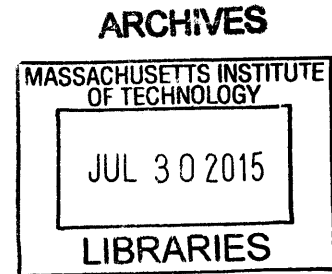


# Droplet deposition on hydrophobic surfaces for agricultural sprays

by

Maher Damak

Ingénieur de l'Ecole Polytechnique  
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by

**Maher Damak**

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on May 8, 2015 in partial fulfillment of the  
requirements for the degree of  
Master of Science in Mechanical Engineering

## **Abstract**

This thesis presents a study of the in-situ precipitation of polyelectrolytes during droplet impacts and its applications in enhancing the retention efficiency of sprays. Large amounts of agricultural sprays are wasted worldwide, due to the poor retention on hydrophobic plants. As the harmful effects of pesticides in particular are more and more pointed out, there is an increasing pressure to reduce their use and make their spraying more efficient. Current solutions, mainly based on surfactants, all have limitations. Here, we present a novel idea based on the modification of the surface of the plant. By precipitating opposite polyelectrolytes, in-situ, we create sparse pinning sites that pin the contact lines of the impacting droplets from the spray and prevent them from bouncing off. We first study the behavior of the impact of two droplets containing oppositely charged polyelectrolytes on a hydrophobic surface. We then study the precipitation process of two polyelectrolytes and develop a model that predicts the outcome of a double drop impact. Finally, we show the macroscopic applications of this study, by using simultaneous spraying. Simultaneously spraying dilute opposite polyelectrolytes on a superhydrophobic surface leads to a large increase in the liquid retention and the coverage of the surface. The behavior has been shown to hold for different polyelectrolytes and surfaces, making this method suitable for a range of applications.

Thesis Supervisor: Kripa K. Varanasi  
Title: Associate Professor of Mechanical Engineering



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# 1. Introduction

Hydrophobic and superhydrophobic surfaces have captured much attention in the past decades due to their remarkable properties.<sup>1,2</sup> Thanks to their tendency to repel water, they can be used in various applications such as self-cleaning<sup>3,4</sup>, improving heat transfer efficiencies<sup>5-8</sup>, biomedical devices to avoid blood clotting<sup>9</sup>, food packaging<sup>10</sup>, and textile<sup>11,12</sup>. Researchers have been inspired by natural superhydrophobic surfaces such as lotus leaves<sup>11,13,14</sup> and butterfly wings<sup>15</sup> to design robust surfaces for these applications.

While repelling water is useful in a wide range of contexts, we may seek, in certain cases, to deposit water or other liquids on a hydrophobic surface. Typically, in agriculture, when pesticides and nutrients are sprayed, we want them to stick to plants and cover their entire surface. Surprisingly, even if designing surfaces to repel water is a difficult problem, the reciprocal problem of making water stick on hydrophobic surfaces is also a difficult problem, and the few solutions that were proposed in the last decades do not completely solve the problem.

The goal of this thesis is to present a new method to enhance the retention of sprays on hydrophobic surfaces. To achieve this, we study the phenomena of spraying and droplet impacts through a large range of length scales. We observe the structure of hydrophobic leaves on the nanoscale. We study the impact of droplets of sizes in the 100-micron to millimeter range. We evaluate the efficiency of sprays at the centimeter scale, and we hope to scale our method to agricultural applications at the kilometer scale. We will review the previous methods to increase the spraying efficiency and propose a novel, more efficient one.

## 1.1. Motivations

Pesticides are an important input in agriculture. They eliminate weeds, insects, microbes and other harmful elements and dramatically increase the crop productivity. Thus, pesticides are extensively used both in the developed and developing world. However, they also have many adverse effects on the environment and on the health of the people exposed to them. It has been found that 98% of insecticides and 95% of herbicides end up in the soil, water, air or other species than those that were targeted.<sup>16</sup> This contributes to soil pollution, water pollution and air pollution. It also endangers many plant and animal species. For example, significant honeybee losses have been attributed to pesticides.<sup>17</sup> Two mechanisms may contribute to pesticide pollution. First, poor retention of pesticides by plants leads to a significant portion ending in the soil, where it may both pollute the soil and contaminate the groundwater.<sup>18</sup> Second, wind drift may take pesticides away from the fields, leading to air pollution as well as soil and water pollution in other locations. Pesticides also have adverse health effects. People who are exposed to them may suffer from severe nervous diseases, reproductive problems and cancer.<sup>19-23</sup>

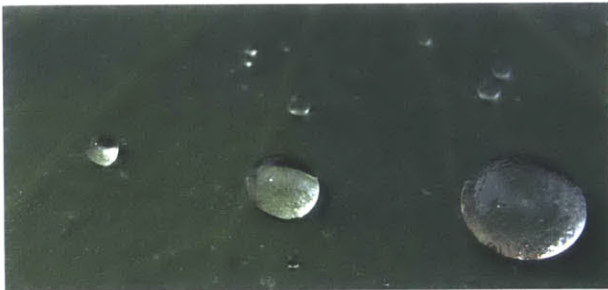
All of these effects are aggravated in the developing world, where less precautions are taken when handling and spraying pesticides. In particular, most farmers use handheld sprayers, and do not wear personal protective equipment while spraying. This is partly due to the lack of resources, but mostly to the lack of awareness of the dangers of pesticides. Moreover, some very toxic formulations, which are forbidden in most countries, may still be in use. For example, "India is one of the few remaining countries still engaged in the large scale manufacture, use and export of some of the toxic chlorinated pesticides, such as *p,p'*-dichlorodiphenyltrichloroethane (DDT), hexachlorocyclohexane (HCH) and pentachlorophenol (PCP)."<sup>24</sup>

A study found that up to 25 million persons in the developing world suffer pesticide poisoning every year, from which 3 million experience severe poisoning.<sup>23</sup>

## 1.2. The problem

Due to all these adverse effects of pesticides, there is an increasing pressure to reduce their use.<sup>18</sup> Therefore, the challenge is to eliminate the sources of deposition inefficiencies in sprays. One of the most important inefficiencies is due to the hydrophobicity of certain plants, which leads to the bouncing or rolling of impacting droplets from the spray (Figure 1-1a). Such hydrophobic plants are common, and they usually get this property from the presence of waxes and hairs on the surface of their leaves.<sup>25</sup> For these plants, most of the sprayed liquid ends up in the soil and do not benefit the plant. The goal is then to increase the efficiency of the pesticide spraying process by making the pesticide droplets stick to the plant and to ensure a better coverage of the surface of the leaves. Several parameters influence the outcome of droplet impacts on surfaces such as the liquid's surface tension and viscosity and the size of the droplets.

a



b



**Figure 1-1: Causes of spraying inefficiency.** (a) Water droplets on a lotus leaf. The leaf is superhydrophobic and impacting or deposited droplets bounce and roll away, leading to very low retentions.<sup>26</sup> (b) Wind drift of pesticides from an agricultural field to a nearby road.<sup>27</sup>

Another important problem in pesticide spraying is the drift of pesticide droplets due to the wind. These droplets are generally of the order of 100 microns and, thus, can be easily carried over large distances by the wind.<sup>28,29</sup> Such a case is shown in Figure 1-1b. Contrary to the retention problem, wind drift is aggravated by a decrease in droplet size. A compromise has then to be found when solving the problem of pesticide retention.

A third problem is the rapid evaporation of pesticide droplets, when their size is very small. This evaporation may occur in the air and upon deposition, limiting the amount of pesticide actually absorbed by the plant.<sup>30</sup>

### **1.3. Constraints for India**

As we seek a solution that could be used and scaled up in developing countries, and India in particular, a set of additional constraints are imposed to a potential viable solution. Most of Indian farmers are marginal farmers, with fields of less than a hectare.<sup>31</sup> From several field visits, it appears that most of these farmers are not aware of the health hazards of pesticides and are not willing to invest large amounts of money in better spraying equipment. Their priority is usually to get new machinery, good quality seeds, fertilizers and pesticides when necessary. Due to the insensitivity to health concerns, there need to be a significant reduction in costs with any new solution for it to be adopted. Pesticides may represent a substantial part in the overall cultivation cost: For example, pesticides account for 40–50%, 25% and 38% of cost of cultivation for cotton, paddy and cole crops, respectively. Some farmers are aware of the problem of poor retention of pesticides and use either commercially available surfactant solutions or more rustic solutions, such as adding honey or “lassi” to pesticides to make them stick better. Usually, farmers do not consider finding more effective solutions to this problem as one of their priorities.

These observations lead to several constraints on the solution. It has to lead to significant improvements compared to existing methods to ensure substantial financial gains. It also has to be easy and cheap to adopt. In particular, it should not involve any expensive new equipment that small farmers would be reluctant to invest in. Ideally, it should work with the sprayers farmers already have, which are mostly handheld sprayers, with a field capacity of 0.1 hectares per hour and generating droplets of 90-160 microns.

## 1.4. Outline of thesis

The poor retention of sprays on plants and hydrophobic surfaces in general has been identified and studied for decades. Several solutions have been proposed. However, as we shall see, they all have some drawbacks and may not work for all surfaces.

In this thesis, we present a novel method for spray retention based on in-situ precipitation of polyelectrolytes during the spraying process. While all previous methods have focused on changing the fluid properties, we argue that, by depositing sparse defects on the surface, we can dramatically change its wetting properties and make impacting droplets stick to the surface. We propose a simple method of altering the surface directly during the spraying process. An outline of the thesis is as follows.

### 2. Droplet impacts and spray retention

We present the fundamentals of wetting and the mechanism of typical drop impacts. We then review the current solutions proposed in the literature to improve spray retention.

### 3. Double drop impacts and polyelectrolyte precipitation

We introduce the mechanism of in-situ precipitation with sprays. We study the formation of polyelectrolyte precipitates in solution and its influence on the behavior of two-drop impacts. We develop a physical model to rationalize the phenomenon and predict the necessary concentration of additives in every case.

### 4. Simultaneous spraying of polyelectrolyte solutions

We show the macroscopic effects of the previous study. Simultaneously spraying opposite polyelectrolytes leads to a much greater retention of sprays and surface coverage.

### 5. Conclusion

We summarize the main results, emphasize the main applications of this technique and present the intended future work.



