were known from a long time. Many religious and cultural text describe the self-cleaning actions of the lotus leaf and use of it is considered as a sacred practice. One of them, an oldest quotation is taken from oriental sacred Hindu texts; *"He who dedicates his actions to the Spirit, without any personal attachment to them, he is no more tainted by sin as a lotus leaf never wettable with water while living in water pond" ||5.10||, Shrimad Bhagavad Gita* [36, 37]. Not surprisingly, the underlined sentence clearly describes the self-cleaning features of the lotus leaves with philosophical intent.

Soon after scanning electron microscopic (SEM) imaging technique entered research laboratory in the late 1960s, the self-cleaning mechanism and role of surface roughness of the plant leaf surfaces could be exploited in great detail. It has been observed that outer layer of all parts of the plants including leaves, flowers, fruits, and covered with hydrophobic protective cuticle layer consists lipid and waxy hydrocarbon polymers which is produced by epidermal cells. The microscopic imaging of lotus leaf reveals that leaf is covered with a two level micro-nano roughness; the micro layer bumps (papillae) are covered with nano scale waxy texture [38]. The wax paraffine wax is hydrophobic (WCA 95°-110°) while the lotus leaf shown WCA as high as 160° in the superhydrophobic region due to micro-nano two level surface roughnesses [10, 39]. Similarly, the two-level surface texture was observed in rose petal surface but with different dynamical wetting parameters [40]. Neinhuis and Barthlot reported various functional assets of natural surfaces, such as plant leaves, animal skins, and other organisms, to understand how surfaces achieve superhydrophilic and superhydrophobic wetting state. Through the analysis of SEM images and existing literature, they identified nearly 20,000 different species [41]. Among these, they documented over 200 water-repellent plant leaves surfaces and found such surfaces having waxy cuticles on lower/upper epidermis [41]. The epidermal cell forms a single papilla or a cell is divided into papillae and scale ranges from 5 µm to 100 µm large cell size. Some leaves also consist hairy (trichomes) like structure on the surfaces. The basic mechanism of surface underneath water droplet interface involves air pockets which is trapped between texture results decrease in actual solid-liquid interfacial contact area. The texture on leaves surface may comprise of micro/nano scale, or micro-nano architecture both depending on natural selection and engineering. The waxy protrusions on leaves were found in various shapes which influences the wetting characteristic of the surface. Interestingly, besides superhydrophobicity of micro/nano-scale protrusions, it has been observed that the waxy trichomes matted surfaces exhibit excellent water repellency due to the trapped air between pair of trichomes. These trichomes found with unicellular, multicellular, or branched one protrude from the epidermal tissues [42]. The hairs are biopolymer composites chiefly comprise of hemi celluloses, cellulose, and lignin [43]. The wetting of natural surfaces can be understood by its surface chemical composition and construct, and, consequently, surface free energy. The surface can be heigh, low, and ultralow adhesion depending on water droplet and surface interaction characteristics as seen in lotus and petal effect.

1.3 A self cleaning action: slipping, rolling and bouncing

Surface roughness is paramount in achieving superhydrophobicity. Surfaces with varying levels of roughness can attain superhydrophobicity through hydrophobic coating, exhibiting both low and high adhesion independently. Low adhesion superhydrophobic surfaces offer self-cleaning properties consistently. The interplay between spontaneous water-repellency and self-cleaning is evident [38]. However, the behavior of droplets rolling on surfaces is contingent upon factors such as low or high adhesion, droplet volume and surface slanting angle. The adherence of contaminant particles to droplets depends on the contact line between the three phases (solid, liquid, air/gas) and the direction of rolling velocity. While a comprehensive model of this process is yet to be developed, it's clear that the hydrophilic/hydrophobic nature of contaminant particles also influences the efficacy of self-cleaning action [44–47]. The presence of a waxy coating on both the rose petal and lotus leaf distinctly illustrates that the degree of adhesion in superhydrophobicity, whether low or high, relies heavily on the types and distributions of surface roughness. While it's known that the hydrophobic or hydrophilic nature of a smooth surface primarily hinges on its surface chemistry, the attainment of extreme superhydrophobicity or superhydrophilicity is uniquely tied to surface texture. Furthermore, this texture can vary, ranging from single-level to two-three or multilevel configurations [48, 49].

