University of Twente

The influence of electrowetting on the behavior of impacting droplets on superhydrophobic surfaces

Bachelor Thesis

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Summary

In this research the concept of bouncing droplets on superhydrophobic surfaces is combined with electrowetting. By applying a voltage it is possible to reduce the number of times the droplet bounces, or even suppress the bouncing by trapping the droplet on the surface. With the use of electrowetting, it is observed that the radius of the droplet increases with voltage. It is shown that this relation is linear.

The linear energies (kinetic en potential) are compared with- and without electrowetting. It is observed that the unaccounted dissipation increases with the electrowetting voltage. The loss in linear energy before and after the first bounce is investigated and it is shown that this energy difference goes quadratically with voltage-squared as predicted by the electrowetting equation.

The voltage at which a droplet is just trapped to the surface is called the critical voltage. It is shown that the critical voltage increases as the height increases. A greater height means more linear energy that has to be dissipated on the surface the make the droplet stick. However, due to the oscillations in the droplet, a greater fall height, generally, still means a greater critical voltage.

The phenomenon of trapping droplets using electrowetting can be extended to a two dimensional situation in which bouncing droplets can be steered. This is done by using a double gap electrode where the droplet impacts on one side of the gap, and a voltage is applied on the other two electrodes at the other side of the gap. Found is that the droplet jumps towards the electrodes over which the voltage is applied.

Harmen Hoek and Arne te Nijenhuis

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Chapter 1

Introduction

When a water droplet falls on the ground, it collapses or it bounces a few times. When the surface, on which the droplet bounces, is superhydrophobic, the droplet can bounce for quite a long time. Hydrophobicity can be found in leaves of certain plants, like the leaf of a Lotus plant, but also in rain clothing. Droplets making contact with superhydrophobic surfaces will most likely jumps off the surface as quickly as possible. But when a voltage is applied (electrowetting) on the surface, the situation changes. Research to the phenomenon with applied voltage to the surface will be discussed in this thesis.

In the experiments a droplet is falling from a certain height and impacts on a superhydrophobic surface. The phenomenon is shown in figure 1.1:

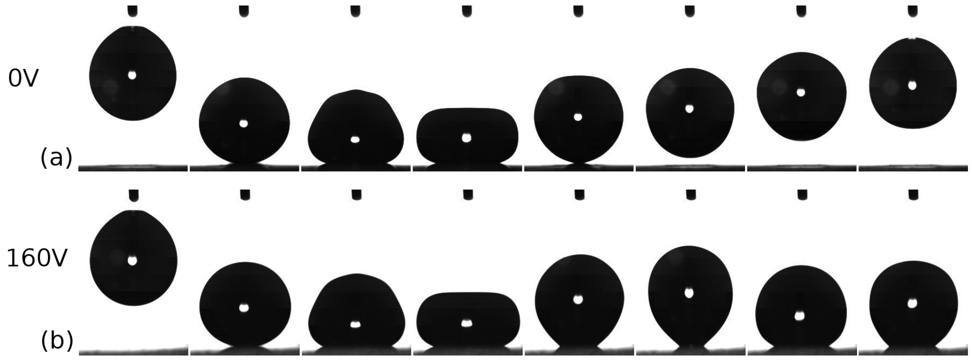

Figure 1.1: Motion of droplet with $0V$ applied (a) and $160V$ applied (b)

It can be seen that the droplet does not stick to the superhydrophobic surface for $0V$ applied to the electrodes in the substrate, but does stick when $160V$ is applied. This difference is due to electrowetting. Electrowetting modifies the wettability of the superhydrophobic surface in a way that the impacting droplet adheres to the surface. The wettability of a surface is the quantification for the degree of hydrophobicity or hydrophilicity of a surface. [1]

Applications of electrowetting can be found in adjustable lenses, electronic displays like e-readers, but also in combination with the coffee stain effect. Next to that, electrowetting is used in the oil industry, for separating oil-water mixtures. The topics discussed in this thesis are useful to get a better understanding of the influence of electrowetting on impacting droplets on superhydrophobic surfaces. That will expand the knowledge of electrowetting in general. [2, 3]

Previously, research has been done by Nottingham Trent University on electrowetting on superhydrophobic surfaces which where coated with Teflon. The droplet which made contact with the surface without making impact. The most important result of the research was that the cosine of the contact angle is proportional to the square of the applied voltage. [4]

Also research has been done on the bouncing of droplets, by University College London. In this research, the water droplet makes impact on the surface of a superhydrophobic substrate. The researchers found that they needed surfaces with contact angles over 151° to make the droplets bounce on a substrate. Their research focuses on determining the hydrophobicity of a surface, with a relationship between contact angle and number of bounces. There was no electrowetting applied in the experiments. [5]

Also research is done by another member of the Physics of Complex Fluids Group on the behavior of droplets under electrowetting when their initial position is at rest, lying on the surface. Parallel to that last study, the experiments reviewed in this report were done to give an understanding of the behavior of falling droplets with the use of electrowetting.

What makes the experiments described in this report unique, is that the combination of electrowetting and impacting droplets on a superhydrophobic surface has never been done before.

The main goal of our project is to research the influence of electrowetting on the bouncing of a droplet on a (super-)hydrophobic surface. To do so, two subgoals were introduced:

- The first, and most important one, is to find the critical voltage at which a falling droplet will be trapped to the surface without bouncing before. The critical voltage will be examined at different fall heights, to get a relation between the energy of the droplet and the voltage needed to trap the droplet on the surface.
- The second goal is to extend the principle of bouncing with electrowetting to a 2-dimensional situation where the droplets are steered using electrowetting.

> Is there a way to apply a voltage on a surface, such that the droplet will be controlled in its motion after the bounce? For example, not jumping in the vertical direction, but making a slight angle to that vertical direction, to move away from the spot where it first bounced.

To find results to the goals written above, first a look will be given at the theoretical aspects, in **Chapter 2**. The theoretical aspects are divided into two parts: the part of the theory for the droplet hitting the surface, and the part when the droplet is in motion through air. Detailed information will be given on (electro-)wetting and the variable which quantifies wetting: the contact angle. Next to that, dissipation of the droplet, both in air and during contact with the surface, will be discussed and unraveled.

In **Chapter 3** the setup, as used during the experiments, will be made clear, as well as the procedure of measurements. Also the substrates used, with their different characteristics, and the way of analyzing the data of the experiments will be reviewed.

In **Chapter 4** and **Chapter 5**, the results and some issues and improvements will be given and discussed. Next to that, some ideas for in following experiments will be suggested.

In the last chapter, **Chapter 6**, the conclusion to the main goals of the experiments are examined.

Acknowledgments
First of all we would like to thank Prof. Mugele for the opportunity of doing a bachelor assignment at the Physics of Complex Fluids group at the University of Twente. His enthusiasm at our first meeting made that we were enthusiastic immediately. We got the freedom to explore what we wanted and even got our own office.

In addition, we would like to thank our first supervisor Dr. Zhantao Wang for the great help in the beginning with our first experiments, and all our questions. Also, our supervisor Dr. Andrea Cavalli for his time and effort in answering a lot of our questions, and the feedback on the concepts of this thesis.

Also Rudy Lagraauw, thanks for the help with your daily supervision. There was no day you did not came by to help us with experiments, Matlab, our report and more.

And of course the rest of the Physics of Complex Fluids group. Thanks! We really felt part of the group and enjoyed the conversations. Special thanks to Daniel Wijnperle and Arjen Pit for the technical support and answering many questions.

Chapter 2

Theoretical Aspects

The theoretical aspects are divided into two sections. The division is based on the situations in which the droplet happens to be. The flight of the droplet through air will be reported in the section "Dynamics of the Droplet". Firstly, the phenomena at the surface will be discussed:

2.1 Surface Phenomena

The surface phenomena of the droplet depend on the physical properties of the surface of the used substrate, the droplet and on the medium in which the phenomena occur. A few of those properties are discussed in the next subsections. Following the physical properties, the theory of electrowetting is discussed.

2.1.1 Wetting

The wettability of a surface is the quantification for the degree of hydrophobicity or hydrophilicity of a surface, when a water droplet is in contact with that surface. Hydrophobicity is the repellency of water by a surface, hydrophilicity is the attraction of water by a surface. Wetting can be divided into two extreme regimes: complete wetting and complete drying. When complete wetting of the surface occurs, the liquid which is brought into contact with the solid, will spontaneously spread to a thin film on the solid. In the case of complete drying, the opposite occurs, the liquid will try to make the least contact as possible. For a small droplet of water, this means that the droplet remains spherical as it touches the surface. [6]

Surfaces carry a specific energy, which depends on the cohesion between the molecules of the substrate, which have a larger attraction to each other than to molecules in the air. Those surfaces can be either solid, liquid or gas. Surface tension results

from this form of cohesion.
All interfaces among two media have a specific surface tension, so does a droplet of water in air, making contact with a solid surface. For this case, a force balance can be drawn. See figure 2.1.

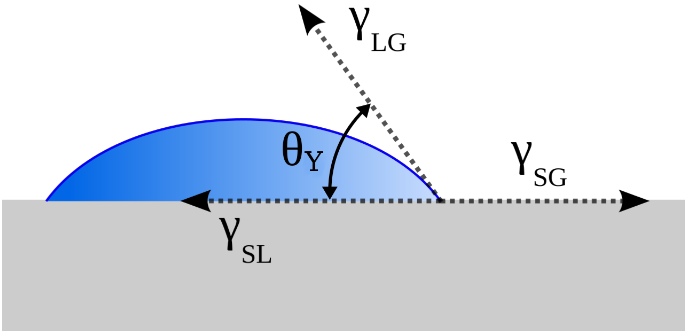

Figure 2.1: Force balance and contact angle [7]

From the force balance at equilibrium in figure 2.1, equation 2.1 can be obtained:

$$\sigma_{SG} = \sigma_{SL} + \sigma_{LG} \cos \theta_Y \tag{2.1}$$

In this static situation, assuming that the surface is flat, the contact angle is referred to as Young's Contact Angle. For a dynamic case, other forces are affecting the contact angle, for example an electrical force, when applying a voltage to the surface. In that situation, the angle is called the equilibrium contact angle. The interfacial tension, σ_{LG}, between the gas and liquid is fixed for the materials used, so this value can be found in literature. The tension of water in air at room temperature is $72.75 mN \cdot m^{-1}$. The other two surface tensions, σ_{SG} and σ_{SL}, depend on the material of the substrate surface used. To determine the contact angle θ_Y between the edge of the liquid and the solid surface, one should know those surface tensions, or by measuring the angle with appropriate equipment. By vector addition, the angle that the droplet shape should make to make the force balance balanced, could be determined. This very angle is called the Young's Contact Angle. [8]