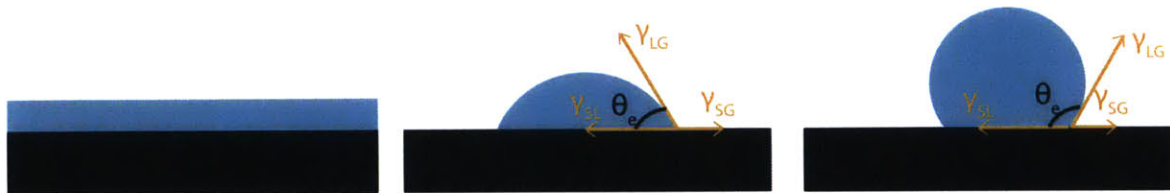
## 2. Controlling droplet impacts on surfaces

### 2.1. Introduction to wetting

#### 2.1.1. Contact angle

When a liquid droplet is deposited on a smooth surface, it may take different shapes. The behavior is dictated by a balance of gravity and the different interfacial tensions. Every interface between two phases comes with an energy cost: Qualitatively, molecules at the interface have fewer neighbors than those in the bulk and, thus, are in a less favorable energy state. Increasing the interfacial area is then energetically unfavorable, and the energy per unit area that has to be spent to increase the area is the interfacial tension  $\gamma$ . This energy per unit area may also be seen as a force per unit length pulling perpendicularly to any given contact line.<sup>1</sup>

For small enough liquid droplets, the influence of gravity, which scales as the third power of the radius, becomes negligible compared to surface tension forces, which scale as the radius. In this case, droplets tend to adopt a spherical shape to minimize their volume for a given volume.



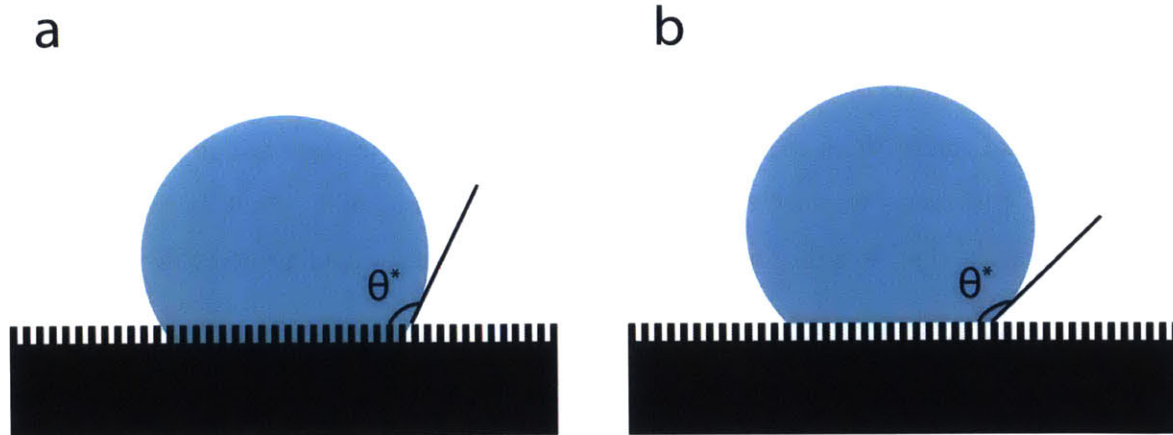
**Figure 2-1: Water on a smooth surface.** The first case corresponds to a positive spreading coefficient: water spreads until it covers the whole surface. The second case is a hydrophilic surface with a negative spreading coefficient. The orange vectors represent the forces acting on the contact line. The third case is a hydrophobic surface.

When a droplet is deposited on a solid surface, three interfacial tensions compete: the liquid/air, liquid/solid and solid/air interfacial tensions. As shown in Figure 2-1, three different outcomes may arise depending on the magnitudes of these tensions. When the liquid spreads on the surface, it decreases the solid/gas area, while increasing the solid/liquid and liquid/gas areas. If we define the spreading parameter as  $S = \gamma_{SG} - \gamma_{SL} - \gamma_{LG}$ , complete wetting of the solid surface by the liquid occurs for  $S > 0$ . If  $S < 0$ , the droplet forms a nearly spherical cap, and a simple force balance on the contact line gives the Young-Dupré equation for the contact angle:  $\cos(\theta_e) = \frac{\gamma_{SG} - \gamma_{SL}}{\gamma_{LG}}$ . If the liquid is water, surfaces with  $\theta_e < 90^\circ$  are called hydrophilic and surfaces with  $\theta_e > 90^\circ$  are called hydrophobic. Superhydrophobic surfaces are defined as surfaces with  $\theta_e > 150^\circ$ . Theoretically, for  $\gamma_{SG} - \gamma_{SL} + \gamma_{LG} < 0$ , the Young-Dupré equation does not have a solution, and we should have complete dewetting. However, this behavior is never observed in practice.<sup>2</sup>

### 2.1.2. Wenzel model

Most real surfaces have some heterogeneities and roughness at the micro or nanoscale, and the previous model developed for smooth surfaces does not apply macroscopically. Because of the heterogeneities, the contact angle can take all values in a certain interval. The minimum contact angle is called the receding angle  $\theta_r$ , while the maximum is the advancing angle  $\theta_a$ . The difference  $\theta_a - \theta_r$  is called the contact angle hysteresis.





**Figure 2-2: Droplets on a rough surface.** (a) Droplet in a Wenzel state: The liquid penetrates between the surface features. (b) Droplet in a Cassie state: The liquid is sitting on top of a patchwork of solid and air pockets.

The roughness of a surface leads to an apparent contact angle different from the Young's angle. One case of wetting is showed in Figure 2-2a and described by the Wenzel model.<sup>3</sup> In this case, the water penetrates inside the roughness of the surface, which makes the Solid/Liquid and Solid/Air contact areas higher than in the smooth case. A simple derivation leads to the Wenzel relation  $\cos(\theta^*) = r \cdot \cos(\theta_e)$ , where the roughness  $r$  is the ratio between the real and the apparent areas. This shows that roughness enhances the intrinsic wetting behavior of a surface. A hydrophilic surface becomes more hydrophilic and vice versa. Although not captured by this equation, a Wenzel state also corresponds to a high contact angle hysteresis, as the droplet is pinned inside the topographical features of the surface, which makes it difficult to move.

### 2.1.3. Cassie model

A second case consists in the droplet sitting on the top of the topographical features of the surface, with air pockets trapped underneath it, as shown in Figure 2-2b. An energy minimization gives the Cassie-Baxter equation for the apparent contact angle:

$$\cos(\theta^*) = -1 + f(\cos(\theta_e) + 1)$$

where  $f$  is the fraction of the solid phase under the droplet.<sup>4</sup>

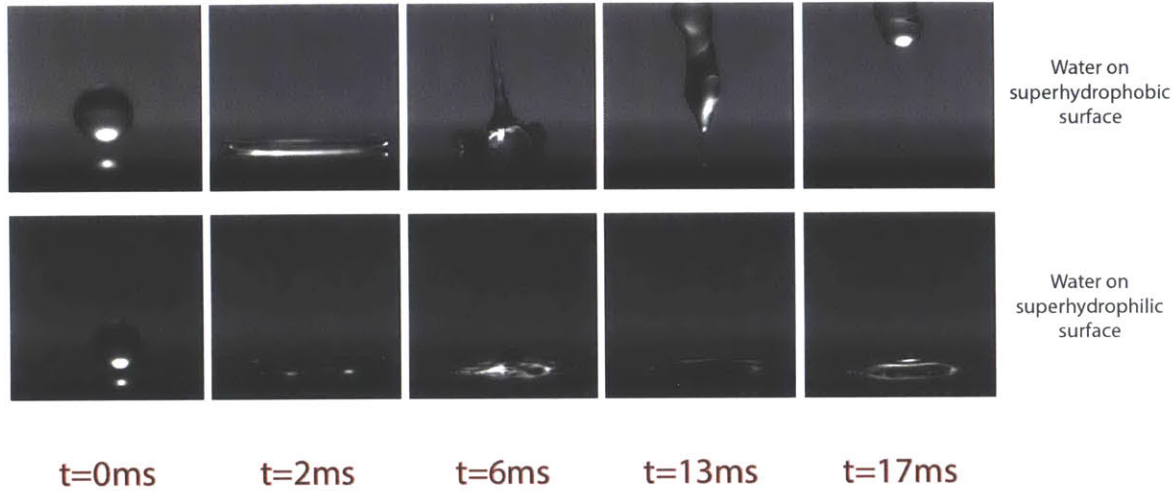
The Cassie-Baxter state is stable when the Young contact angle is larger than a critical angle  $\theta_c$  given by  $\cos(\theta_c) = \frac{f-1}{r-f}$ . However, this state is often observed for angles lower than the critical angle. It is then a metastable state. A Cassie state usually has a low contact angle hysteresis because the area of contact with the solid, which is responsible for the pinning, is significantly reduced. It promotes then fast shedding and low adhesion of liquid droplets.

When a droplet is in a metastable Cassie state, it may undergo an irreversible transition towards the stable Wenzel state when appropriate conditions are met. In particular, when the pressure in the droplet is sufficiently increased, the liquid may penetrate the surface features. A particular mechanism is of interest here: When a droplet impacts a surface with a velocity  $V$ , it has an additional dynamic pressure term that scales as  $\rho V^2$  (Bernoulli pressure). If the velocity is high enough, the impacting droplet may get irreversibly pinned in a Wenzel state upon impact, even if it would have been in a Cassie state if it had been gently deposited. When this transition happens, the impact behavior may be significantly altered.<sup>5,6</sup>

## **2.2. Droplet impacts on solid surfaces**

Drop impacts on solid surfaces can lead to different outcomes depending on the properties of the solid, the fluid and the impact. Rioboo et al. showed experimentally six possible outcomes that are deposition, prompt splash, corona splash, receding break-up, partial rebound and complete rebound. Snapshots of high-speed videos of the deposition and complete rebound cases are shown in Figure 2-3 for a hydrophilic and a superhydrophobic surface. Deposition occurs when the liquid spreads on the surface then stops. Splash is when the droplet is atomized into tiny droplets directly upon impact. Receding break-up is the fragmentation of the droplet in the receding phase following spreading as a whole drop. Rebound occurs at the end of the receding phase when the whole droplet or part of it is expelled from the surface due to a remaining excess energy.

When retention of the liquid is sought, it is clear that the best scenario is the deposition one, where the droplet just spreads on the surface and stays there. Conversely, complete rebound represents the worst scenario, where no liquid is retained.<sup>5,7-9</sup>



**Figure 2-3: Snapshots of water droplets impacts.** In the first case, water impacts an OTS-coated, nanotextured silicon surface (Receding contact angle:  $162^\circ$ ). It expands, recedes and bounces off. In the second case, the surface is a nanotextured silicon surface (Contact angle close to  $0^\circ$ ). The droplet expands and is then deposited on the surface.

Except for the last paragraph of this section, all the described impacts are normal impacts on horizontal surfaces. To describe the phenomenon, let us consider the impact of a droplet of diameter  $D$  and velocity  $V_0$  of a fluid of density  $\rho$ , viscosity  $\mu$  and surface tension  $\sigma$ . The solid is characterized by its roughness and the contact angles (equilibrium, advancing and receding) it makes with the liquid. If  $d$  is the radius of the spreading film upon impact, we can define the spread factor  $d^* = d/D$ .