The way droplets bounce off surfaces can create a self-cleaning effect, closely tied to how liquids interact with solid surfaces. This phenomenon of droplet bouncing and self-cleaning, observed on both smooth and textured surfaces, is gaining recognition for its technological significance. When a water droplet hits a superhydrophobic solid surface, it goes through a sequence of events: initially spreading out upon contact, then retracting and bouncing off [50]. This rapid transition occurs within a few milliseconds, necessitating high-speed imaging techniques to capture. Various studies have detailed the conditions under which droplets can continuously impact and bounce off. Superhydrophobicity plays a critical role, enabling self-cleaning through droplet bouncing, contingent on the droplet's kinetic energy surpassing the interfacial energy. Micro- and nanotextured surfaces aid droplet impact via capillary pressure from trapped air beneath the liquid. Researchers note that the bouncing and deformation of droplets rely on factors like contact angle and its hysteresis, both influenced by the rheological properties of the liquid, such as density and viscosity [51]. Surprisingly, the contact time of the droplet isn't influenced by its impact velocity [52]. Additionally, the kinetic energy of the impacting droplet strongly impacts bouncing, alongside parameters like droplet velocity and impact height [53].

1.4 Biomimetics of surfaces

Nature ingeniously developed remarkable multifunctional surface properties using minimal resources. In order to mimic the functionalities of various leaf surfaces, they typically possess a hierarchical structure with textural dimensional features spanning from the macroscale down to the nanoscale. It wasn't until 1997, with the unveiling of the *Lotus Effect*, that scientists and engineers began venturing into the realm of bio-inspired design [54]. The rise of low surface energy coatings is attributed to their self-cleaning properties. There are two primary methods for creating a self-cleaning surface: (i) creating roughness on a hydrophobic material, and (ii) applying a hydrophobic coating to a hydrophilic rough surface. In both scenarios, surface texturing should be optimized to sustain the Laplace pressure at the solid-liquid interface [55]. Optimizing texture involves more than just adjusting porosity; shape of the texture plays a crucial role in creating minimal solid-liquid contact areas. As a consequence of the constraints posed by current Wenzel and Cassie-Baxter theories, accurately estimating the optimal texture shape and configuration for self-cleaning surfaces is quite challenging. Looking ahead, selecting multifunctional surfaces will become increasingly intricate. However, one can overcome these hurdles by studying the myriad multifunctional superhydrophobic surfaces found in nature, each boasting remarkable structured designs. Leveraging nature's ingenuity offers a straightforward approach to learning from and preserving it. Until now, researchers have investigated numerous texture of natural surfaces, yet determining the optimal surface geometry for self-cleaning remains challenging [41]. Continuing this exploration of natural surfaces to create artificial superhydrophobic surfaces, researchers drawn obvious inspiration from plant leaves.

The research focuses on natural plant leaves, which exhibit functionalities of significant commercial interest. The wetting properties of these leaves are studied to understand how nature achieves such remarkable functionality. Surface structures inspired by these natural designs can be fabricated using various methods to replicate specific wettability characteristics. There exist numerous physical techniques for crafting surface structures ranging from micro to nano scales. In contrast to chemical processing methods, physical fabrication techniques excel in providing controlled patterns [56]. Nonetheless, these varied fabrication processes differ significantly from one another, each presenting distinct advantages and disadvantages compared to alternative methods. Various physical techniques, such as lithography [57], nanomanipulation, nanolithography, laser direct writing, soft lithography, and electrospinning, are capable of fabricating micro and nanostructures [58, 59]. Lithography, also known as photoengraving, involves replicating a pattern into a reactive polymer film substate, resist, which is then used to replicate the pattern into an underlying thin film [60]. Over the past half-century, many lithography techniques have also been developed, utilizing different lens systems and exposure radiation sources, including photons, electrons, X-rays, neutral atoms and ions [61]. Nanomanipulation and nanolithography are based on scanning probe microscopy (SPM). Moreover, Laser direct writing combines laser-assisted deposition with a high-resolution transformational stage to create patterned microstructures from a wide range of materials [62]. Depending on the desired surface texture, soft lithography and electrospinning techniques are employed to produce the required surface morphology, as discussed below:

1.4.1 Soft lithography

Soft lithography encompasses a range of non-photolithographic techniques based on self-assembled monolayers (SAMs) [63]. It serves as an alternative to photolithography and facilitates both micro- and nanofabrication replication. Techniques within soft lithography include contact printing, micro-transfer molding, micro-molding in capillaries, and replica molding [64]. Microcontact printing, for instance, utilizes an elastomeric (polydimethylsiloxane (PDMS)) stamp with relief patterns to generate patterned SAMs on planar and curved substrates [65]. Nanoimprint lithography, developed for fabricating patterned micro/nanostructures, follows a straightforward method: a stamp with desired features is first fabricated, typically through optical or electron beam lithography. Next, polymer material is spun onto a substrate where nanostructures are to be created. The stamp is then pressed onto the polymer layer at a temperature above the glass transition point for a specified duration to induce plastic deformation. Upon cooling, the stamp is separated from the polymer, leaving behind patterned polymer on the substrate, ready for further processing or direct use as a device component [66]. To replicate natural plants leaf surface textures, we utilized molding techniques , involving engraving the desired substrate texture onto a polymer film [67]. Initially, two polymer solutions are necessary. The first polymer solution is poured onto the desired substrate and allowed to dry, resulting in a negative polymer replica that mirrors the texture of the substrate. This negative replica film serves as a stamp. Subsequently, the second polymer mold is poured onto the negative replica and dried. Peeling out the polymer film yields a positive replica, effectively fabricating the desired substrate.

1.4.2 Electrospinning

The electrospinning technique can be employed to fabricate hairy matted surface textures in biomimicry [59]. Utilizing electrostatic force, this method transforms polymer solutions into ultrafine fibers ranging from several micrometers to nanometers in diameter. With the potential to create fibrous surfaces, electrospinning stands as a promising technique for manufacturing matted surfaces on a commercial scale. The electrospinning process necessitates a high-voltage power supply, a polymer solution, and a cylindrical spinning/static plate collector. Here are the steps involved: Initially, load the desired polymer solution into a disposable syringe and secure it onto a holder with appropriate distance from collector. To maintain a consistent flow, one employs a syringe pump to push the polymer solution steadily. Next, apply a high voltage to the conducting needle tip of the flowing solution and the fiber collector. Over a specified time, the flowing polymer solution will generate fibers on the collector. Finally, the polymer fibers were retrived from the collector and allowed to dry them as needed. Numerous parameters must be taken into account to achieve the desired diameter of fibers during biomimicry, where fibers may resemble microspheres. Factors such as polymer solution viscosity, flow rate, applied voltage, distance from needle to collector, and environmental humidity can largely influence fiber diameters [68]. To ensure efficient fiber production, multiple parameters were fine-tuned in the electrospinning setup. Controlling the spinning speed of the cylindrical collector is necessary to collect straight fibers, whereas a static plate collector is utilized for non-woven fiber networks. By adjusting different parameters, this method can generate a wide range of micro/nanofibers. The electrospinning technique has been reported to produce numerous fiber structures, including but not limited to cylindrical, bead-on-string, flattened ribbon, porous surface, side-by-side, branched, tubular, multichannel fibers [69]. This diversity highlights the versatility of electrospinning technique.

1.5 Electrowetting

Various methods, including temperature and pressure [70], dielectrophoresis [71], and electrowetting (EW) effects [72], have been demonstrated to effectively alter the liquid droplet shape. Electrowetting is a fascinating phenomenon where a conductive liquid droplet can be precisely manipulated on a solid surface at the microscale. This intriguing behavior is rooted in the principles of electrostatics. Remarkably, as far back as 1857, Lippmann noted alterations in the capillary rise of mercury when subjected to electric charges [32]. This observation laid the foundation for what is now known as Lippmann's law of electrowetting, marking the first formal description of electrocapillarity. Over time, this concept evolved, leading to the development of techniques like Electrowetting on Dielectric (EWOD), which represents a sophisticated method aimed at activating and transporting liquid droplets with precision on a solid substrate, offering exciting possibilities for various applications.

1.5.1 Electrowetting on dielectric (EWOD) surfaces

EWOD involves the electrical manipulation of an electrolytic-liquid droplet on a dielectric surface under an applied voltage [73]. Devices utilizing EWOD are increasingly prevalent due to their distinct advantages, such as minimal power consumption, swift response times, and versatile adjustability [32]. These benefits yield a wide array of applications spanning from lab-on-chip technologies to display systems and optical lenses. To perform EWOD experiment, we have attached a direct current (D.C.) power supply to the contact angle meter as discussed later. In EWOD, a conducting electrode was applied to the liquid droplet and another one bottom of the dielectric surface. The variation of CAs with applied D.C. voltages were measured in static CA mode. Depending on system, the applied voltage increases up to contact angle saturation (CAS) region, i.e., CA become independent of applied voltage [74].