2.1.2 Contact Angle

The contact angle is a variable used to quantify the wettability of a surface. When the surface tension of the solid-liquid interface is larger than the surface tension of the solid-gas interface, the contact angle has to compensate for that, as can be seen in figure 2.1. In the case of hydrophobicity the contact angle is larger than 90°. When the contact angle is smaller than 90°, the liquid has a larger contact area with the solid surface. The regime of contact angles between 0° and 90° is called

the hydrophilic regime. When the contact angle is over 160°, the solid surface is superhydrophobic.
Determining the wettability of a surface is quite easy with the contact angle, because only a sideview of the droplet with a camera is needed to determine the angle. [8]

2.1.3 Wenzel and Cassie-Baxter

The wettability of a surface depends on the type of the used material, but surface roughness is also affecting the wettability. When a surface is rough, the state of the droplet is typically divided in two models: the Wenzel model and Cassie-Baxter model, both named after the researchers who came up with the models. The difference between those two states is quite easy; Wenzel describes the homogeneous wetting regime, and Cassie-Baxter the heterogeneous wetting regime. See figure 2.2 for a visual explanation of the difference between the models. Below the droplet in the Cassie-Baxter state, there is an air layer. The air is trapped between the liquid and the roughness of the surface. For superhydrophobic purposes, it could be convenient to use pillars like in figure 2.2b. Experimentally it is hard to discover if a droplet is in a Cassie-Baxter-state for substrate with a structure of nanoroughness, because it is not easy to see if there is air between the droplet and the surface. [6]

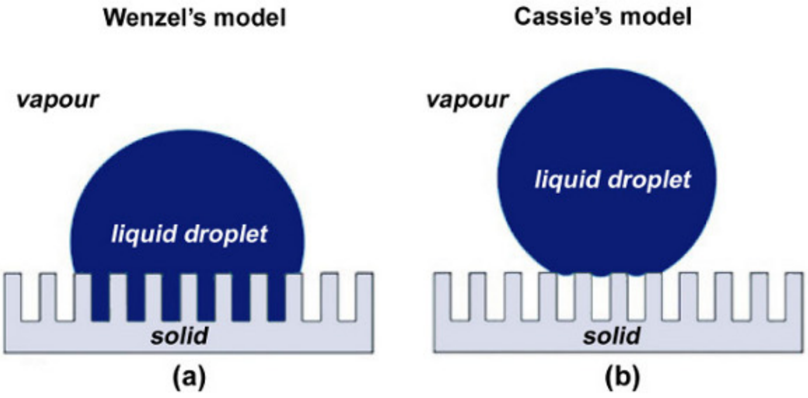

Figure 2.2: Droplet in Wenzel state (a) and Cassie state (b) [9]

2.1.4 Electrowetting

Electrowetting can be used for the controlling of the behavior of a drop, when in contact with a surface. The principle of electrowetting is the change of the contact angle of a liquid when an electric field is applied between the liquid and the underlying surface, see figure 2.3:

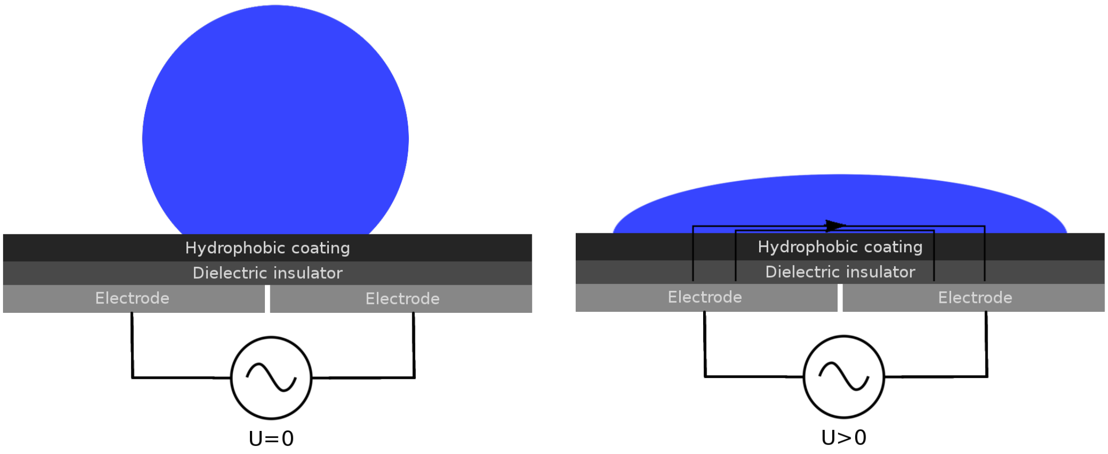

Figure 2.3: Electrowetting at $U = 0$ (left) and $U > 0$ (right)

The reason for the change in contact angle is the electrostatic force that result from the ions in the water which want to get close to the ions of the dielectric substrate and expand the droplet in sideways motion. This electrostatic force can be represented as a vector in figure 2.1 which reduces the length of the σ_{SL}-vector. The effective surface tension between liquid and solid, after applying a voltage, becomes:

$$\tilde{\sigma}_{SL}(U) = \sigma_{SL} - \int_0^U \rho_{SL}\,\mathrm{d}\tilde{U} = \sigma_{SL} - \frac{\varepsilon_r \varepsilon_0}{2\sigma_{LG} d} U^2 \qquad (2.2)$$

In equation 2.2 ([1]), ρ_{SL} is the surface charge, U the applied voltage to the substrate, ε_r the relative permittivity of water, ε_0 the dielectric constant and d the thickness of the substrate.

As can be seen in 2.2, the surface tension between solid and liquid gets smaller for increasing voltage. By equation 2.1 the contact angle will decrease in order to keep the equation balanced. So, the contact angle of the liquid on a substrate depends on the applied voltage to the surface as well as the combined dielectric constant ε_r and thickness d of the layers on top of the substrate. The values of the variables just named, can be combined in the electrowetting number η, a non-dimensional number which compares the strength of electrowetting and capillary forces. When the cosine of Young's Angle, the contact angle for a static situation, is added to the electrowetting number, one can estimate the contact angle of the liquid on the substrate when a voltage is applied. See equation 2.3 which is called Lippmann-Young or Electrowetting equation:

$$\cos\theta_c = \cos\theta_Y + \frac{\varepsilon_r \varepsilon_0 U^2}{2\sigma_{LG} d} = \cos\theta_Y + \eta \tag{2.3}$$

In this equation ([1]) θ_Y is Young's Angle and θ_c is the equilibrium contact angle which is measured at the applied voltage U. Also, ε_0 is the permittivity of vacuum and σ_{LG} is the surface tension between liquid and gas. Reversely, when the contact angle and applied voltage are known, the thickness of the substrate can be estimated by using the Lippmann-Young equation.

2.2 Dynamics of the Droplet

When a droplet falls from an initial height and bounces on a substrate, dynamics is an important topic to review, because energy loss can be explained by dynamic behavior. The motion of the droplet from needle to surface, and reverse, can be divided into two situations. The first situation is the droplet traveling through air. The second situation is when the droplet is in contact with the surface of the sample.

Before analyzing both situations, the total energy and the conservation of energy will be reviewed. The kinds of energy that can be linked to the droplet are kinetic, potential and oscillation energy.

The motion of the droplet through the air is quite straightforward when the droplet is assumed to be a perfect sphere. The kinetic energy can be calculated with equation 2.4 and the potential energy with equation 2.5. They combine for all the energy in the droplet in air when the droplet is perfectly spherical. Unfortunately, the shape of the droplet is constantly changing, while its volume remains constant. That is a reason that the droplet will not reach the same height as where it initially started its fall.

$$E_{kinetic} = \frac{1}{2}mv^2 \tag{2.4}$$

$$E_{potential} = mgh \tag{2.5}$$

In equation 2.4 and 2.5 m is the mass of the droplet, h the initial drop height, g the gravitational acceleration and v the speed at a certain moment.

The oscillation energy is the energy which is not stored in the motion of the center of mass, but in the shape of the droplet. As will be told in Chapter 3, Legendre Polynomials are useful for calculations with the shape of the droplet. When the droplet is in contact with the surface of the substrate, it will spread in the horizontal direction. A part of the kinetic and potential energy which the droplet has in air, will be stored in this sideways motion. When the droplet has maximized its radius, all energy stored in the oscillation is potential oscillation energy. After and before the maximum radius, there is also kinetic oscillation energy present in the droplet.

The total energy balance is stated in equation 2.6:

$$E_{total} = E_{kinetic} + E_{potential} + E_{oscillation} + E_{dissipation} \tag{2.6}$$

This energy-equation should remain constant throughout the whole process. The last term of equation 2.6 depends on the four other energies and the fact that energy in the system should be conserved. [10]

2.2.1 Dissipation

Dissipation is the term for the energy lost by the droplet. Dissipation is accounted for in the energy balance (equation 2.6), because otherwise the principle of conservation of energy inside the system will be violated. Conservation of energy means that the energy will be dissipated inside the system.
There are a few reasonable possibilities for the droplet to dissipate energy. Because the contact time of the droplet is much shorter than the time the droplet is in flight, internal dissipation during flight should be considered a serious contributor to the total dissipation. Dissipation during flight can be, for example, the oscillations of the droplet in air.

The energy of the center of mass of the droplet can decrease in two ways: One of them is related to the shape of the droplet. Some of the energy of the droplet changes into surface energy, so that the droplet gets another shape. But also internal flow is related to the shape of the droplet. This internal kinetic energy does not affect the speed of the droplet, but it does determine the motion of the droplet around the center of mass. Next to the changing shape, energy can be lost in viscous dissipation as result of internal shear forces. This can happen both inside and outside the droplet, air friction for example. The energy lost by viscous dissipation is typically converted into heat.

When a voltage is applied to the surface, the droplet will lose extra energy. The electrical energy applied is in accordance with equation 2.7:

$$E_{electric} = \frac{1}{2}CU^2 = \frac{1}{2}\varepsilon_r\varepsilon_0\frac{A}{d}U^2 \tag{2.7}$$

In this equation, C is the capacitance of the dielectric layer of the substrate, determined by the area A, the thickness of the layer d and the relative permittivity ε_r.