By observing the evolution of the spread factor over time, one can distinguish four phases in the impact process. The first is the kinematic phase. The spread factor increases as  $t^{\frac{1}{2}}$  and the behavior is the same for all impact outcomes. This phase is very quick, lasting about one tenth of the spreading time. The subsequent phase is spreading, and it is driven by the kinetic energy of the drop, unless the impact velocity is very small, in which case the intermolecular forces drive the spreading.<sup>9</sup> At the end of the spreading phase, the spread factor reaches a local maximum. In the following relaxation phase, the droplet

may begin to recede. In a different study, Rioboo et al. compared experimentally the impact on wax (Receding angle:  $\theta_{rec} = 95^\circ$ ), glass ( $\theta_{rec} = 6^\circ$ ) and PVC ( $\theta_{rec} = 12^\circ$ ), keeping all fluid and impact parameters constant.<sup>8</sup> They found that the receding motion happens only for the wax surface. Generally, the more a surface is hydrophobic, the more a droplet is prone to recede, all other things remaining equal. At the end of the receding stage, the surface energy and remaining kinetic energy from the spreading phase may not be completely dissipated. In that case, they cause a vertical jet to form. The jet can remain attached to the surface and eject one or several drops due to the Rayleigh-Plateau instability (Partial rebound), or it can detach as an intact droplet (Complete rebound).<sup>7</sup> If there is no energy left to cause the bouncing, the droplet will just remain on the surface at the end of the relaxation phase. It is the equilibrium phase.

The dimensionless numbers that are mainly used to describe drop impacts are the Reynolds number  $Re = \frac{\rho V_0 D}{\mu}$ , the Weber number  $We = \frac{\rho V_0^2 D}{\sigma}$  and the receding contact angle. These numbers evaluate the ratios between the important forces that come into play in the process: Inertia, viscosity, capillarity and contact line pinning. However, these numbers are not sufficient to characterize the physics of drop impacts, and no full description of the different outcomes has been found based on these numbers. This is due to the presence of other effects that are difficult to quantify such as the surface defects and roughness features and the onset of internal instabilities in the drop. Moreover the spreading of the liquid lamella involves multiple velocities and length scales that are different from the initial ones and vary rapidly with time, which modifies the balance of forces and changes the models that should be used to describe the droplet at a particular time. Only tendencies can be pointed out. Increasing the Weber number by increasing the impact velocity, increasing the droplet size and/or decreasing the surface tension generally promotes bouncing and less deposition, when the surface is hydrophobic. However, if the velocity is sufficiently large, a Cassie to Wenzel transition may occur, and only a partial rebound may be observed, with a fraction of the droplet being deposited. Increasing the viscosity of the liquid should dissipate more energy during the impact and diminish the chances of bouncing. However, viscous forces are usually small compared to inertia and surface tension, and the influence of viscosity is limited. The

receding contact angle is also a key parameter: the largest the angle, the highest the chances of rebound.

The bouncing of a droplet highly depends on surface hydrophobicity. Such a behavior is generally not observed on hydrophilic surfaces, while on superhydrophobic surfaces bouncing can be observed even for very low Weber numbers. Richard and Quéré showed multiple rebounds of a spherical drop of Weber number 0.07, with a restitution coefficient as high as 0.9.<sup>10</sup>

Drop impacts on inclined surfaces often lead to partial or complete rebounds. In that case, to describe the phenomenon, most authors use a normal Weber number  $We_N$  based on the normal component of the velocity.<sup>7</sup>

### **2.3. Current solutions to enhance spray deposition on hydrophobic plant surfaces**

The parameters that influence the retention of a liquid on surfaces have been enumerated and their impact studied to determine those that can be used to enhance the retention of agricultural sprays. Most methods are aimed at modifying the liquid properties, as, in agriculture, the plant surfaces are given and difficult to change. Here the most important properties of the sprayed liquid are the viscosity, surface tension and size of the droplets. Based on these parameters, several drift retardants and surfactant solutions have been proposed.<sup>11-16</sup> Many studies performed spray experiments directly on plants and measured the retention. This approach is usually taken because predicting the outcome of the impact of individual pesticide droplets on leaves based on the properties of the liquid is difficult.

### 2.3.1. Surfactants

A surfactant is a chemical compound that reduces the surface tension of the liquid. It usually consists of molecules that have a hydrophobic tail and a hydrophilic head, which favors their adsorption on the surface. The surface tension is thereby lowered, since the energy cost of increasing the surface area decreases, due to the surfactants' affinity to the surface. Since the surface tension drives the receding part of the droplet impact process, reducing it may prevent the bounce-off of a droplet, because there remains no sufficient energy to propel the droplet after the receding. To evaluate the effect of surfactants on plants, studies have been carried out to measure the volume retention of sprays and the coverage of the plant after spraying and to understand the characteristics of the plant that make surfactants efficient.

A researcher team performed experiments on seven different plant species. They measured their contact angles and the adhesion of spray droplets with different levels of surfactants.<sup>11</sup> They confirmed the very good correlation between adhesion and contact angles previously reported for a wide range of leaves.<sup>13</sup> They also proved that the retention increases when surfactants are added and that higher concentrations of surfactant lead to higher retention. This increase was noticed on all leaves from the hydrophilic to the hydrophobic ones, which demonstrates that the retention is enhanced by surfactants.

Uniformity of the spray is also important and it can be characterized with coverage. It was studied by Yu et al. who found similar trends as for retention when spraying on crabapple leaves.<sup>14</sup> They measured the coverage area after depositing one droplet of a known diameter. They did several experiments with different drop sizes and found that the use of a surfactant greatly increases the coverage area on the leaf (up to 96% increase). However, they found that the evaporation time was significantly decreased when a surfactant was added: a 29% decrease in evaporation time was observed for 343 $\mu$ m droplets.

To understand the origin of the different retention rates, researchers also performed spraying experiments on several plants: black nightshade, chamomile, quackgrass, winter wheat, pea and tomato.<sup>15</sup> They claimed that the microroughness of the surface of the leaf was a critical parameter in determining retention, based on the scanning electron microscopy images they obtained. They also tested the effect of surfactants. Unlike the previous studies they found that they had no effect when the sprayed leaves were hydrophilic. For hydrophobic leaves they were shown to enhance retention, and a linear relation between retention and the logarithm of surfactant concentration was observed.

The limited range of surfactant efficiency, and the difference in behavior may be explained by the concept of dynamic surface tension.<sup>17</sup> Surfactants lower the surface tension of static droplets by positioning themselves at the surface. However, in an impact process, the droplet experiences large and quick deformations, and the surfactants may not have time to completely reposition themselves at the surface during the process. A surfactant timescale larger than the impact timescale leads to an effective surface tension during the impact that is much higher than expected and may limit the effects of surfactants.

### **2.3.2. Viscosity modifiers**

Viscosity modifiers or drift retardants are chemicals composed of polymers and whose effect is essentially to increase the viscosity of the solution. By increasing the viscosity, the viscous dissipation is increased in all the phases of the droplet impact process, and if enough energy is dissipated, droplet bounce-off may not be possible.

It was found that, unlike the effect of surfactants, the coverage area of a drop was not significantly increased by the addition of drift retardant into the solution.<sup>14</sup> In some cases there was a slight increase compared to water, while in other cases the reverse effect was observed. Similarly, a research group tested the influence of viscosity modifying adjuvants on deposition efficiency for different drop sizes ranging from 170 to 800 $\mu\text{m}$ . For these sizes, no effect of viscosity modifiers was observed.<sup>11</sup> On the contrary, another

study showed a significant increase in evaporation time when a drift retardant was added to the solution (30% increase for 343 $\mu\text{m}$  droplets).<sup>14</sup> This very limited effect on retention is in agreement with the fact that viscous forces are much smaller than capillarity and inertia in an impact process.

### 2.3.3. Droplet size

The size of the sprayed droplets is also a crucial parameter for retention. For a fixed nozzle, this size depends on the viscosity and surface tension of the sprayed liquid.

Researchers measured the volume median diameter of a spray function of the surface tension.<sup>16</sup> They showed that this volume decreased with adding surfactants (up to 17% decrease). It is also theoretically shown that for sprayed liquids, the dominant oscillation wavelength is  $\lambda = \frac{4\pi\sigma}{\rho_a U_r}$ , and the droplet size is proportional to this wavelength, so it is proportional to the surface tension.

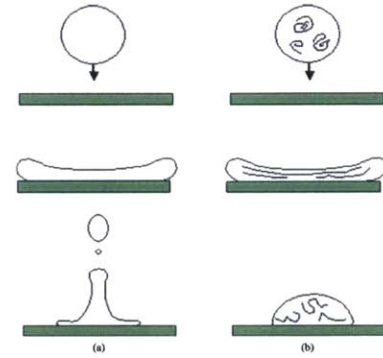
Researchers also studied the effect of droplet size on retention for four different plant leaves: cocklebur, morning glory, velvet, and coffee senna leaves.<sup>11</sup> They found that the deposition efficiency decreases linearly with the droplet size: respectively by 16, 10, 8 and 6% per 100 $\mu\text{m}$  for the four previous leaves. On the contrary, increasing the droplet size limits the evaporation. The time required for a spherical drop to evaporate is given by  $T = \frac{1}{\lambda} D^2$ , where  $\lambda$  is a constant.<sup>18</sup> Therefore using small droplets has an ambiguous effect on the global efficiency of the spraying: it leads to better retention but the droplets evaporate faster and are more prone to wind drift.

### 2.3.4. Non-Newtonian effects

More recently, Bergeron et al. proposed a new method to increase retention in agricultural sprays.<sup>19</sup> It consists in adding small amounts of a high-molecular weight polymer additive to the solution. They showed that this allows changing the rebound behavior to a slow retraction that leads to the deposition of the droplet. In the retraction



phase, the capillary number  $Ca = \frac{V_{ret}\eta}{\sigma}$  can be defined, where  $V_{ret}$  is the retraction speed and  $\eta$  is the fluid viscosity. This number shows the competition between viscous effects that tend to slow the droplet and capillary effects that accelerate the retraction. The capillary number is very small for usual impacts of Newtonian fluids. For the small amounts of polymer used, the viscosity and surface tension of the solution are almost not altered. They argued that the observed effect comes from non-Newtonian effects, particularly the extensional viscosity of the polymer solution  $\eta_e$ . The extensional viscosity represents the viscous dissipation when a fluid is stretched.  $\eta_e = \Gamma \cdot \eta_s$ , where  $\eta_s$  is the shear viscosity and  $\Gamma$  is the Trouton ratio. For a Newtonian fluid,  $\Gamma = 3$ , but for non-Newtonian fluids it can be as high as  $10^4$ , and while the capillary number is usually negligible, multiplying it by four orders of magnitudes makes it significant, and viscous dissipation becomes the main source of energy dissipation.<sup>20</sup>



**Figure 2-4: Effect of high molecular weight polymers on droplet impacts.** In case (a) a typical water drop bounces off the surface while in case (b) polymer additives in the drop provide a high extensional viscosity, which dissipates the energy needed to propel the drop off the surface.<sup>14</sup>

At the microscale, stretching the fluid during expansion and retraction unfolds and deforms high molecular weight polymers (Figure 2-4) and the process drains energy out. It results in preventing the rebound of the drop on surfaces where a water drop would bounce off. Significant improvements in deposition on rough surfaces have been witnessed.