1.6 Characterization techniques

Various analytical techniques can be employed to analyze surface topography and texture. Depending on the desired information and the scale of surface texture, imaging techniques such as optical microscopy and scanning electron microscopy (SEM) are commonly used. Additionally, surface profilometers and atomic force microscopy (AFM) are employed for analyzing textures at the micro to nanoscale. Interfacial interactions between water droplets and solid specimens can be assessed through physical contact angle characterization. Moreover, high-speed cameras are used to capture the dynamic droplet profile. The details of some characterization techniques are given below.

1.6.1 Optical microscopy

The advanced optical microscopy, combined with coupled device (CCD) cameras, enables the capture of high-resolution color images of surface topography. This technique utilizes visible light and adjustable magnifying lenses to achieve detailed imaging with the desired magnification levels. The optical microscopy can capture submilimiter to few microscale. It is capable of capturing surface features ranging from sub-millimeter to a few micrometers in size. Additionally, the system can record real-time video of movements in the sub-millimeter range when paired with a high-speed digital camera.

1.6.2 Scanning electron microscopy (SEM) and FE-SEM

SEM is a prevalent technique utilized for examining surface morphology, encompassing shapes and sizes. It operates by directing a focused beam of electrons onto a conductive specimen surface, interacting with surface atoms to render surface topography [75]. Traditional SEM imaging occurs under high vacuum conditions and necessitates involved sample preparation, such as dehydration, fixation, and conductive surface coating tailored to the surface characteristics. Recently, low-voltage SEM has emerged as a promising alternative, eliminating the need for a conductive coating layer [75, 76]. Nonetheless, our current infrastructure utilizes SEM (*JSM 6390 LV, JEOL®, Japan*), while advanced Field Emission Scanning Electron Microscopy (*FE-SEM, JSM7200F, JEOL®, Japan*) is employed for capturing micro/nanostructures. In both imaging techniques, a conductive coating layer is still requisite for observing leaves and artificial polymer surface textures. Prior to imaging characterization, meticulously section the sample specimen to an appropriate size, considering the dimensions of the instrument holder, for dehydration. Subsequently, affix it to the specimen holder with double-sided tape, ensuring precision, to facilitate the application of a metallic (Platinum) layer, 6-7 nm thick, onto the surface using sputtering technique [77]. Subsequently, images of the specimen are captured from various locations with different magnifications as needed. The precise SEM imaging details for each sample are provided in the respective chapters where the technique is utilized.

1.6.3 Surface profilometer

Profilometers are instruments designed to measure surface texture roughness, typically using a micro-scale stylus probe that physically contacts the surface to detect height variations along a given length. The mechanical movement of the stylus over the surface is converted into electrical signals, which are then used to generate surface texture profiles. A stylus profilometer, specifically a contact-based type, involves the stylus tip directly touching the measuring surface and following a specific path to capture the surface topography. The profilometer operates with a mechanical feedback system that ensures the stylus probe maintains contact with the surface. However, due to the probe's high sensitivity, it is prone to potential damage, particularly to the delicate cantilever tip. Therefore, the dimensions of the stylus tip are critical, with the radius needing to be small and the contact pressure kept minimal to avoid damaging the surface or the instrument.

1.6.4 Atomic force microscopy (AFM)

Atomic Force Microscopy measures the forces between a fine tip and a surface texture at the sub-micron to nanoscale. Depending on the surface type, the scanning probe can operate in various modes, including contact, tapping, or non-contact mode. The AFM records the height profile of the surface as it is scanned, allowing for the generation of a 3D image of the surface topography.

1.6.5 Contact angle (CA) measurements

The contact angle serves as a physical measure of how a liquid droplet interacts with a solid surface. When a liquid droplet is deposited onto a solid surface, its surface tension dictates the formation of a spherical cap shape on the solid [78]. To determine the apparent static contact angle (WCA) of such a droplet, shadowgraphic images are captured using a high-speed camera. By employing basic geometrical analysis, the CA of the droplet can be determined accurately. To facilitate image capture and contact angle analysis, we utilize an advanced CA meter from *Kyowa*

Interface Science®, Japan . Various mathematical approaches, such as the tangent method, height-width method, or $\theta/2$ method, along with curve fitting techniques using specialized software integrated into the contact angle meter, can be employed to analyses the contact angle geometrically [79].