The loss of extra energy due to the applied voltage will happen because the droplet will spread more over the surface and will also spread faster. Also, the droplet finds it harder to depin from the surface again. The spreading could result in larger oscillations and larger viscous dissipation, because there is a lot of shear in the droplet when it spreads on the substrate. With those energy losses in mind, the energy loss should probably be related to the electric field and its electrostatic force. By equation 2.7 and earlier research it can be expected that the loss in energy will be proportional to U^2. [4]

Restitution coefficients can give an approximation of the amount of energy dissipated between two bounces. The restitution coefficients (ϵ) are a ratio between the maximum height after the impact of the droplet on the surface and the maximum height before the impact. Typically the coefficient is below unity, because, due to dissipation, the droplet will not reach the same height as it did before. The coefficient of restitution can also be calculated by comparing two velocities, one before and one after impact of the droplet. Restitution coefficients are very useful for plotting data, as is done in a few graphs in this report.

Chapter 3

Experimental Aspects

This chapter describes the experimental aspects of the experiments carried out. Firstly the setup is discussed, after that the substrates are discussed. At the end of the chapter, the measuring procedure and data analysis will be explained.

3.1 The setup

The experimental setup used is shown in figure 3.1. The sample is placed on the microscope table (Nikon Eclipse TI) as shown with the letter 'a' in figure 3.1. A millimeter-sized drop of ultra clean deionized water with physical properties of: kinematic viscosity $\mu = 1 * 10^{-3}\ Pa \cdot s$, surface tension $\sigma = 0.0646\ N/m$ in air at room temperature and density $\rho = 996.9\ kg/m^3$ is dropped on the superhydrophobic surface using a syringe-pump (KD Scientific Legato 270) with a precision tip needle (b) with a diameter of 1.90 mm. The drop detaches from the needle by its own weight, obtaining a uniform radius of ± 1.1 mm. The volume of the drop is controllable using the syringe-pump and is set to 5.3 μL for these experiments. The fall height is controllable and is a parameter for our experiments. The electrodes in the substrate for electrowetting are connected to an AC voltage source (Agilent 33210A) (c). The voltage is then amplified 400 times using a voltage-amplifier (TREK PZD700). Voltage is a main parameter for our experiment. The AC frequency is set to 10 kHz. [10]

The free fall, impact and bounces of the drop are recorded using two cameras, one for the side view (d) and one for the bottom view (e). The sideview camera (Photron Fastcam SA3) is lighted using a backlight (f) (Schott KC1500) and is set to a frame rate of 2500 or 5000 fps, a shutter time of 1/frame and a resolution of 512x512. The bottomview camera (Photron Fastcam SA5) is lighted using a lamp (g) (Nikon Intensilight C-HGFI). The image of the bottom view can be enlarged using lenses inside the microscope with a magnification of respectively 10, 40, 80 and 120. The bottomview is only used for monitoring the condition of the surface and for alignment if needed.

Two typical stills of the recording of the sideview and bottomview camera are shown besides the letters 'h' and 'i' respectively in figure 3.1:

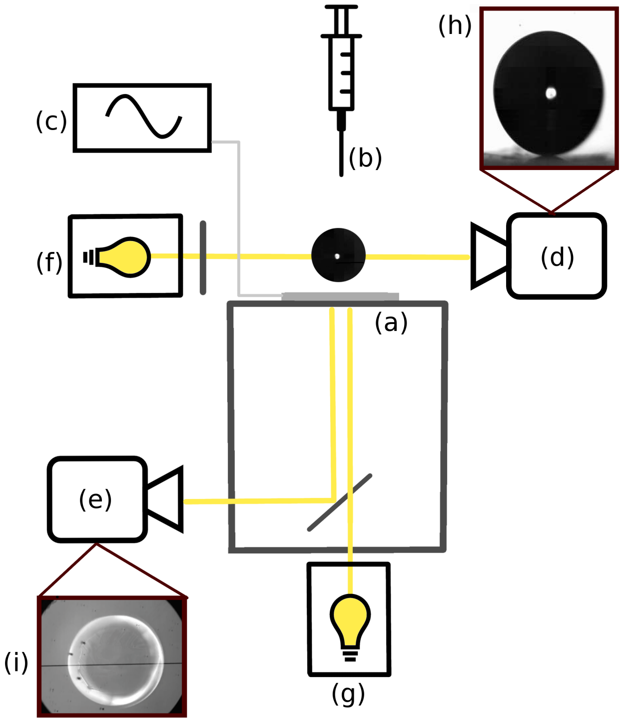

Figure 3.1: Schematic representation of the setup (a) microscope table (b) needle (c) AC voltage source (d) sideview camera (e) bottomview camera (f) sideview lamp (g) bottomview lamp (h) typical sideview recording (i) typical bottomview recording

Besides this setup, an Optical Contact Angle measuring device (OCA from Dataphysics) is used for precise measurements of the contact angle of drops on the hydrophobic surfaces at rest.

3.2 Analysis of used samples

In order to explain the results, it is useful to understand and characterize the surfaces used.

During the experiments, several types of surfaces where used as samples. The surfaces are based on two main structures: a structure with pillars and one with nanoroughness. Both types have their advantages and disadvantages. Pillars are more stable, but suffer from the Wenzel effect: the water between the pillars can destroy the pillars by the vibration of the water or some kind of erosion. Nanoroughness is not limited by the Wenzel effect at rest, but is damaged when using electrowetting at relatively high voltages, as will be discussed in Chapter 4. Mostly because of this reason, the nanoroughness was used during the experiments at a maximum voltage of $180V$.

A typical surface is built up from several layers, as shown in figure 3.2. The bottom layer consists of electrodes for electrowetting. These thin electrodes are placed on a glass substrate by etching in a HCl-solution. The middle layer is a dielectric insulator. This insulator prevents shortcuts between the electrodes and makes it possible that nanoroughness is etched on the substrate. The top layer is a hydrophobic coating for hydrophobicity, as will be reviewed in the next section.

3.2.1 Sample preparation

Two kinds of surface structures were used during the measurements. One with nanoroughness on top, and one surface structure with pillars. Both will be discussed in this section.

Nanoroughness
The superhydrophobic surfaces were prepared in the cleanroom using photolithography technique. A representation of a typical sample can be found in figure 3.2:

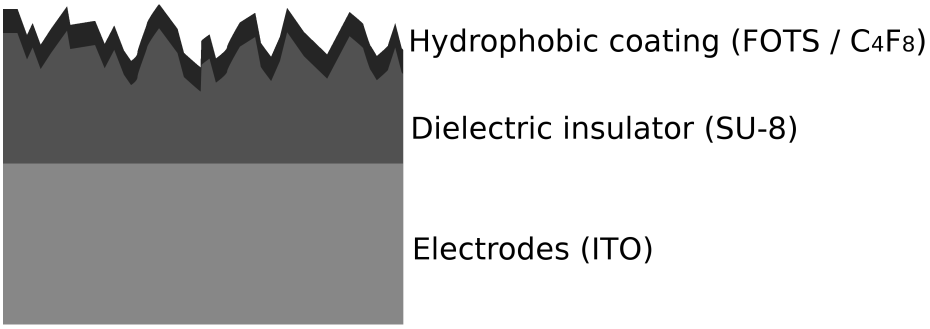

Figure 3.2: Schematic representation of an intersection of the substrate

Glass covered with electrodes made out of Indium Tin Oxide (ITO) is spincoated with a 4.6 μm thick SU-8 photoresist in order to make a thin homogeneous insulating layer. The purpose of this layer is to prevent the surface from making contact with water and getting dirty which both could cause a shortcut between the electrodes.
Using plasma etching with an oxygen plasma for 120 or 150 seconds, a thin nonhomogeneous layer of SU-8 is etched off the coating, creating a nanoroughness in the photoresist layer. Because SU-8 itself is not superhydrophobic, a superhydrophobic layer needs to be created on top of the SU-8. After development of the photoresist layer using UV light, a layer of a few μm of C_4F_8 or (tridecafluoro-1,1,2,2,-tetrahydrooctyl)-trichlorosilane (FOTS) is damped on top of the SU-8 to make the surface hydrophobic. The thickness of the FOTS-layer depends on the duration of the damping and amount of FOTS used. The thickness of C_4F_8 is also subject to the length of the procedure.
Both the structure of the top layer and the coating make the substrate hydrophobic. Combined together, the substrate can be superhydrophobic ($\theta_c > 160°$).

Pillars
The superhydrophobic pillar surfaces are created in a similar manner as the nanoroughness structures. This time however, the dielectric layer of SU-8 photoresist is kept intact and directly developed using UV light. This creates an homogeneous layer of the dielectric with a thickness of a few μm. On top of this layer, the microstructure with round- or squared pillars (diameter of 5 μm, height of 5 μm and center-to-center distance between the pillars of 10 μm) is created using a mask and exposure to UV-light.

A schematic representation of the structure of the pillars on the surface is given in figure 3.3:

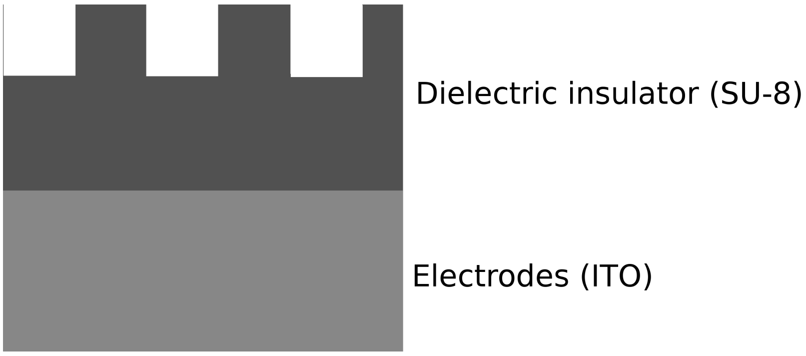

Figure 3.3: Schematic representation of the superhydrophobic pillar surface

In the experiments, mostly substrates with FOTS were used, with a nanoroughness structure which had been treated with an exposure to oxygen plasma for 120 seconds.

3.2.2 Structures of the electrodes

Two types of electrodes were used; interdigitated electrodes (IDE's) and two electrodes with a gap in between.

Electrodes with a gap
A simple way to apply an electric field to a drop is with the use of an electrode. Two electrodes of ITO are deposited with Pulsed Laser Depostion (PLD) on a thin glass substrate. The electrodes are placed apart from each other with a gap of 50 μm between them.
By applying a voltage over the two electrodes as shown in figure 3.4, an electric field will appear causing water droplets to stick to the surface when a voltage is applied, as described in chapter 2.1.5.