This explanation has, however, been subsequently challenged, and the reason of this rebound suppression may be an interaction between the polymers and the surface instead of non-Newtonian effects, which makes it unlikely to be a universal method that works on every surface.<sup>21</sup> This method also doesn't significantly improve the coverage of the surface since the equilibrium contact angle of the polymer droplets is the same as for pure water.

## 2.4. Modifying surface properties: A new way to control deposition

While all previous solutions focus on modifying the fluid properties, we propose here to arrest impacting drops by changing the surface properties so that droplets are more prone to being deposited upon impact. This can be achieved by depositing some hydrophilic particles on the surface that will act as pinning sites and locally reduce the receding contact angle. Moreover, keeping in mind that the final application is pesticide spraying, we seek a simple way to deposit these particles that can be done during the spraying process.

A naïve way to do this is to add hydrophilic particles to the sprayed liquid, hoping that they would attach to the surface during the impact and pin the droplet. We performed such experiments by adding hydrophilic silica particles of the order of 10 microns to the liquid and observing the impact of a droplet of that liquid, on a superhydrophobic surface, with a high-speed camera. Snapshots of the impact are shown in Figure 2-5. The impact behavior is not changed with the addition of these particles, and we still observe a typical complete rebound. The silica particles, which are hydrophilic, prefer to stay in the bulk of the liquid than to deposit on the surface, and, therefore, do not contribute to pinning the droplet.

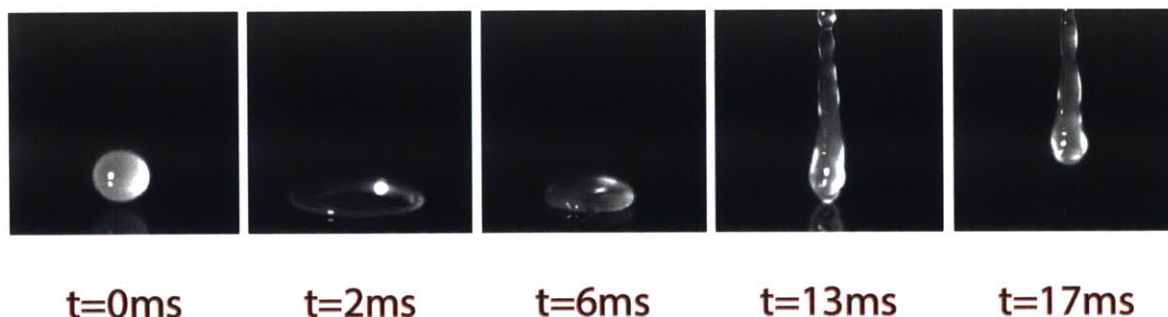


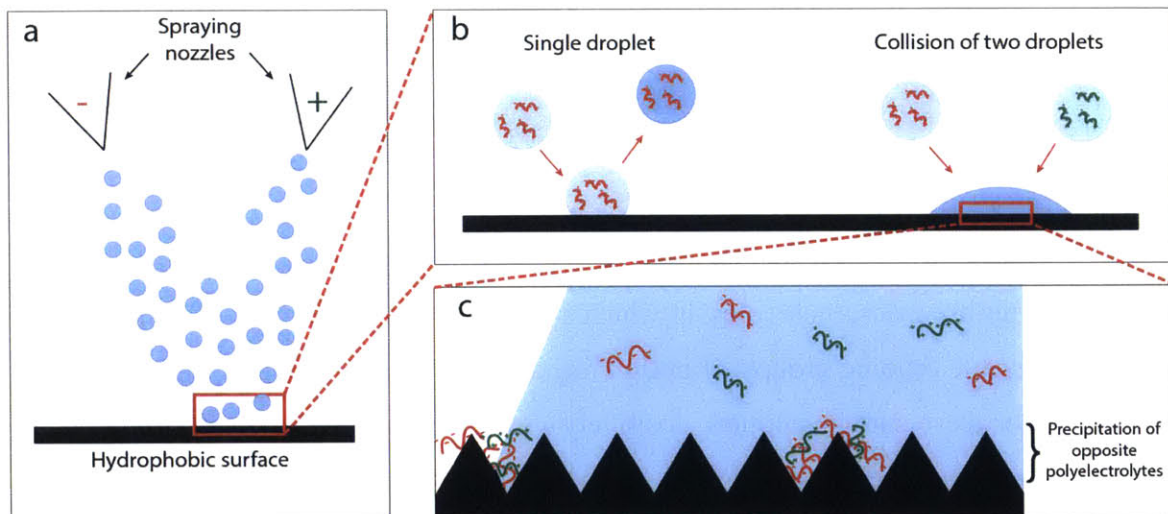
Figure 2-5: Impact of a water droplet containing silica particles on a superhydrophobic surface.

Directly adding hydrophilic particles into the solution is not an effective solution. To overcome this problem, we propose to alternatively grow the hydrophilic spots directly on the surface during the impact process. This will be the object of the next chapter.

### 3. Polyelectrolyte additives and double droplet impacts

#### 3.1. Concept

To make droplets stick to a hydrophobic surface, we propose to slightly modify the target surface properties by depositing sparse hydrophilic defects. These defects would act as pinning sites for the contact line of impinging droplets and prevent them from bouncing. As shown before, the hydrophilic defects cannot be directly added to the droplet. The defects are thus created through in-situ precipitation of a chemical compound during the spraying process. To do this, we add small quantities of oppositely charged polyelectrolyte molecules that interact and precipitate in solution. We add each type of polyelectrolyte to a separate solution and spray them simultaneously, as shown schematically on Figure 3-1a. When droplets of water or one polyelectrolyte solution hit a superhydrophobic surface, they bounce off, as can be seen in the cartoon of Figure 3-1b. However, in the simultaneous spraying process, when two droplets containing opposite polyelectrolytes come into contact, a precipitation reaction will take place and a hydrophilic residue will deposit on the surface and pin the droplets, therefore suppressing the bouncing.



**Figure 3-1: Schematic of simultaneous spraying and two-droplet impacts.** (a) Simultaneous spraying of oppositely charged polyelectrolyte solutions. (b) Single polyelectrolyte droplets bounce on a hydrophobic surface. Two opposite polyelectrolyte droplets impacting simultaneously stick to the surface. (c) A zoom on the contact line shows that sparse defects are formed on the surface and can pin the receding contact line.



Only a few precipitate compounds will form in the roughness of the surface. Most of the polyelectrolyte molecules will remain dissolved in the solution, due to the short reaction time. However, the small number of formed defects may be sufficient to arrest the droplet. As shown in Figure 3-1c, during the receding phase, when the contact line encounters one of the deposited defects, it may get pinned. This process dissipates some energy and the retraction phase is slowed down, eventually leading to droplets sticking to the surface in the favorable cases.

In the following subsections, after quickly presenting some of the main properties of polyelectrolytes, we will study the two-drop impact process shown in Figure 3-1b and determine how it is affected by adding polyelectrolyte molecules to the droplets. We will directly observe the deposited precipitate on the surface through microscopy. We will then define a criterion predicting the transition between bouncing and sticking for two impacting droplets. Observing and rationalizing the precipitation process when two droplets come into contact will lead to a scaling law quantifying the number of defects formed. This law will be used to determine the density of defects on a surface upon a two-drop impact and predict whether the outcome will be bouncing or sticking. We will finally transpose these individual droplet results to sprays and show that simultaneous spraying of polyelectrolyte solutions on superhydrophobic surfaces leads to a substantial increase in the deposition and retention of the liquid.

### **3.2. Polyelectrolytes and zeta potential**

Polyelectrolytes are macromolecules, in which a substantial portion of the constitutional units has ionizable or ionic groups, or both. They are usually water soluble, and their charged groups dissociate in solution. Positively charged polyelectrolytes are called polycations and negatively charged ones are polyanions. Polyelectrolytes combine the properties of polymers and salts: Their solutions are viscous for high enough concentrations, and they are conductive. There are many biological polyelectrolytes such

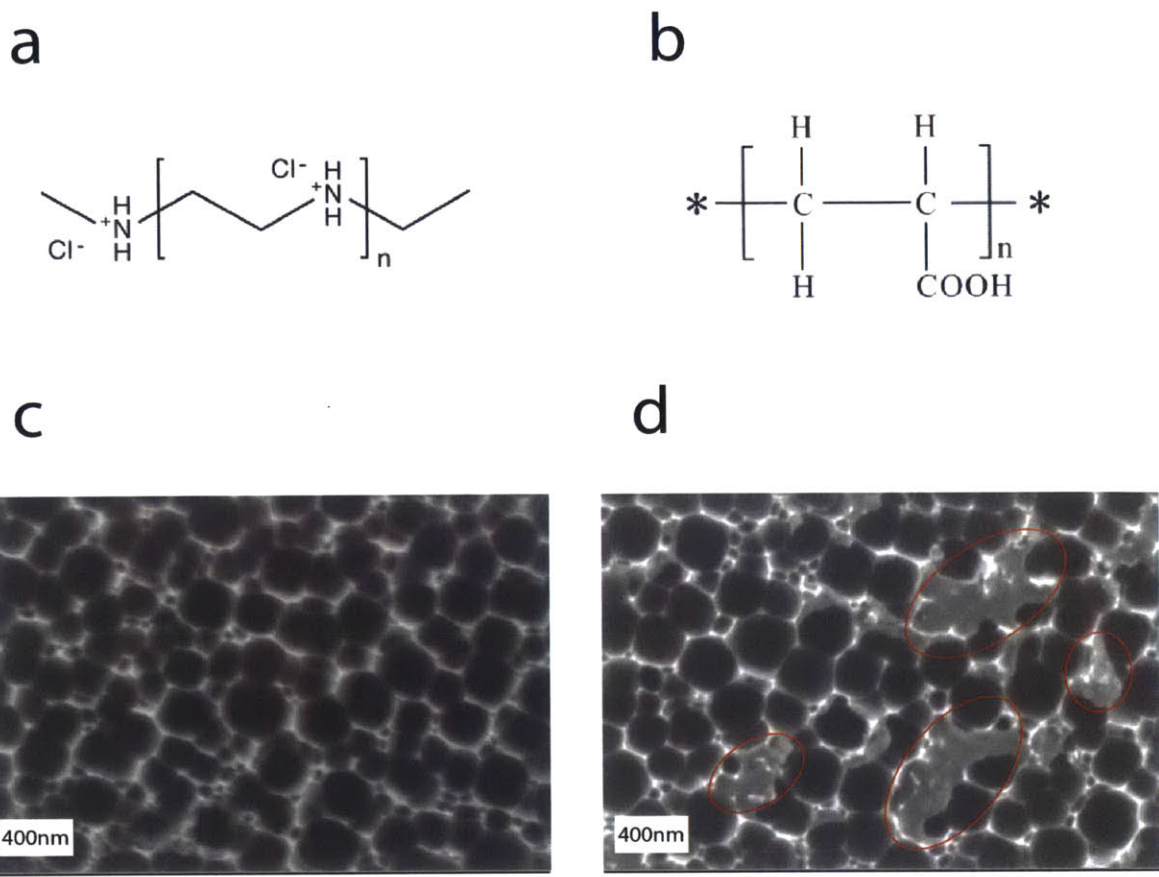
as polysaccharides and DNA<sup>1,2</sup>, and, due to their unique properties, both natural and synthetic polyelectrolytes are used in a wide range of applications.<sup>3-5</sup>