In the tangent analysis, the droplet's form is envisioned as a segment of an abstract circle's circumference. This approach involves locating the center of this theoretical circle and determining the contact angle by measuring the angles formed by tangent lines extending from the circle [80]. Conversely, in the $\theta/2$ method, the droplet's configuration is similarly regarded as a portion of a theoretical circle, but the contact angle is derived from the angles formed by lines connecting the droplet's extremities and apex to the solid surface [81]. However, when employing curve fitting techniques, where the droplet's contour is presumed to conform closely to a true circle or ellipse, the least squares method is utilized. This method entails fitting a curve to the observed data points within a specified range, optimizing the fit to the droplet's shape . In addition to static analysis, dynamic CA can be assessed through droplet extension/contraction (or captive drop) and sliding techniques. These methods are employed to gauge contact angle hysteresis (CAH) and droplet behavior on a solid surface. In the captive drop approach, the droplet's volume is alternately increased and decreased, and the corresponding CAs were measured. The observed CA during volume augmentation and reduction is termed the advancing and receding CAs, respectively. The disparity between these values is referred to as CAH. Conversely, the sliding method entails tilting the solid substrate with deposited droplet, causing the droplet to initiate rolling or sliding at a particular inclination. This angle is designated as the sliding or roll-off angle (α), with the advancing and receding angles defined at the lower and upper ends, respectively. Both techniques are suitable for determining the CAH of a droplet on a solid surface, though the latter method additionally provides information on sliding and rolling behavior.

1.6.6 High-speed imaging of droplet impact

The dynamic behavior of droplets on hydrophilic and (super)hydrophobic surfaces has garnered substantial interest from the scientific community, particularly with advancements in high-speed cameras that allow for capturing droplet impact events at high frame rates, reaching up to ∼310,000 *fps* at reduced resolutions. To capture the droplet impact on leaf surfaces, a monochrome high-speed camera (*Phantom LAB3a10, Micro® LAB*) with high resolution (1280 × 1024 pixels) and frame rate (∼2000 *fps*) was used.

1.7 Motivation of the present work

As earlier discussed, many leaf surface textures, such as those of lotus leaves, rose petals, and taro leaves, exhibit well-ordered, repetitive two-level micro-nano structures [40, 82, 83]. The uniform distribution of these micro- and nanostructures provides sufficient roughness for isotropic superhydrophobicity, while also allowing for high adhesion forces to water. Numerous researchers tried to fabricate artificial polymer films, with well-defined micro/nano structures obtained by duplicating the such leaf surfaces [84, 85]. Feng *et al.* reported fabrication of artificial polymer film inspired from rose petal using soft lithography technique [26]. Sun *et al.* reported artificial lotus leaf by nano-casting using PDMS polymer [86]. Bhushan *et al.* reported lotus leaf like biomimetic hierarchical surfaces fabricated by replication of a micropatterned master surface and self-assembly of two kinds of tubular wax crystals, which naturally occur on the superhydrophobic leaves of *Tropaeolum majus (L.)* and *Leymus arenarius (L.)* [87]. The second category of leaf surface construct can also give a prodigious water repellences owing to its amazing hairy matted subsurfaces. To name a few are, plant leaves, such as lady's mantle (*Alchemilla vulgaris L.*) leaf, poplar leaf, ramee leaf, silver ragwort etc., [88, 89]. Normally, these hairs are trichomes with unicellular, multicellular, or branched protrude from the epidermal tissues [88]. Gu *et al.* reported electrospun artificial silver ragwort surface [88]. Ye *et al.* reported highly reflective and superhydrophobic surface inspired by hairy matted poplar leaf [89]. In addition to isotropic wetting, numerous researchers have endeavoured to replicate naturally inspired surfaces that exhibit anisotropic wetting characteristics coupled with self-cleaning attributes [90]. Zhu *et al.* reported rice leaf mimicking with the binary structural arrays that comprises two components: an organized stripe array and a droplet row array [90]. In another study, Nagashima *et al.* described a technique for constructing bioinspired hierarchical patterns employing the bottom-up approach, while allowing for tunable anisotropic wetting characteristics [91]. The dynamic behaviour of droplets on hydrophilic and hydrophobic surfaces has gained significant attention from the scientific community, particularly with the advent of high-speed cameras. Understanding phenomena such as droplet bouncing, self-cleaning, and droplet transport has become crucial [50]. Various research groups have explored factors like reducing contact time, surface structure effects, impact velocity, and droplet viscosity [50, 92–94].