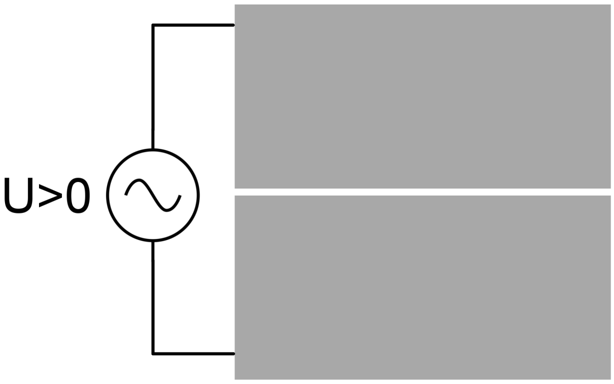

Figure 3.4: Schematic representation of electrodes with a gap

Interdigitated electrodes (IDE)
The interdigitated electrodes (see figure 3.5 on next page) are made out of ITO. The IDE is placed on a thin glass substrate as well, by the manufacturer. By applying a voltage over the two electrodes on both sides of the IDE, an electric field will appear all over the surface.

The biggest advantage of using two electrodes with a gap in between is that the chance of a shortcut is smaller than when using IDE electrodes. However, the effective area on which can the experiments with electrowetting can be done, is smaller for the substrate with a gap than for IDE, that is why most experiments described in this report were done with IDE samples.

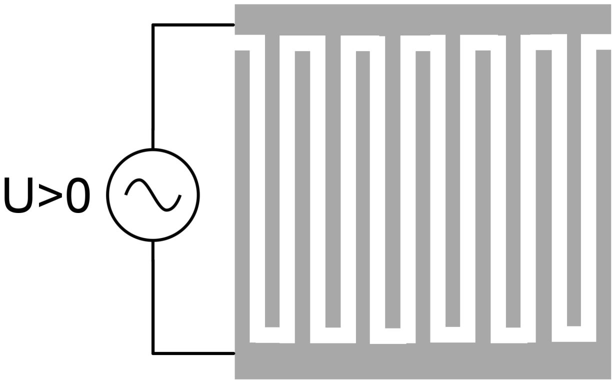

Figure 3.5: Schematic representation of interdigitated electrodes

3.3 Surface characterization

Nanoroughness
In figure 3.6, the surface of an unused substrate can be seen, with topview. This picture is made with an Atomic Force Microscope (AFM). In Chapter 4, a comparison is made between a used sample and an unused sample. What can be seen in figure 3.6 and figure 3.7, is that the roughness of the substrate is not very high, but there is definitely a height difference in the substrate, roughly 1.5 μm.

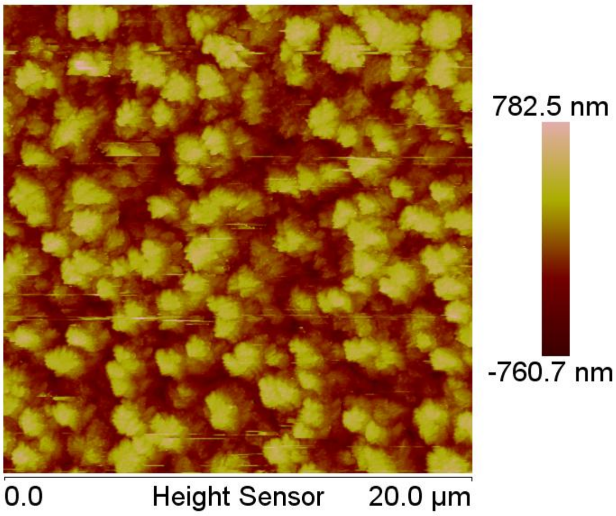

Figure 3.6: Surface image with AFM of nanoroughness

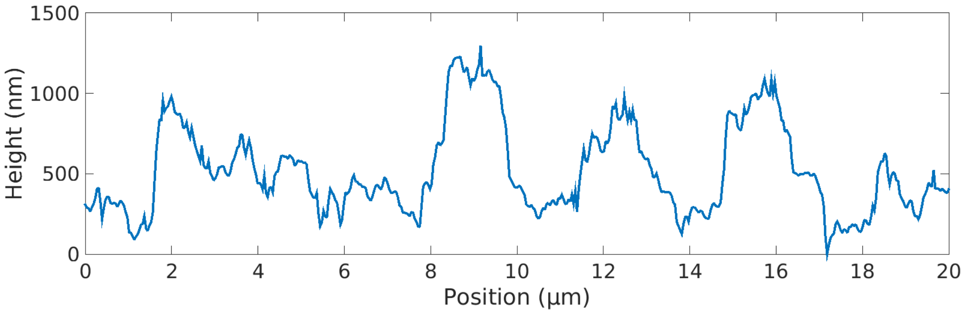

Figure 3.7: Cross-section of substrate

Pillars

In figure 3.8, the surface of a pillar structured sample is shown. The structure is in accordance with the values given in paragraph 3.2.1 ”Sample Preparation”. The different colors behind the pillars is the pattern of the interdigitated electrodes.

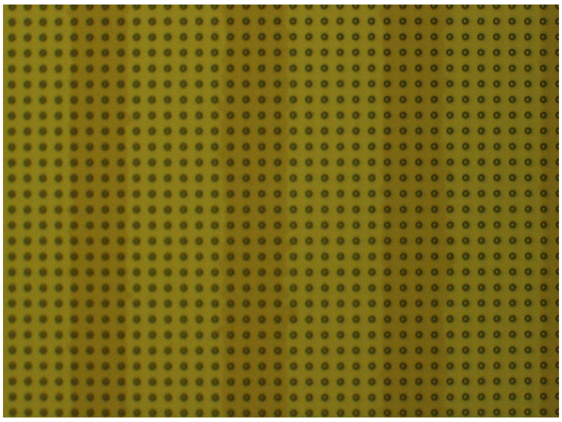

Figure 3.8: Surface image with AFM of a pillar structure

3.4 Measuring Procedure

Measurements were done with the setup described in paragraph 3.1, "The Setup". After setting the height of the needle to an appropriate height, so that the droplet was captured in sight of the camera, the bouncing experiments were started. For voltages in a range of 0 to (at some times) 400 V, measurements were done by capturing the motion of the droplet with both the sideview and bottomview camera. To obtain enough data at a certain height, the whole substrate needed to be used. That was only possible with IDE-substrates, because with those substrates a field can be applied over the whole substrate.
Next to that, the assumption was made that nanoroughness is homogeneous over the whole surface. With both those two things in mind, around 50 measurements were done on one substrate. For bouncing experiments on different heights, contact angle measurements and the AFM measurements, a batch of nine substrates was used.

3.4.1 Calibrations

In order to measure exact distances from the videos, the video of the experiments have to be calibrated, to get to know the pix/mm for later data analysis purposes like the height of the droplet relative to the surface. For calibrations, a needle with a known diameter ($1.90mm$) is placed in front of the camera. The number of pixels the needle in the video occupies is counted and with the known diameter of the needle, a calibration is done.

3.5 Analyzing Procedure

For analyzing the data obtained from the measurements, some mathematics was needed, as well as appropriate data-analyzing software like MATLAB and ImageJ. Below both tools are discussed.

3.5.1 Oscillation modes

The videos from the sideview camera are analyzed using Legendre Polynomials. The Legendre Polynomials are used to decompose the complex oscillations of the droplet into simple eigenmodes. The modes of droplet shapes from n=0 to n=5 are given in figure 3.9:

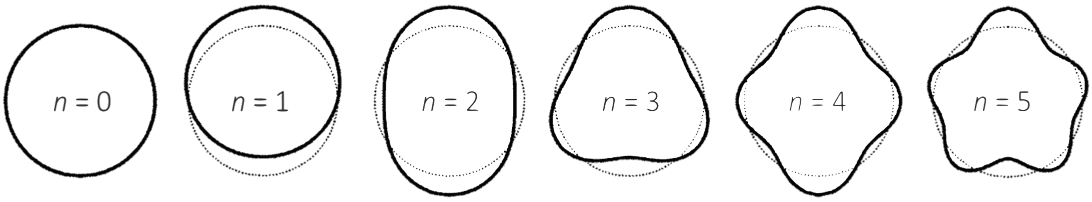

Figure 3.9: Legendre Polynomials n=0 to n=5, [10]

When a droplet is analyzed, and the modes are linked to their coefficients a_n, with n as mode number, a (a_n,t)-diagram can be plotted. With this diagram, it can easily be seen which shape the droplet has during flight by looking at which coefficient has the most dominant amplitude in the graph. From this graph the frequency of the droplet can also be determined by looking at the time of a few periods of a mode. A typical form of a (a_n,t)-diagram is given in figure 3.10:

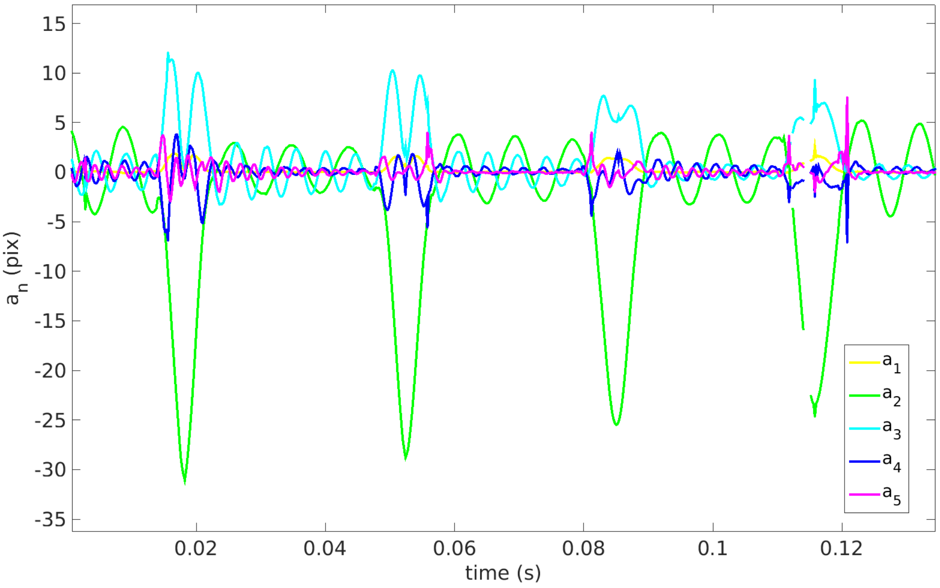

Figure 3.10: Typical Legendre-result

3.5.2 Matlab

For analyzing the videos obtained by the sideview camera, the computer software MATLAB R2015a from Mathworks is used as data analyzer.