Polyelectrolytes can be strong or weak, depending on whether they fully or partially dissociate in solution. Weak polyelectrolytes are not fully charged in solution and their charged can be tuned by changing the pH. To quantify the electric interactions of polyelectrolytes, the zeta potential is commonly used. The zeta potential is the electric potential in the interfacial double layer surrounding the polyelectrolyte, at the location of the stationary layer of fluid attached to the molecule.<sup>3,6</sup>

When two solutions of opposite polyelectrolytes are mixed, and when the zeta potential of the molecules is sufficiently high, the oppositely charged polyelectrolytes attract each other and bind together, forming a bulk precipitate in the solution.

### **3.3. Double drop impacts**

To study the effect of precipitation on drop impacts, we used two polyelectrolyte molecules. Linear Polyethyleneimine (LPEI) was the positively charged polyelectrolyte, with  $\text{NH}_2^+$  groups in solution (Figure 3-2a), while Polyacrylic Acid (PAA) was the negatively charged polyelectrolyte, with  $\text{COO}^-$  groups in solution (Figure 3-2b). We chose a pH for which both zeta potentials are sufficiently high to have a substantial interaction between the two polyelectrolytes. At this pH (around 4.5), we observed that mixing solutions of these two polyelectrolytes resulted in an insoluble precipitate spontaneously forming in the solution. It consisted in an amorphous whitish residue floating in the solution, and made the liquid more viscous. This is the first reason why simultaneous spraying was privileged over directly spraying the solution containing the precipitate: Viscous solutions are difficult to spray, that is, they require high energies to be atomized, which is not desirable in our applications. Moreover, spraying a solution that already contains hydrophilic precipitates would not work, as explained above.



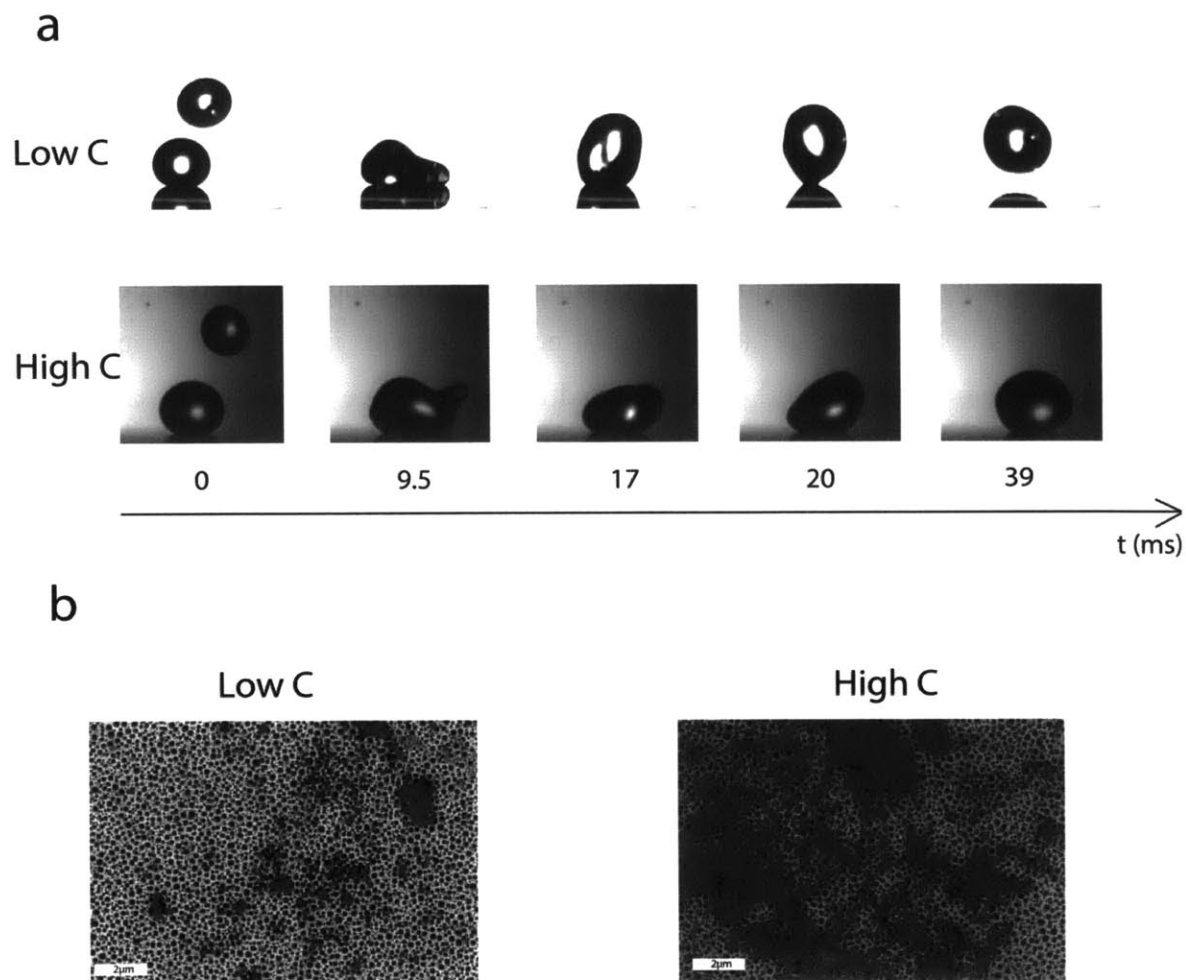
**Figure 3-2: Polyelectrolytes and their precipitates.** (a) LPEI molecule. (b) PAA molecule. (c) SEM image of a nanograss OTS-coated silicon surface. (d) SEM image of the same surface after the impact of two opposite polyelectrolytes. Several precipitates are deposited on the surface.

To overcome this limitation, we propose to form the hydrophilic defects directly in-situ, through the precipitation of polyelectrolytes on the surface during the impact process. Concretely, two sprays, each containing one of the opposite polyelectrolytes, are sprayed simultaneously, and, when their droplets come into contact on the surface, they form precipitates between or atop the roughness of the surface. Separately, the polyelectrolyte solutions are very dilute and thus have similar physical properties (viscosity, surface tension...) as pure water.

The typical superhydrophobic surface we use is a nanograss texture, composed of random features of typical size and spacing around 200nm, and coated with a hydrophobic modifier, leading to a contact angle of 165° and a hysteresis smaller than 5°. Figure 3-2c shows a scanning electron microscope image of the surface from atop where we can see

the nanotexture. After spraying with the two polyelectrolyte solutions, we took another image of the same surface (Figure 3-2d) and could observe the formation of sparse defects of polyelectrolyte precipitate on the surface. These defects will be pinning sites for the receding contact line of a droplet.

To determine the local behavior of two droplets with opposite polyelectrolytes simultaneously impacting the surface, we performed experiments involving the impact of a droplet on another still droplet, on a superhydrophobic surface for different values of the radius, velocity and polyelectrolyte concentration (For simplicity, the concentration of both polyelectrolytes was always the same). Snapshots of the two-drop impact process, taken with a high-speed camera at 10,000 frames per second, are shown in Figure 3-3a, for two values of the polyelectrolyte concentration.



**Figure 3-3: Double drop impacts and precipitate formation for different polyelectrolyte concentrations.** (a) Snapshots of the impact of a PAA drop on an LPEI drop with low (2mM) and high (50mM) concentrations. The bouncing is suppressed with a high concentration. (b) SEM images of a surface after simultaneous spraying with low (10mM) and high (50mM) concentration polyelectrolytes.

The behavior we observe is similar to that of single drop impacts: The droplets coalesce then undergo an expansion phase, reach a maximal lateral radius then start retracting. For pure water or low concentrations, the receding phase continues until the droplet bounces off. For high enough concentrations, the receding phase will be inhibited and the droplet will remain pinned on the surface, due to the defects formed during the impact. As seen on the figure, the process lasts around 20ms, which is comparable to the contact time of single droplets of similar radius.

Figure 3-3b shows the defects formed by sprays of solutions with different concentrations. Defects density, and thus the ability to arrest impacting droplets,



increases with concentration, as thought intuitively. The objective is then to generate just enough defects to make the sprayed droplets stick to the surface.

To determine the concentration that will allow droplets to stick, we must analyze the forces that act during the receding phase of a droplet impact. There are three forces: inertia, capillarity and viscosity. In drop impact scenarios, viscosity can be neglected, as the capillary number, which compares the magnitude of viscous and capillary forces, is of the order of  $10^{-3}$ . The relevant forces are then inertia and capillarity. In energy terms, the droplet comes with a kinetic energy, which is converted into surface energy in the expansion phase. In the receding phase the surface energy is converted back into kinetic energy, and at the end, if the droplet still has enough energy, it will bounce. Since we neglected viscosity, the only way for the droplet to lose energy is through the pinning forces on the surface. We assume then that the droplet will bounce if the work of pinning during the receding phase is lower than the initial kinetic energy, and will stick otherwise.

The kinetic energy is

$$E_k \sim \rho R^3 V^2$$

The work of pinning is

$$W \sim \sigma R^2 (\Delta\theta_{nat} + \Delta\theta_{defects})$$

R is the radius of the droplet, V is its initial velocity,  $\rho$  is the density,  $\sigma$  is the surface tension and  $\Delta\theta$  is the contact angle hysteresis.

For a superhydrophobic surface, the natural hysteresis is negligible. The added hysteresis due to the defects is proportional to the number of defects on the contact line.

$$\Delta\theta_{defects} = \alpha N_{pinning\ sites}$$

In order to determine the outcome of an impact process, we must then evaluate the number of defects that are formed during the process.