In addition to natural/bioinspired artificial surfaces, electrowetting (EW) provides a dynamic method for controlling liquid behavior using an electric field. To manipulate droplet on leaf surface, many researchers tried by EW. Mats *et al.* reported EW on superhydrophobic dried *Colocasia* leaf surface, it requires a high voltage (above 0.3 kV) to alter droplet CA. To observe a CA change of 30°, the applied voltage was up to 1.6 kV [95]. Also, Feng *et al.* reported electrowetting on leaf (EWOL). The lotus leaf surface was operated up to 400 V. However, the dielectric film of lotus leaf is not an equipotential plate which results asymmetric deformation of droplets [96]. Krupenkin *et al.* reported electrowetting on nanostructured superhydrophobic surfaces to complete wetting [97]. However, based on EW phenomena, Kuiper *et al.* reported EW variable-focus liquid lens based on two immiscible liquids [98]. Berge *et al.* reported a lens of 6 mm diameter, a cylindrical glass housing filled with -chloronaphtalene as the insulating liquid (a drop of about 15 µl of the insulating liquid is injected with a syringe) and Na_2SO_4 solution in water as a conducting liquid. This was the first report of variable EW liquid lens [99].

In summary, research into natural surface wettability—including isotropic and anisotropic wetting, and dynamic droplet behaviours including rolling to bouncing—has driven technological advances. Inspired by natural surfaces, researchers have developed artificial surfaces that replicate special surface structures to control liquid droplet effectively for applications from self-cleaning surfaces to microfluidic devices. To achieve precise control of droplets on nature inspired artificial surfaces, electrowetting enhances this capability, offering a versatile tool for accurate droplet manipulation across diverse applications, from programmable droplet actuation to liquid lenses.

An extensive review of the literature on naturally occurring plant leaves highlights the vast potential of bioinspired surface structuring for advancing both specific applications and fundamental understanding. Nature's diverse array of surface textures, each with unique multifunctional properties, continues to captivate researchers, yet the question of which surface structures are most effective remains open. While there has been significant global interest in the development of artificial surfaces, particularly in terms of surface wettability—covering aspects such as isotropic and anisotropic wetting, as well as dynamic droplet behaviors like rolling and bouncing—the wettability characteristics of natural plant leaf systems and their bio-mimetic counterparts have not been fully explored, necessitating more targeted research.

There is still much to explore in this emerging field. By mimicking and thoroughly understanding natural systems, it is possible to fabricate artificial structures with controlled micro- to nanoscale features, ensuring a strong structure-property relationship. These artificially mimicked surfaces could be highly beneficial for microfluidic devices, enabling precise control of droplet transportation, splitting, merging, and self-cleaning. Among the techniques available for such control, electrowetting stands out as a powerful tool for enhancing droplet manipulation on artificial surfaces. This technique holds significant potential for applications ranging from lab-on-a-chip technologies to healthcare diagnostic systems.

1.8 Scope of this thesis

Drawing inspiration from the specific plant leaf surface structure and their biomimetics from isotropic to anisotropic wetting, electrowetting aspects and considering the important points aforementioned, the following chapters have been established to address the aims of this thesis. This thesis is organized into seven chapters, each addressing specific aspects of wetting and its implications. The following provides a concise overview of each chapter:

- **Chapter 1:** The chapter provides a concise history and overview of key subjects related to surface wettability, droplet rolling, and droplet bouncing on natural plant leaf surfaces. It summarizes surface characterization, biomimetic techniques, and recent advancements in bio-inspired wettability, focusing on self-cleaning surfaces inspired by the *lotus effect* and largely, by superhydrophobic plants. Additionally, the chapter briefly discusses electrowetting and offers a comprehensive literature review. The research motivation and scope of the thesis are also outlined.

- **Chapter 2:** In the preceding chapter, an overview of the subjects and definitions relevant to our study was provided. This chapter addresses the general mechanisms and mathematical equations related to droplet wetting dynamics. It includes discussions on the effects of surface roughness through the Wenzel and Cassie equations, as well as the phenomena of electrowetting on dielectric (EWOD).