The videos are loaded into MATLAB as a collection of matrices with a matrix for every frame. Each matrix contains a videoframe converted to greyscale values. From these matrices, the background (without the drop) is subtracted leaving a video with only the motion of the drop itself. From this data, the contour of the drop can be extracted as a function of time using Laplacian edge 2detection. With this contour, a mathematical approximation for the drop shape can be obtained using Legendre polynomials as discussed before.

An example of this shape mode decomposition is shown below, in figure 3.11.

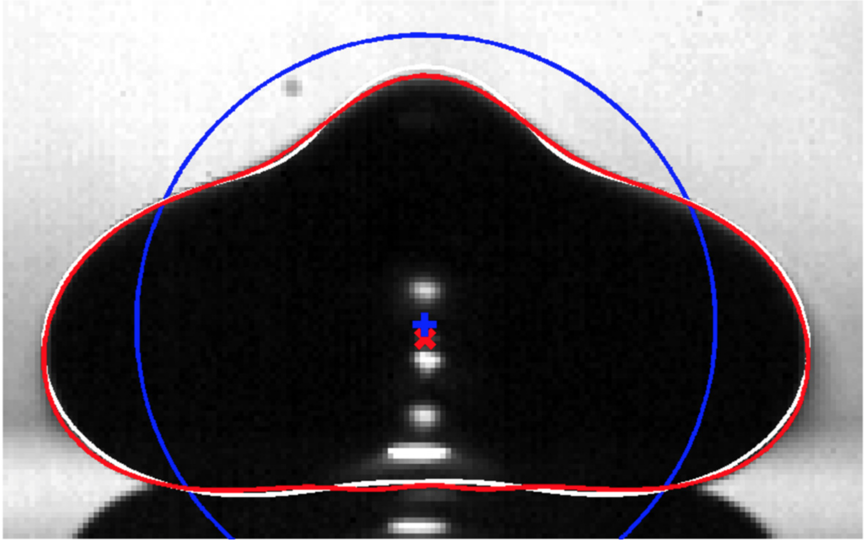

Figure 3.11: *"Sideview analysis: shape mode decomposition of the droplet interface, during the bounce. The spherical decomposition is shown for the n=0 mode (blue), and superpositions up to order n=4 (white) and n=10 (red). Also the center of decomposition* y_0 *and the center of mass* y_{cm} *are indicated by the blue + and red x symbols, respectively."* [10]

With this mathematical approximation in MATLAB the center of mass, velocities, maximum radius, restitution coefficients and more variables can be determined.

Chapter 4

Results

4.1 Bouncing profile of the droplet

The most obvious result of the experiments is the qualitative bounce of the droplet in a frame-by-frame figure. In figure 4.1 a result of a bounce sequence is shown for a droplet which lands on a surface with no voltage applied and for a droplet landing on a surface with a voltage of 160V applied (electrowetting):

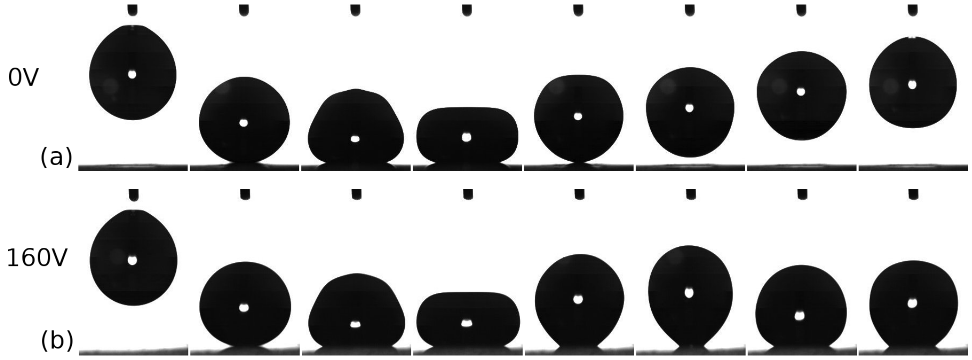

Figure 4.1: Bounce sequence for a droplet with 0V applied (a) and 160V applied (b)

As can be seen in the figure, the droplet, which is not affected by any voltage (row a), jumps from the surface after impact. The other droplet (row b) sticks to the surface, due to loss of energy. That is because a sufficient part of the linear energy of the droplet is dissipated by the effect of electrowetting.

From another dataset of measurements, the graph of motion of the center of mass of the droplet was obtained for measurements with $0V$ and $130V$. The bouncing profile is the motion of the center of mass (COM) of the droplet and is plotted with height on the y-axis in *mm* and time on the x-axis in seconds. See figure 4.2.

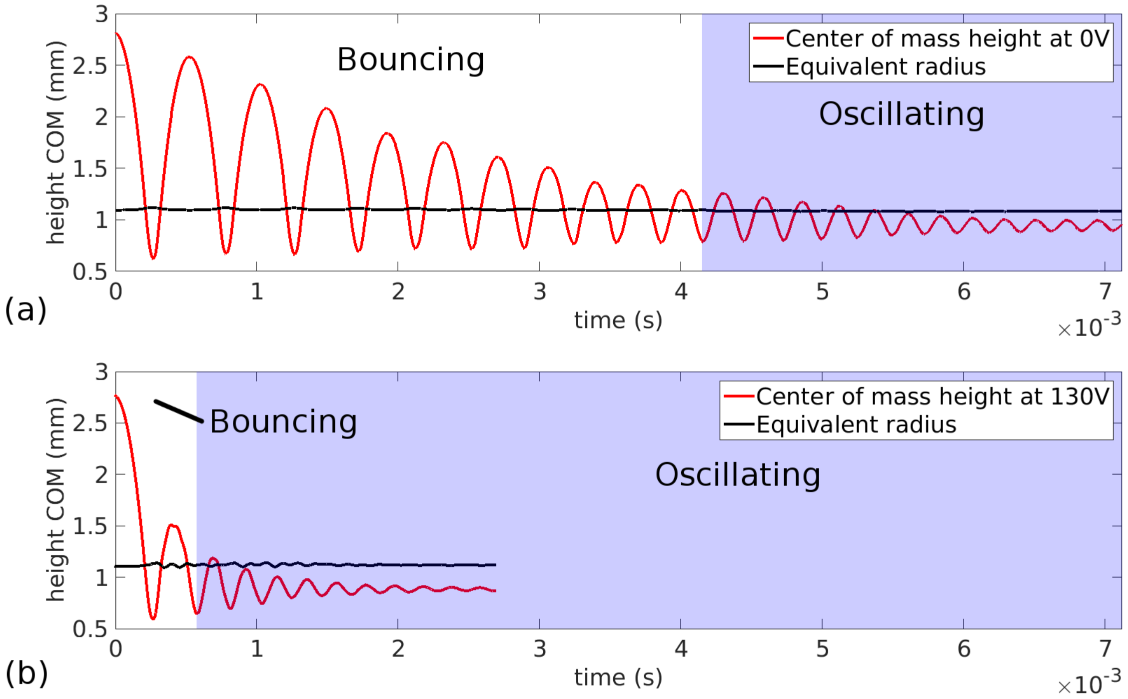

Figure 4.2: COM-height for a droplet with 0V applied (a) and 130V applied (b)

The obvious difference between the two measurements is that the droplet affected by the 130V is bouncing just two times, because of energy dissipation by electrowetting, and the droplet at zero voltage bounces ten times. The blue zone in the graphs is the oscillation regime, that is when the droplet is stuck on the surface, but still oscillates in the vertical direction, as can be seen in the figure. The equivalent radius is the radius the data-analyzing software determines by calculating the volume of the droplet. The volume calculation depends on the edge of the droplet detected and the radius determined from this detection. In the data movies the assumption is made that the droplet is perfectly spherical.

In figure 4.3 the number of bounces of the droplet as function of the voltage is shown for three different heights. Clearly, in the graph a decrease in number of bounces is visible for increasing voltage applied over the substrate. However, due to the large error boxes, a clear relation between the number of bounces and the voltage can not be extracted from the figure.

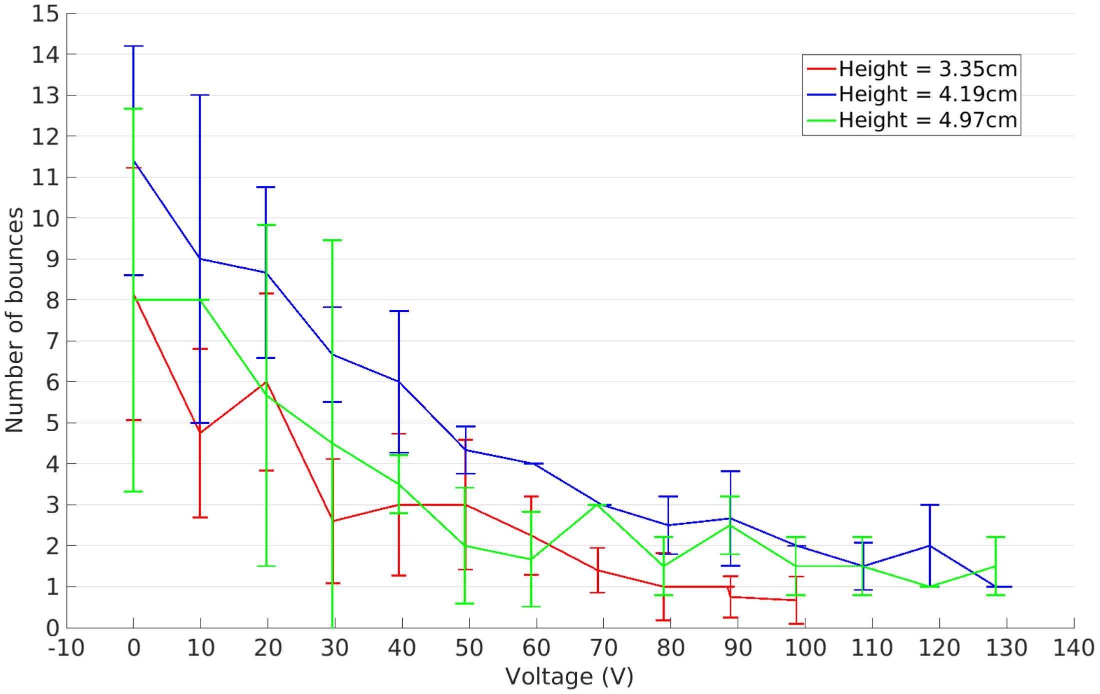

Figure 4.3: Number of bounces of droplet vs. voltage

4.2 Energies

A droplet falling and bouncing has two major form of energy: linear energy (kinetic and potential) and oscillating energy. When electrowetting is used, a fourth form is introduced: electrical energy which in fact is a form of dissipation in which the linear- and oscillating energy is converted.