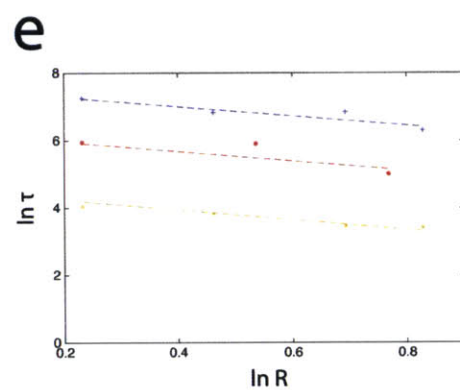
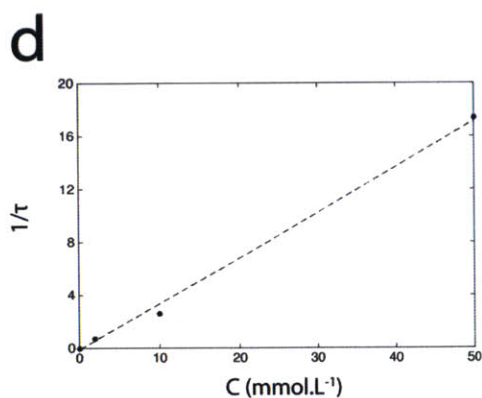
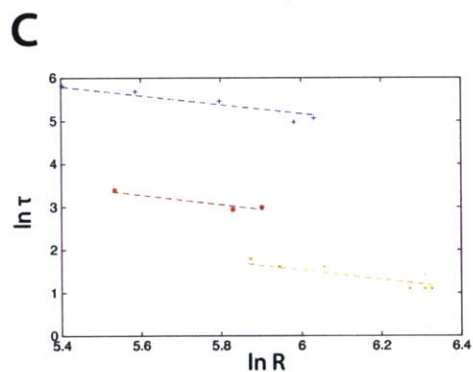
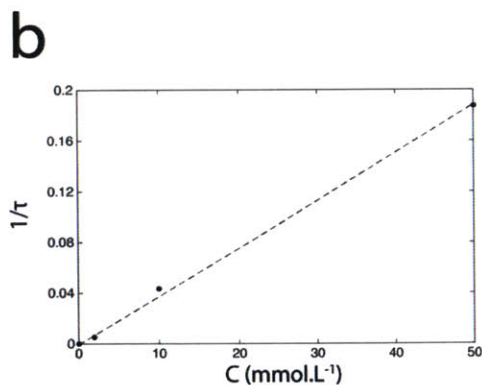
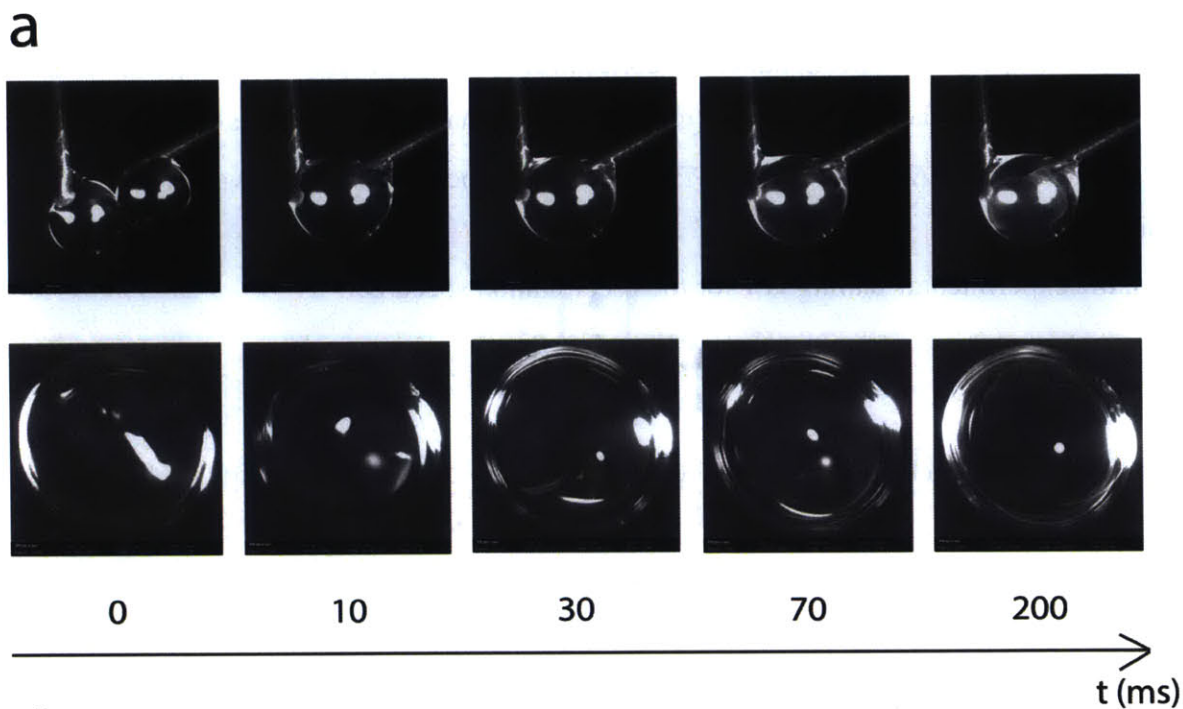
### 3.4. Formation of the precipitate

In the next part of this investigation, we seek to understand and rationalize the formation of the polyelectrolyte precipitate when two droplets coalesce. We performed coalescence experiments between two droplets containing opposite polyelectrolytes, while imaging with a high-speed camera. Two sets of experiments were conducted, one with the droplets in the air, the other on a hydrophobic OTS-coated glass surface. Figure 3-4a shows snapshots of the precipitate formation in coalescing droplets in air and on the surface. A whitish residue appears inside the droplet and starts growing. We repeated the same experiments for different droplet sizes and concentrations. The quantity we measured to quantify the phenomenon was the time  $\tau_{exp}$  from the coalescence till a precipitate could be observed in the video. We argue that this can give a measure of the speed of the precipitation reaction  $V_{precip}$

$$V_{precip} = \frac{dN}{dt} \propto \frac{1}{\tau_{exp}}$$

where N is the number of defects formed.

$\tau_{exp}$  is a subjective quantity that highly depends on the imaging conditions (light, angle, lens, frame rate...). However, when maintaining the same experimental and imaging conditions, relative values of  $\tau_{exp}$  can be used to compare precipitation speeds when the concentration and droplet size are varied. Each experiment was repeated several times, and consistent values of  $\tau_{exp}$  were obtained.



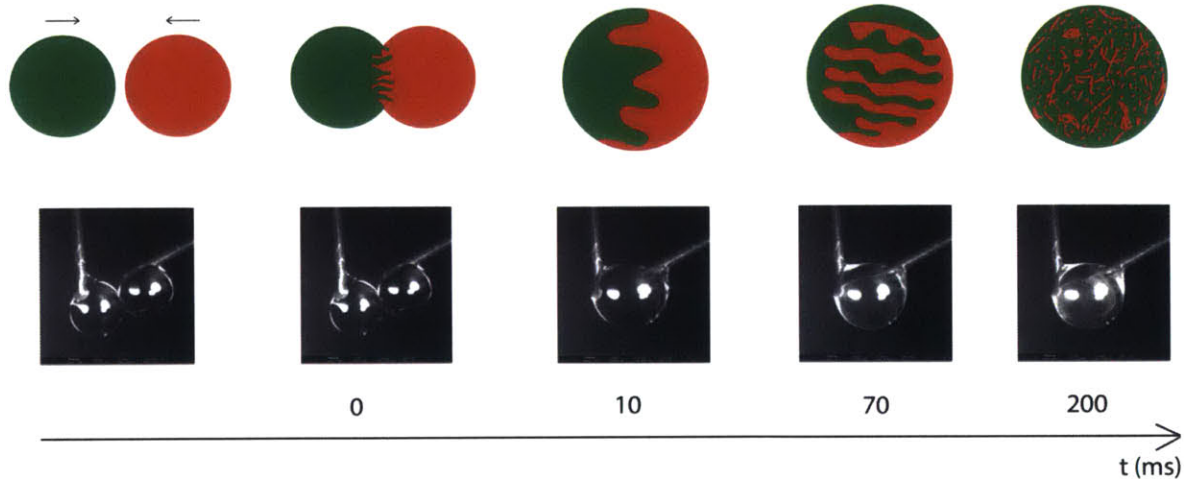
**Figure 3-4: Snapshots and timescale analysis of the polyelectrolytes precipitation.** (a) Snapshots of two droplets upon gentle coalescence, in air and on an OTS-coated glass surface. (b)-(d) Inverse of the time of precipitate visualization on the video, in air and on the surface, respectively, as a function of the polyelectrolyte concentration. (c)-(e) Logarithm of the time of precipitate visualization, in air and on the surface, respectively, as a function of the droplet radius.

The results are presented in Figure 3-4. The plots in (b) and (d) show that the precipitation speed is proportional to the concentration of the polyelectrolytes, both in air and on the glass surface. The plots in (c) and (e) show that  $\ln(\tau_{exp})$  varies linearly with  $R$  with a slope of  $(-3/2)$  in both cases. This means that the reaction speed varies as the radius power  $(3/2)$ .

Thus, the experimental scaling law for the precipitation speed is:

$$V_{precip} \propto CR^{\frac{3}{2}}$$

To rationalize this behavior we hypothesize that, at short times, the precipitate formation is limited by the mixing of the two liquids. When the two droplets coalesce, they need some time to get completely mixed, as shown schematically on Figure 3-5. During the mixing phase, only a fraction of the polyelectrolyte molecules have come into contact and are able to interact. The mixing is driven by inertia and capillary forces and thus happens over a time of the order of the inertial-capillary timescale  $\tau_i = (\frac{\rho R^3}{\sigma})^{1/2}$ .



**Figure 3-5: Schematic of the mixing of two coalescing droplets and the corresponding snapshots for opposite polyelectrolyte mixing.**

In the case of Figure 3-5, this timescale is around 100ms, which is of the same order as the observed precipitation time.

The precipitation speed is proportional to the number of “precipitation sites”, or the number of molecules of one polyelectrolyte that can interact with the other

polyelectrolyte. This number is proportional to the concentration and the volume of the droplet. , The precipitation speed is inversely proportional to the timescale for droplet mixing, which will allow opposite polyelectrolytes to come together and precipitate.

$$V_{precip} = \frac{dN}{dt} \propto CR^3 \frac{1}{\tau_i}$$

We recover the experimental scaling law

$$V_{precip} \propto CR^{\frac{3}{2}}$$

### 3.5. Criterion for the bouncing/sticking transition

Using the previous results, we can come back to the energy balance model we developed earlier to determine the bouncing/sticking limit.

The number of pinning sites on the contact line is

$$N_{pinning\ sites} \propto V_{precip} \tau_{contact} \frac{1}{R^2}$$

We divide by  $R^2$ , as we are interested in the number of defects on the contact line, and not in the entire volume.