- **Chapter 3:** This work investigates the unusual wettability of the Indian jujube (*Ziziphus mauritiana*) leaf, where the adaxial (upper) surface is hydrophilic, while the abaxial (lower) surface, with its hairy, matted texture, exhibits superhydrophobic properties. The superhydrophobicity and adhesion of tender, mature, and senescent leaf states are analyzed, revealing that tender leaves have the highest water contact angle (WCA ∼151°) and increased roll-off angle. In contrast, mature and senescent leaves show strong adhesion, even at a ∼90° tilt. To biomimic the abaxial leaf texture, electrospun polyvinylidene fluoride (PVDF) fibers were fabricated, replicating the leaf's properties with a WCA of ∼145.7° and high contact angle hysteresis (CAH) of ∼49.4°. The nonwoven fiber network aligns with the worm-like chain (WLC) model, describing the fiber structure's growth and spread.

- **Chapter 4:** In this chapter, we report unusually high anisotropic superhydrophobicity, unidirectional self-cleaning, and biomimicking of sword-lily (*Gladiolus hortulanus*) leaf comprising three-levels of distinct surface structures: the first one includes; micro-scale striation, micro-protrusions (micro-papillae) while the other one features nano-scale waxy flakes. Observably, the static anisotropic wetting and rolling of water droplets are more favourable in the parallel (or, striation) direction than in the perpendicular direction. Inspired from such water repellency of the sword lily leaf surface, here bio-mimicked polystyrene (PS) leaf construct is developed through a soft lithographic technique. The biomimicking process using low molecular weight polyvinyl alcohol (PVA) and polystyrene (PS) as negative, and positive replica; respectively. The natural sword lily leaf surface and bio-mimicked PS construct are examined with care, emphasizing microstructure and roll off conditions. In addition, a relevant theoretical treatment is also highlighted.

• **Chapter 5:** This study investigated the surface morphologies and both static and dynamic wettability of four distinct types of leaves namely, *Mesua, Litchi, Ziziphus,* and *Kalanchoe*, aiming to establish a correlation effects of droplet impact and surface texture between them. The surface morphology of these leaves plays a crucial role in determining the static and dynamic wettability of water on them. Despite this, under droplet impact conditions, the leaves demonstrated significant complete and partial rebounding behaviour, likely due to the low and high adhesion from the densely packed micro and nanofeatures. Our thorough investigation includes an in-depth analysis of droplet impact studies, revealing the complex dynamics that dictate droplet behaviour on hydrophobic to superhydrophobic surfaces. Additionally, we broadened our analysis to examine droplet impact on macro to nanostructures, evaluating their effect on the droplet maximum spreading, contact time, and rebound states.

• **Chapter 6:** This study investigates the application of electrowetting (EW) in a fluidic microlens system comprising two immiscible liquids: a 0.01 M KCl solution as the conducting liquid, and silicone oil (and Johnson's mineral oil) as the insulating medium. By applying a DC voltage, the curvature of the interface between the insulating oil and the conducting liquid is altered due to changes in the contact angle, resulting in a variable focal length. The findings demonstrate that significant contact angle changes with applied voltage enable focal length adjustments at low voltages for microliter-sized droplets. However, at higher voltages, contact angle saturation limits the extent of tunability. These liquid microlenses hold potential for integration into micro-optical systems and tunable compound eye systems.

In addition to planar liquid lenses, a simulation study was conducted on an adaptive liquid lens using electrowetting on dielectric (EWOD) technology. The model involved three insulating liquids—silicone oil, *n*-hexadecane, and *n*-tetradecane—within a cylindrical chamber coated with two different hydrophobic dielectric surfaces; Parylene-C and Teflon-AF. The simulation revealed that by applying a bias voltage above 90 V precisely modulates the interfacial layer between the immiscible liquids, offering a transition in the lens curvature from a diverging to a converging profile. The study further explored the effects of applied voltage and dielectric layer thickness on this curvature transition and the resulting focal lengths, providing valuable insights into the practical challenges and considerations for developing industrial-grade liquid lens designs.

- **Chapter 7:** This chapter provides a comprehensive summary of the key findings and conclusions drawn from the research discussed throughout the thesis. It also outlines the limitations encountered during the study and suggests potential directions for future research efforts.