The linear energy is the form of energy that is influenced most by electrowetting. During the contact with the surface, kinetic energy is then converted into electrical energy.

In figure 4.4 and 4.5 the linear energies are compared with the bouncing profile of the droplet at $0V$, and at $130V$.

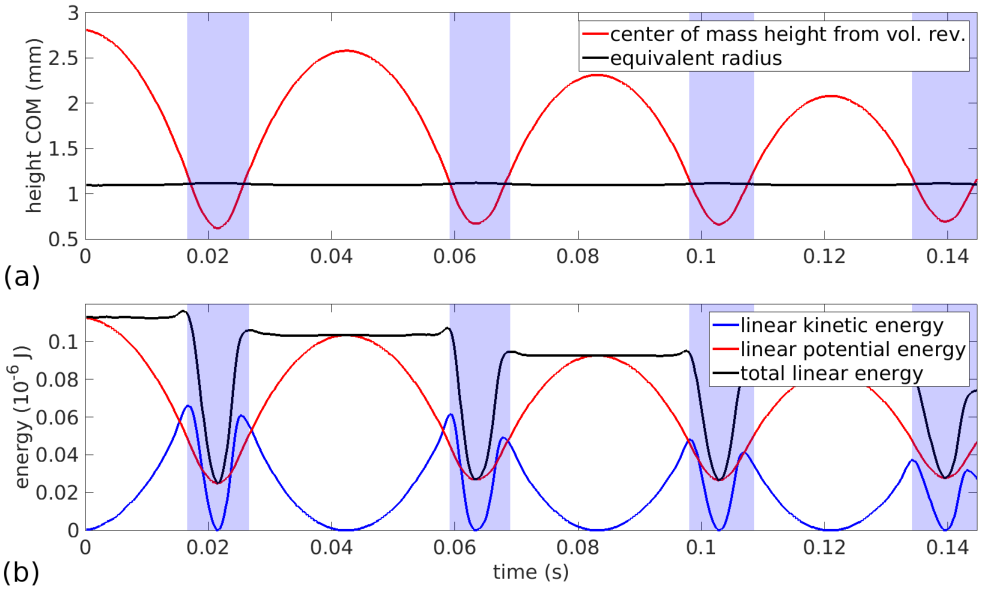

Figure 4.4: (h,t)- and (E,t)-diagrams for droplet bounce at 0V

In the energy-diagram of figure 4.4, the linear energy is plotted against time. The kinetic energy is zero when the droplet is at the top and bottom of its trajectory, because the velocity is zero at those instances. Between those values the speed of the droplet is highest at the moment just before impact on the surface and just after jumping off the surface.
The linear potential energy depends on the COM-height of the droplet with respect to the surface. Thus, the potential energy scales with the bounce profile.
The total linear energy is, more or less, constant during the flight in air, but is lower when the droplet makes contact with the surface. So the energy must be stored in another way. The most reasonable way is probably storing energy in the surface,

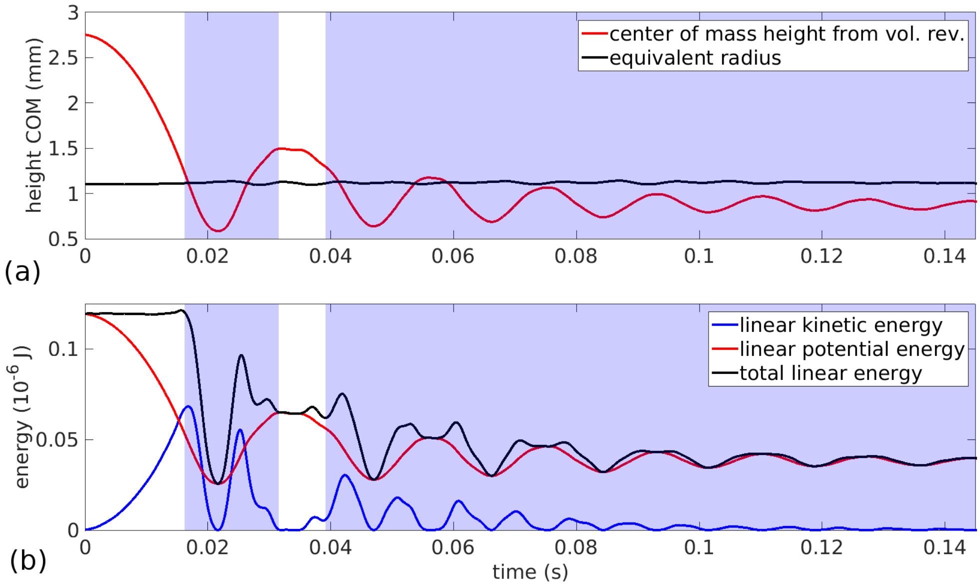

Figure 4.5: (h,t)- and (E,t)-diagrams for droplet bounce at 130V

during contact, in the sideways motion of the droplet, as described around figure 4.10 and in the paragraph ”Dissipation” in Chapter 2.

The difference between the energy-diagram in figure 4.4 and figure 4.5 is mostly that the total linear energy loss after a bounce with 130V is much greater than the loss with 0V applied. The effect of the voltage on the dissipation is seen quite clear here, since the y- and x-axis are equivalent between both plots. Due to the massive energy-loss at 130V, the droplet is not able to bounce more than one time, so the oscillating regime starts after approximately 0.04 seconds.

The influence of electrowetting to the components of linear energy, after the first bounce, can be shown in a linear energy plot as well, with the $60V$-curve added. See figure 4.6:

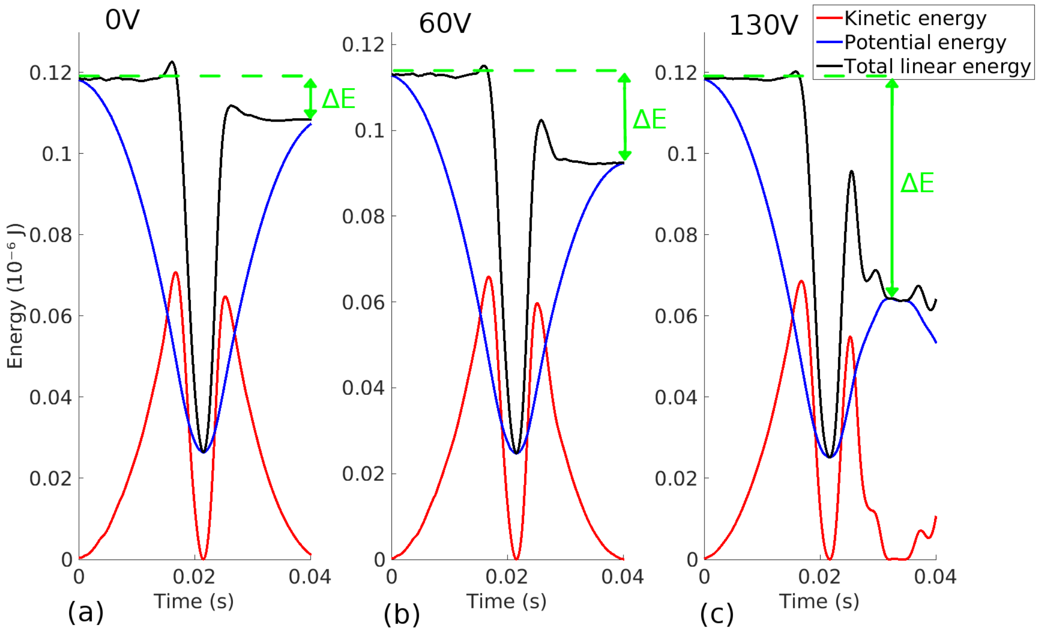

Figure 4.6: Energy loss after first bounce for 0V, 60V and 130V

The decrease in the total linear energy is due to dissipation. In figure 4.6b en 4.6c the influence of electrowetting on the amount of dissipation, after the first bounce, is illustrated for two separate voltages. The difference in the total linear energy for the droplet before the bounce and after the bounce is calculated at the moment that the kinetic energy is zero, when the droplet is at its maximum height.

In figure 4.7, the relation between the absolute loss in total linear energy (as illustrated in figure 4.6 and voltage is shown. Next to that, the restitution coefficient is plotted against voltage. Both show a relation which goes with U^2. This implies that the droplet is affected by the electric energy which is stored in the electrodes on the substrate, by equation 2.7.

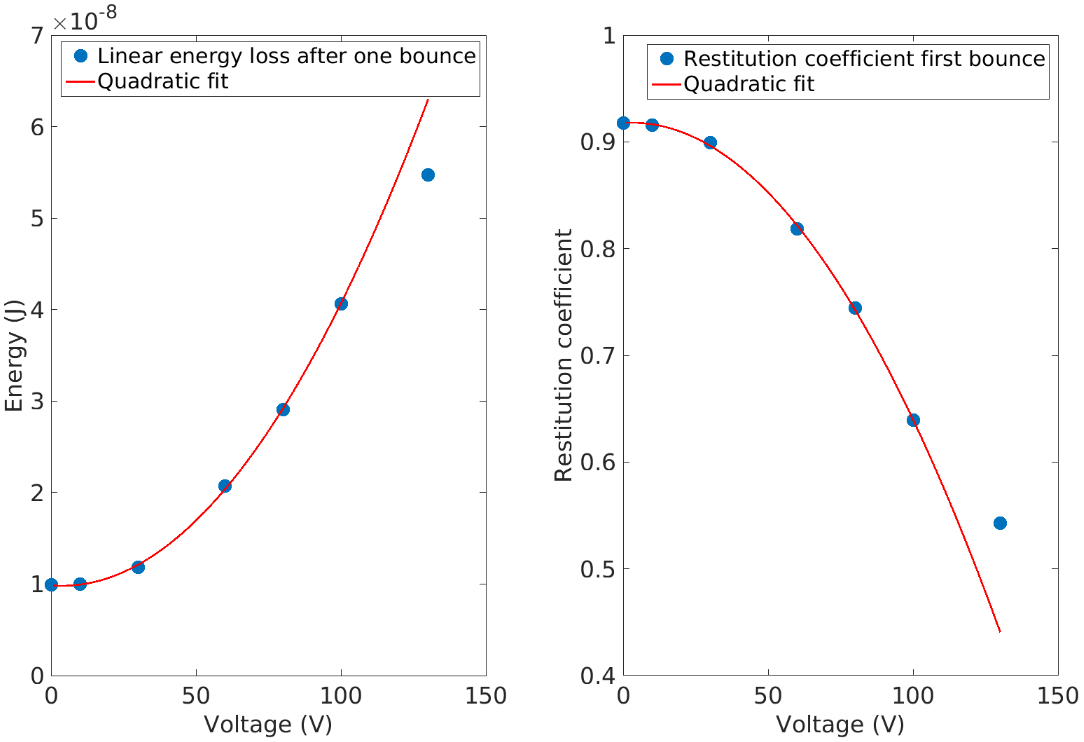

Figure 4.7: Loss of total linear energy (left) and restitution coefficient vs. voltage (right)

4.3 Influence of voltage on droplet radius

When a droplet hits a surface, the droplet spreads as a result of energy conservation where translational energy (linear energy) is converted into surface energy. The diameter of the droplet at the surface depends on the initial fall height and the applied electrowetting voltage. When the fall height of the drop is kept constant and the electrowetting voltage is set as a certain value, the base diameter of the droplet can be varied by changing the voltage, as shown in figure 4.8. The drop radius is bigger when the voltage is larger, as this corresponds to an increased wettability of the substrate. For this experiment, a substrate with a gap electrode is used to allow higher voltages to be applied.