$\tau_{contact}$  is the contact time. As stated earlier, the mechanism of a two-drop impact is similar to the mechanism of single drop impacts. In particular, it is governed by inertia and capillarity, and we suppose that the contact time follows the same scaling law previously shown for single droplets  $\tau_{contact} = \left(\frac{\rho R^3}{\sigma}\right)^{1/2}$ .

The work of pinning is then

$$W \sim \sigma R^2 \Delta\theta_{defects}$$

$$W \sim \sigma R^2 \cdot \beta CR$$

where  $\beta$  is a proportionality constant to be determined experimentally.

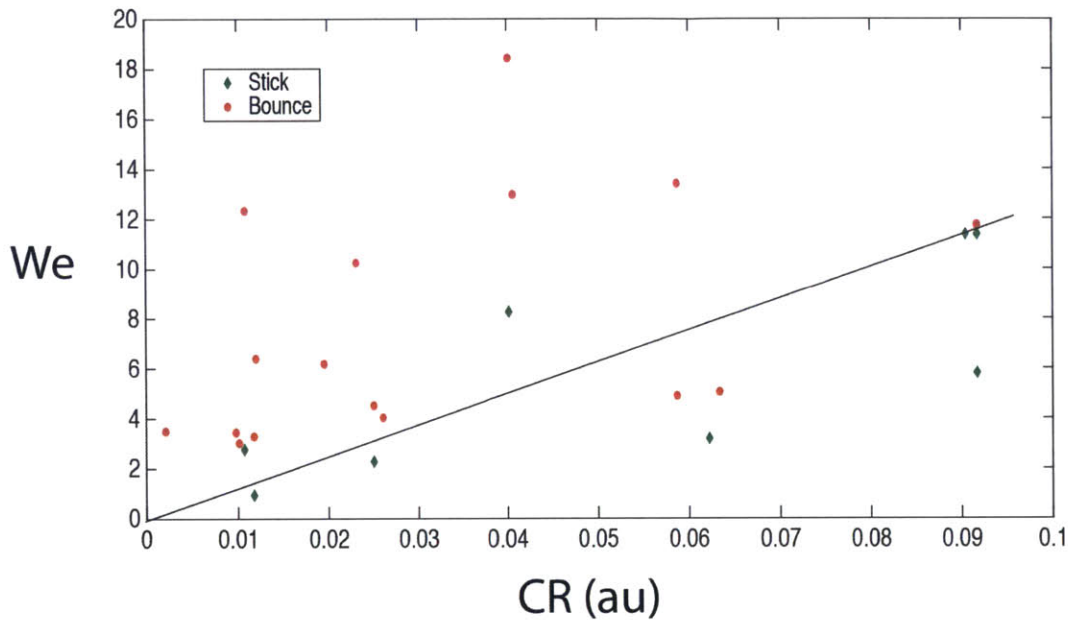
The condition for the droplet to stick is

$$\rho R^3 V^2 = \sigma R^2 \cdot \beta CR$$

which is equivalent to,

$$We \sim \beta CR$$

where  $We$  is the Weber number,  $We = \frac{\rho RV^2}{\sigma}$ , which is the dimensionless ratio of the fluid's inertia and surface tension.



**Figure 3-6: Outcome of a two-drop impact in a Weber number - CR plot.** Below the solid line pinning forces are larger than inertia and pinning of the droplet is expected, while bouncing is expected above the line. Experimental results generally match this trend.

Figure 3-6 is a plot of the Weber number as a function of CR (in arbitrary units). The solid line has a slope  $\beta$ , and represents the transition between the bouncing and sticking regimes: Any point above the line should bounce because it has too much kinetic energy, while points below the line experience large pinning forces that completely dissipate the initial kinetic energy. We see that the outcomes in our experiments follow well this rule and most of them fall on the predicted side of this figure.

In practice, we can then do a few experiments to determine  $\beta$ , and then, for any size and impact velocity of a pair of droplets, we can determine if they will bounce or stick. On a larger scale, for sprays, we can use the same criterion to determine if we will be able to

deposit the sprayed liquid on a hydrophobic surface, or if the surface will repel most of it and remain dry.





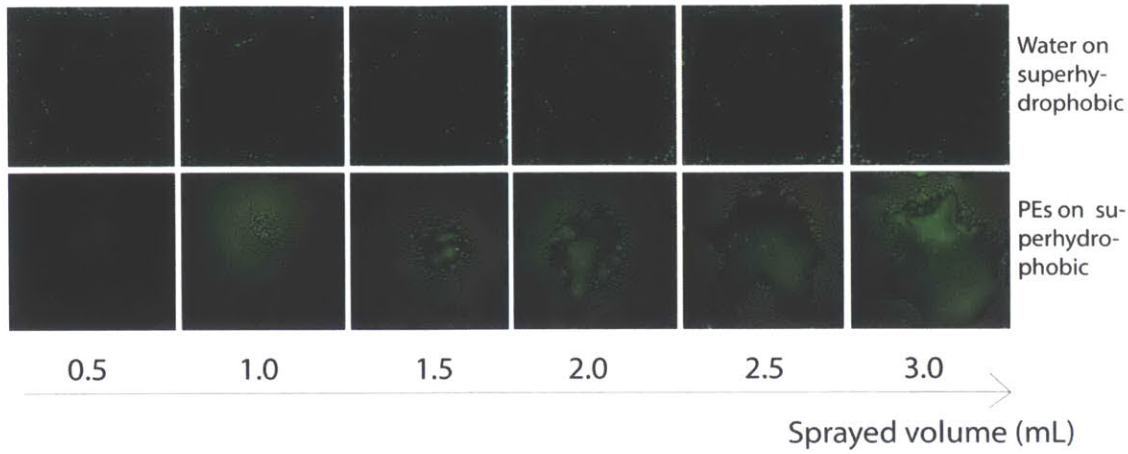
## 4. Simultaneous spraying of opposite polyelectrolyte solutions

To enhance the efficiency of agricultural sprays with the concepts developed in the last chapter, we use simultaneous spraying of oppositely charged polyelectrolytes. We have seen that two droplets impacting the surface together will form a precipitate on the surface that will pin the contact line and, if the concentration is high enough, will prevent the rebound of the droplet. When we simultaneously spray the polyelectrolytes, a large number of droplets of one polyelectrolyte comes into contact with droplets of the opposite one on the surface and form the precipitate. This allows the sprayed liquid to stick on the surface and largely improves the retention of sprays.

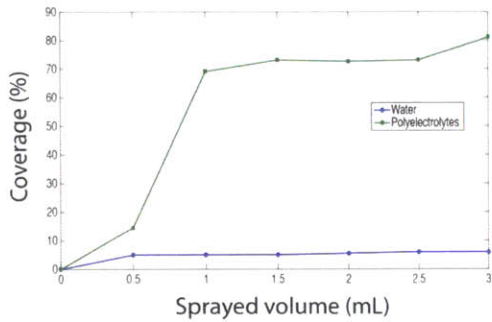
The retention of sprayed liquids was measured for different surfaces and liquids. Sprayers were used to deliver fixed amounts of liquid to the surface in the form of jets of fine droplets, at constant jet velocity and cone angle. Two metrics were used to quantify the retention. First, the mass of the liquid retained by the sample was measured after every spray by weighing the sample.<sup>1,2</sup> The second metric was the coverage of sample, i.e., the area covered by the liquid divided by the total area of the substrate<sup>3</sup>. The first characterizes how much liquid can stick to the surface, while the second quantifies the uniformity of the coverage.

Figure 4-1a shows images of the surfaces as different liquids are sprayed. A fluorescent dye was added to all the sprayed liquids for better visualization. As expected, for a superhydrophobic surface, very little water stuck, as the surface cannot be wetted. When polyelectrolytes were simultaneously sprayed on the superhydrophobic surface, much more of the liquid remained on the surface. Figure 4-1b shows the coverage of the surface in these two cases, determined by image treatment of the previous photographs. For water, coverage did not exceed 7% after 3mL were sprayed. For the case with polyelectrolytes, the coverage was 70% after 1mL and reached 80% when 3mL of liquid were sprayed.

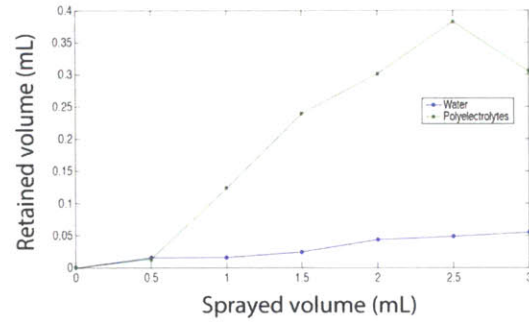
a



b



c



**Figure 4-1: Spraying water and oppositely charged polyelectrolytes (LPEI/PAA) on a superhydrophobic surface.** (a) Snapshots of a superhydrophobic surface after spraying fixed volumes of water and LPEI/PAA. A fluorescent dye was added to allow visualization. (b) Coverage of the surface by the liquid in the same experiments. (c) Retained volume of liquid after spraying water and LPEI/PAA.

The retained volume exhibits similar trends. It is shown in Figure 4-1c as a function of the sprayed volume. We can see that in the case of water, very little volume is retained, while for polyelectrolyte spraying the retained liquid is increased by more than tenfold. The retained mass is even similar to the retained mass of water on a superhydrophilic surface that we measured in separate experiments. After a linear increase phase, the retained mass eventually reaches a limit, because the sample cannot hold more liquid, and spraying more pushes away the liquid accumulated on it. This limit explains the decrease observed in the last data point.

From the spraying conditions in our experiment (droplet size and velocity) we can use the previous two-drop model to estimate the concentration at which the transition from bouncing to sticking occurs. We find a concentration of 10mM, and, indeed, we experimentally observed large enhancements in collection for concentrations of 20mM, while nothing happened for 2mM.

To confirm the generality of the phenomenon and the role of opposite polyelectrolyte precipitation in the process, we performed similar experiments with different polyelectrolytes. The superhydrophobic surface was the same as before, and the polyelectrolyte solutions were Chitosan (10mM) and Alginate (10mM). Chitosan and Alginate are biocompatible polyelectrolytes that would be particularly suitable for agricultural applications. Three experiments were carried: (1) Spraying only water, (2) spraying only Chitosan and (3) simultaneously spraying Chitosan (positive polyelectrolyte) and Alginate (negative polyelectrolyte). Figure 4-2 shows the retained volume as a function of the sprayed volume for the three cases. We can see that spraying only the Chitosan solution on the superhydrophobic surface leads to a very small retention, approximately equal to that of water. Similarly to the previous case, when oppositely charged polyelectrolytes were sprayed, a much larger retention was observed, with a linear increase at the beginning, leading to a retained mass ten times larger than the case of water or Chitosan spraying.