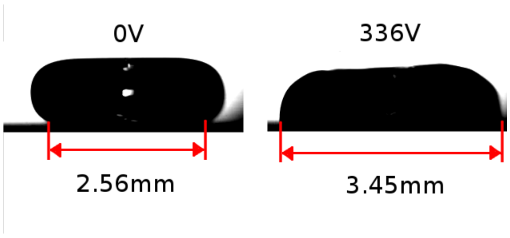

Figure 4.8: Maximum drop radius after impact for both 0V and 336V

When the voltage is increased, a linear relationship between the maximum radius of the droplet during impact and the voltage is observed as shown in figure 4.9:

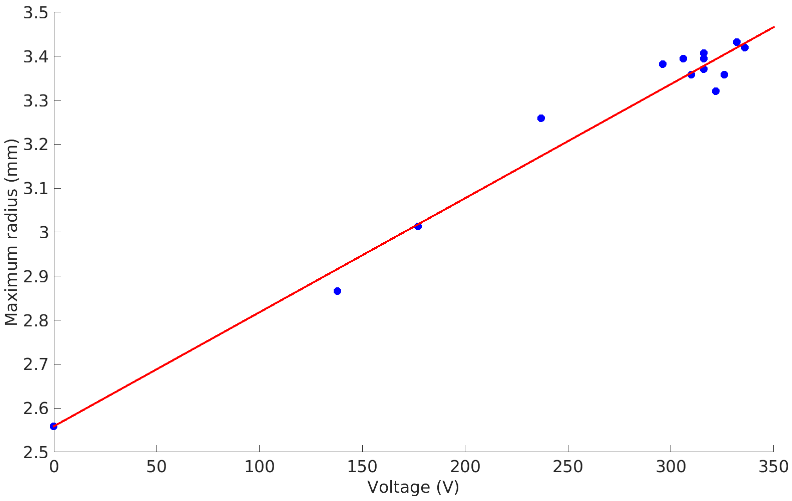

Figure 4.9: Linear relation between R_{max} and voltage

4.4 Critical voltage

Before the result of critical voltage is shown, a explanation will be given why the critical voltage could not have been found in this measurement, and why it might not be possible to find it experimentally.

4.4.1 Linear Energy loss due to oscillation

In the bottom graph of figure 4.10 the restitution coefficient is plotted against time for 45 bounce experiments without electrowetting. The restitution coefficients are obtained by the heights of the bounces. The ratio of the height of the current and next bounce is the restitution coefficient plotted.

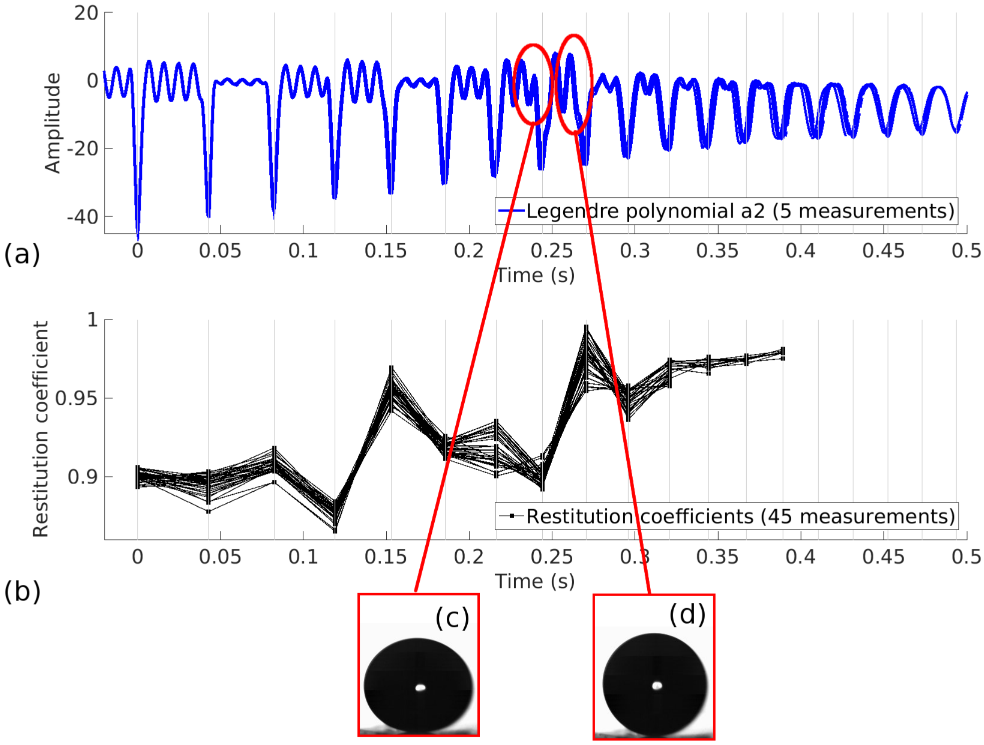

Figure 4.10: Legendre Polynomial coefficient a_2 and restitution coefficients

The most remarkable observation of these restitution coefficients is the fact that for all experiments the restitution coefficients are going up and down similarly during an experiment. The restitution coefficient after the fourth bounce is smaller than the restitution coefficient after the fifth bounce. This indicates less linear energy loss after the fourth bounce than after the fifth bounce.

To describe this phenomenon, the second Legendre coefficient is plotted against time for five bounce experiments in the top graph of figure 4.10. The second Legendre polynomial (a_2) describes the stretch of the drop in x and y direction. A positive amplitude of the the polynomial implies a horizontal stretch, a negative amplitude implies a vertical stretch of the droplet.

What appears to be the case is that this stretched shape of the droplet, described by the second Legendre polynomial, just before impact is an important factor for the amount of linear energy loss. When the oscillation is at such a point that the droplet just before impact is stretched in the vertical direction (and thus wants to stretch in the horizontal direction), the linear energy loss is less than when the drop is stretched in the horizontal direction (and thus wants to stretch in the vertical direction).

This can be seen in the top graph of the figure. An abrupt change in the middle of the oscillation caused by the impact, as encircled with the left red circle in the figure, causes the drop to lose more linear energy than when the oscillation is in sync with the impact, as encircled with the right red circle. These abrupt changes in the oscillation of the droplet explains the change in linear energy loss during a bounce experiment without electrowetting and probably also with electrowetting. More linear energy is converted to oscillation energy when the oscillation of the bounce is out of sync with the oscillations.

4.4.2 Critical Voltage

Applying electrowetting to a bouncing drop will cause a droplet to stick to the surface. A relatively low voltage will make the droplet only stick for a short time, because when enough surface energy is converted back into linear energy, the droplet will lift off the surface again.

When a high voltage is applied to the droplet (order of 150V), the loss in linear energy to surface (electrical) energy is so big that the droplet will not be able to lift off the surface again. The droplet is stuck to the surface.

The voltage at which the droplet just sticks, is called the critical voltage. A voltage just below the critical voltage will not make the droplet to be trapped to the surface. This critical voltage is a function of many surface parameters but also fall height. A greater fall height means more linear energy, so more energy that has to be dissipated in order, for a droplet, to stick to the surface.

During the experiments, three fall heights were used in order to find a relationship between the fall height and the critical voltage.

Because of unstable substrates, which will be reviewed in 4.6, it was not possible to apply any voltage near the critical voltage without destroying the superhydrophobicity of the surface. Therefore, with the use of extrapolation an approximation of the critical voltage is obtained using the measurements of the number of bounces (figure

4.3). The voltage, at which a line through all measurements crosses the 0-bounces line, is the critical voltage. Because of the large error in measurement, calculating the minimum and maximum slope from these measurements makes it possible to obtain an error. The resulting relationship is shown in figure 4.11.

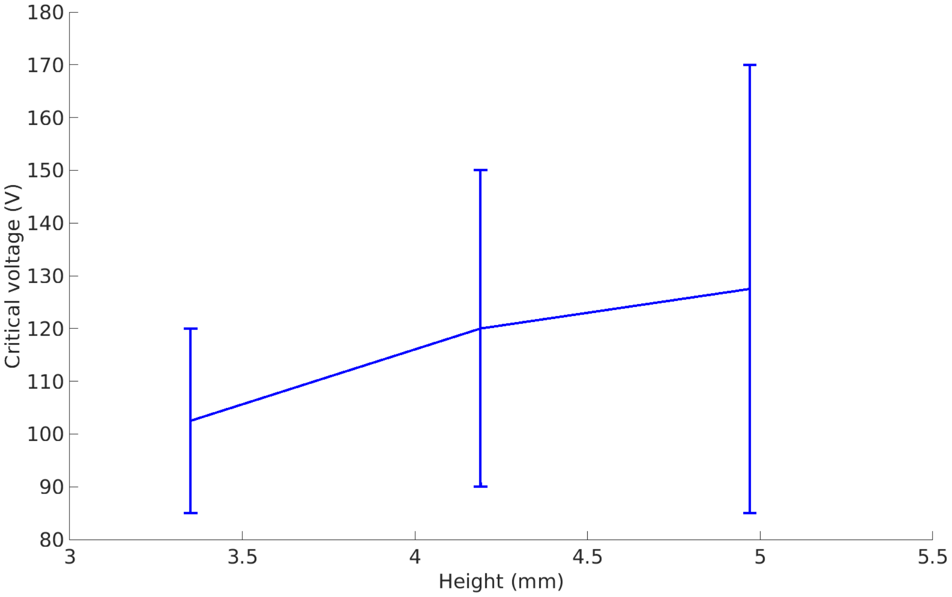

Figure 4.11: The critical voltage for three heights obtained with the use of extrapolation. The error is obtained using a minimum and maximum slope.