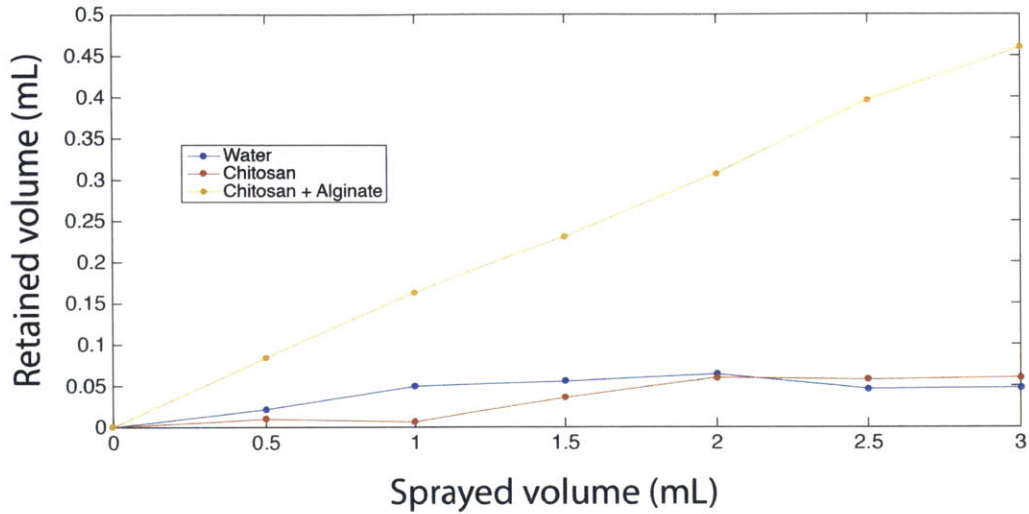
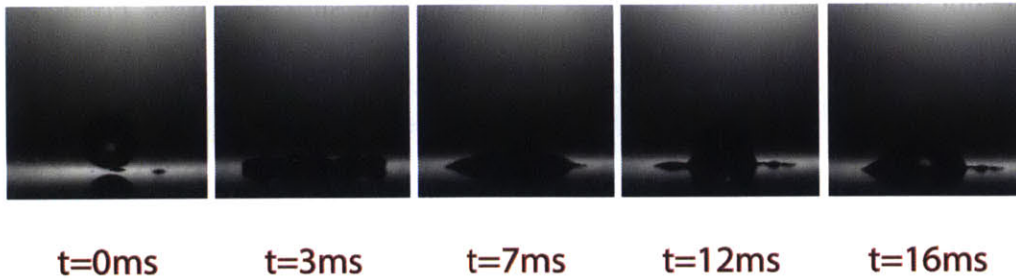


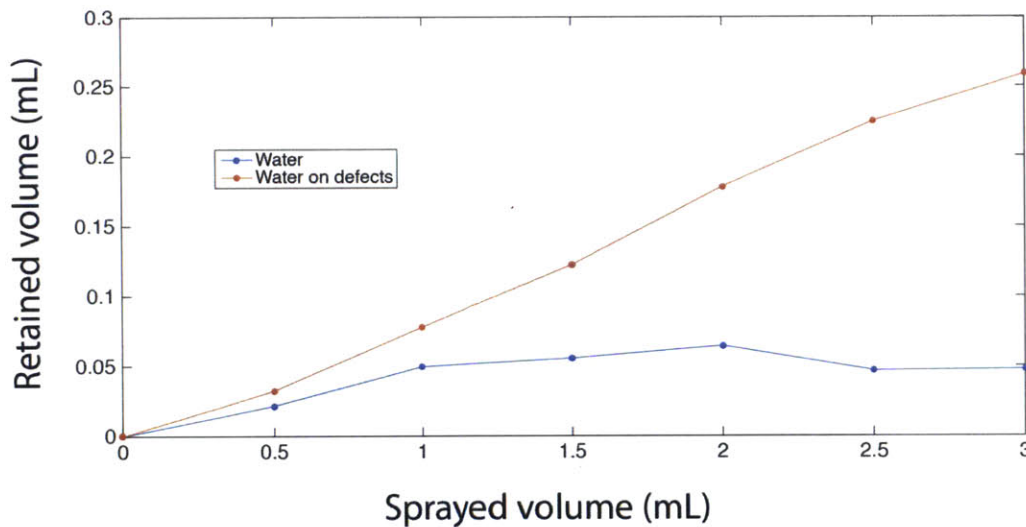
Figure 4-2: Retained volume of water, Chitosan and simultaneous Chitosan and Alginate sprays.

Once precipitates have formed on the surface, it becomes prone to droplet deposition even if the droplets do not contain polyelectrolytes. If single water droplets impact the surface, they will be subject to pinning during the receding phase of the impact, in the same fashion as for double drop impacts. If there are enough defects, rebound will not be possible and the droplet will be deposited. Snapshots of the impact of a water droplet on a superhydrophobic surface, on which defects have been deposited with simultaneous spraying of Chitosan and Alginate, are presented in Figure 4-3a.

a



b



**Figure 4-3: Water spraying on a superhydrophobic surface after precipitation.** (a) Snapshots of the impact of a single droplet on a surface on which Chitosan and Alginate have previously been sprayed. (b) Retained volume versus sprayed volume for water on the superhydrophobic surface and water on the superhydrophobic surface after Chitosan/Pectin spraying.

We tested the retention of water after defects were formed. The superhydrophobic surface used was the same as before, and the polyelectrolyte solutions were Chitosan (10mM) and Alginate (10mM). Two experiments were carried: (1) Spraying only water on the superhydrophobic surface and (2) spraying water on a surface on which simultaneous polyelectrolyte spraying was previously performed. Figure 4-3b shows the retained volume as a function of the sprayed volume for the two cases. Spraying only water on the superhydrophobic surface leads to a very small retention. Spraying pure water after

forming a precursor layer by polyelectrolyte spraying leads to a linear increase in the retained mass, with a slope six times larger than for water directly on the superhydrophobic surface. This is the result of the pinning sites that were previously deposited by spraying the opposite polyelectrolytes.

In addition to experiments on our model superhydrophobic surface (OTS coated nanograss), we performed experiments on plant leaves to verify that the concept still works. Similar results were obtained. Figure 4-4 shows a picture of a lotus leaf after simultaneously spraying polyelectrolytes on it. Lotus leaves are among nature's most superhydrophobic surfaces, and we can see here that it is completely wetted in the region of spraying. This is the most difficult case one would have to deal with, and other plants or surfaces will be more prone to spray retention.



**Figure 4-4: Photograph of a lotus leaf after spraying opposite polyelectrolytes (Chitosan/ Alginate).**

## 5. Conclusion

In this thesis, we have reviewed the existing methods to improve the retention efficiency of agricultural sprays and outlined their limitations. We have then demonstrated a new mechanism to enhance spray deposition on hydrophobic surfaces through in-situ precipitation of polyelectrolytes. We have shown how defects formed on the surface can pin the impinging droplets, and presented the advantages of creating these defects in-situ. We then elucidated the mechanism of precipitate formation in coalescing droplets and determined how it affects the drop impact behavior. This led to a criterion characterizing the transition between bouncing and sticking droplets or sprays. This method allows the surface modification and deposition of the liquid of interest in one single step. This technique can work with different types of polyelectrolytes, as long as their zeta potential is high enough to interact. We have shown that adding Chitosan and Alginate to the sprayed solutions largely enhances the spray retention. These polyelectrolytes are polysaccharides that are non-toxic, biocompatible and biodegradable, which makes them excellent candidates for plant treatment.<sup>1,2,3</sup>

It is known that low retention of pesticides on hydrophobic plants is a major problem in agriculture.<sup>4</sup> By adding small amounts of polyelectrolytes to the sprays, the quantity of pesticides used could be significantly reduced, while the coverage is increased, offering a full protection to the plant and limiting the toxic effects of pesticides. Water spraying is also commonly used in various regions to prevent frost formation, and full coverage of the plant is crucial there.<sup>5</sup> This solution can thus help save large amounts of water. This method can also be used for other agricultural sprays, paints, and any other process that involves sprays or droplet deposition.

By focusing on solving the spray retention problem for the Indian agriculture, we have achieved a simple and easily implementable solution that could be used for various types of sprayers and liquids. This technique could be used in both the developing and developed world, which makes it an example of reverse innovation, where a product that

is developed for the needs of the developing world turns out to be a viable solution in more economically developed settings.

This work may be further developed by understanding the interactions between the polyelectrolyte molecules. Using that to tune the number and structure of defects we want to form may lead to a more controlled deposition of liquids on the surfaces of interest.

Analyzing the dynamics of sprays and the mixing of the droplets in simultaneous spraying may also lead to a more efficient way to spray the liquids.



## 6. Methods and materials

### 6.1. Fabrication of superhydrophobic surfaces

Plasma etch with O<sub>2</sub> and SF<sub>6</sub> was performed on silicon substrates to make a silicon nanograss texture. The latter is a superhydrophilic surface with contact angles around 0°. To make it superhydrophobic, the surface was coated with a hydrophobic modifier (Octadecyltrichlorosilane). Advancing and receding contact angles of DI water on a nanograss silicon surface treated with the hydrophobic modifier were measured with a goniometer (Model 500, ramé-hart) at 25 °C to be 165°±2° and 160°±3°, respectively.

### 6.2. Polyelectrolyte solutions

Four polyelectrolyte molecules were used. All the polyelectrolytes were obtained from Sigma- Aldrich and used as received. The properties of the used solutions are in Table 1.

| Polyelectrolyte                        | Molar weight (kg/mol) | Concentration (mM) | pH      | Zeta potential (mV) |
|--|-----------------------|--------------------|---------|---------------------|
| <b>Linear polyethyleneimine (LPEI)</b> | 20                    | 2, 10, 20, 50      | 4.3-4.7 | 43                  |
| <b>Polyacrylic acid (PAA)</b>          | 20                    | 2, 10, 20, 50      | 4.3-4.7 | -45                 |
| <b>Chitosan</b>                        | 60                    | 10                 | 4.4     | 52.3                |
| <b>Alginate</b>                        | 60                    | 10                 | 3.1     | -33.7               |

**Table 1:** Molar weight, concentration, pH and zeta potential of the polyelectrolyte solutions used in the experiments

The pH was adjusted using HCl for all solutions except the Chitosan solution that was adjusted by adding acetic acid.

### **6.3. Spraying method**

An airbrush was vertically fixed, 21cm above the horizontal sample. The pressure of the air supply to the airbrush was maintained constant throughout the whole set of experiments so as to keep the same jet velocity and cone angle. The liquid was delivered to the airbrush by inputs of 500 $\mu$ L using a syringe. The samples (2"x2") were chosen to be bigger than the spray cone (more than 98% of the sprayed liquid hits the sample).

### **6.4. Coverage determination**

A small quantity of fluorescent dye (Fluorescein sodium salt) was added to the sprayed solutions. Imaging under UV light was realized after each spray, and image processing using ImageJ was performed to determine the fraction of the surface covered by the liquid.

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