This result is inconclusive. Because of the large error it is not possible to draw any conclusions besides the fact that the critical voltage might be higher for larger falling heights. This is expected by energy conservation where linear energy is converted into electrical energy. More linear energy means more electrical energy to trap the droplet, so a greater voltage needed. However, as explained before, this trend might not always be the case due to droplet oscillations.

4.5 Steering bouncing droplets

The intriguing phenomenon of trapping droplets using electrowetting can be extended to a three dimensional situation in which bouncing droplets can be steered using electrowetting. This steering can be achieved using a double gap electrode schematically shown in figure 4.12.

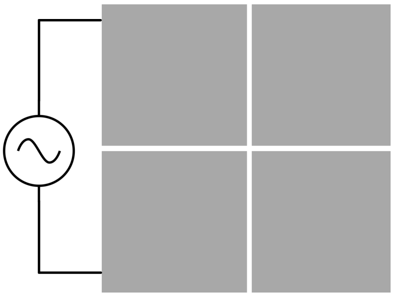

Figure 4.12: Sample with two gaps, four electrodes

When a voltage is applied over the left two electrodes and the impact of the droplet is on the right side of the gap, the droplet is observed to bounce towards the left two electrodes. This phenomenon is shown in figure 4.13 where a sequence of stills from a movie is shown in time. The red lines represents the horizontal position of the droplet after the first bounce. Without an electric field, the droplet bounces perfectly in the center, as expected. When an electric field is applied, the drop is bouncing towards the place where the electric field is at largest. This attraction is primarily caused by the electric field created by the voltage difference over the two electrodes on the other side of the gap, since the electrodes do not make contact with each other. In this way it is possible to steer a droplet while bouncing.

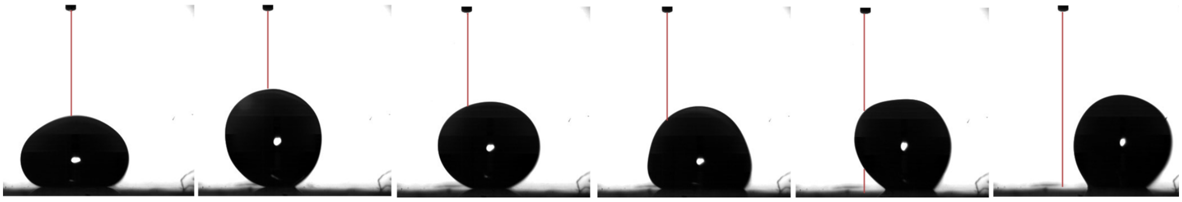

Figure 4.13: A sequence of stills when steering droplets at 148V. The red line represents the center where the droplet would bounce when no voltage is applied

In order to prevent other parameters to influence this result, it was made sure that the experimental table was perfectly flat and the measurements were done under the best possible circumstances. The experiment was successfully repeated with the similar result when the other two electrodes were connected and when bounced on different spots.

4.6 Surface damage due to electrowetting

Not all substrates and measurements worked out that well. A lot of problems came by on the road to the good datasets. In the following section problems on the substrate are reviewed.

Substrate stability experiment

When a droplet hits the superhydrophobic surface with nanoroughness without using electrowetting, the drop bounces nicely for about 10 to 15 times, even after 79 measurements, see figure 4.14. When electrowetting is applied, the number bounces of the drop is less, as expected. Measuring again without electrowetting, after 36 measurements with electrowetting, the droplet is expected to bounce 10 to 15 times again on the substrate. However, this is not the case and only one bounce can be observed as can be seen in figure 4.14:

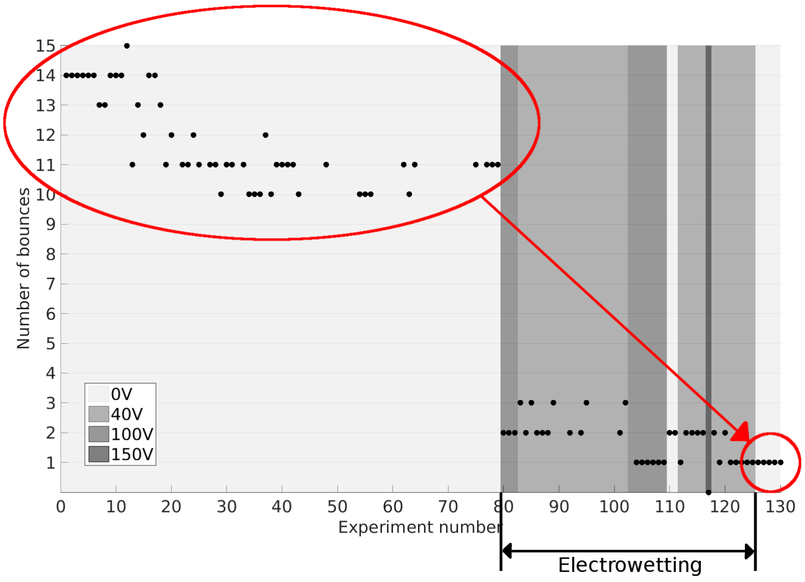

Figure 4.14: number of bounces for 130 consecutive experiments

This result can be accounted to the fact that the surface is damaged during the application of electrowetting. Electrowetting in combination with bouncing can cause damage to the nanoroughness structure on the surface. In the next section, the AFM analysis on this problem is discussed.

AFM analysis

A comparison of two substrates analyzed with the Atomic Force Microscope before and after using electrowetting can be seen in figures 4.15 and 4.16:

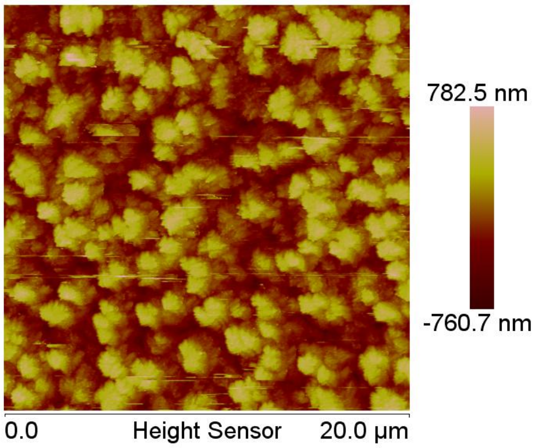

Figure 4.15: AFM before using electrowetting

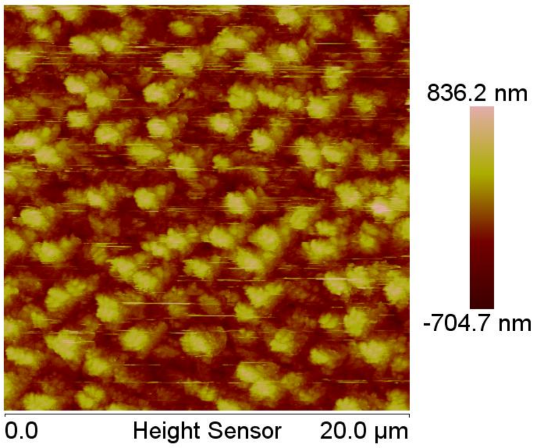

Figure 4.16: AFM after using electrowetting

The cause of this damage could be the force that is applied by the removing tissue (Kimtech) to remove the droplet from the surface after the measurement. When the droplet is in a Wenzel state, this might cost some work, because the droplet has to pulled out of the structure of the substrate, on which the droplet can be adhered.

Because of the two problems on the substrates written in this section, most of the experiments done, contained data which was not usable for any proper data analyzing.

Chapter 5

Discussion

Several aspects of the measurements done were not ideal, those will be reviewed in this section.

To begin, the obtained movie of the droplet was 2-dimensional, which means that the detection of the droplet was also 2-dimensional. That way, when the droplet bounced into the direction of the camera or away from the camera, it would not be noticed in the sideview movie, or just a little, as shown in figure 5.1. This could have influenced the measurements a little.

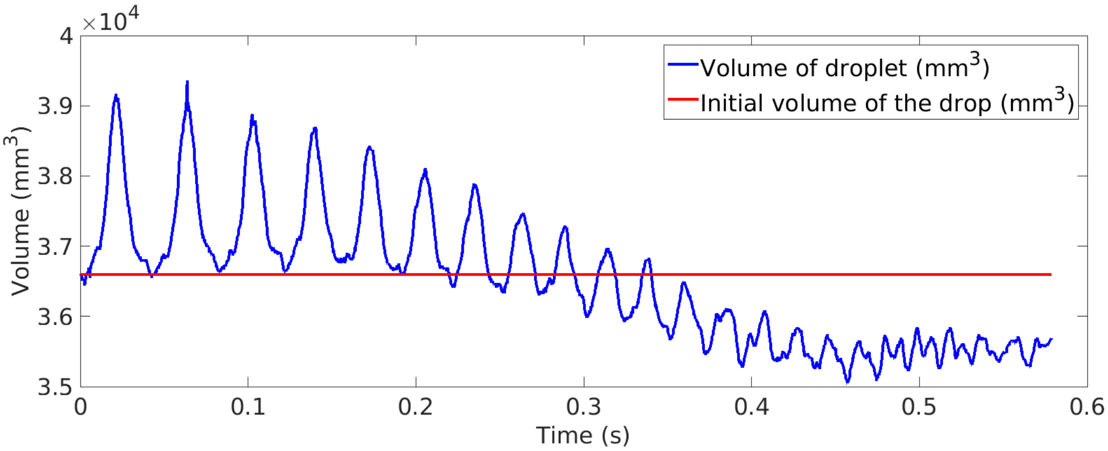

Figure 5.1: Calculated volume of the droplet with 2D-sideview vs. time

In addition to that, the substrates used for the experiments were not stable enough to still work at voltages over 300V. Above that voltage, shortcut would occur in the substrates. To make more stable substrates (non-destructive), the dielectric layer should be thicker.

One of the most difficult aspects of this research was finding reliable and homogeneous substrates. The usage of both bouncing and electrowetting makes traditionally used substrates for just bouncing or electrowetting hard to use. As shown in section 4.6 the substrate gets destroyed when electrowetting is applied, and vice versa, when a substrate is used for electrowetting, that it is not suitable for bouncing. This lack of knowledge of producing stable substrates makes that it would be a research by itself to study the substrates finding a superhydrophobic surface that is suitable for bouncing and electrowetting at the same time.

The repeated measurements of the number of bounces at a specific voltage in section 4.6 is not constant. There are several possible explanations for this:
First of all, the surface is not 100 percent homogeneous. At some places the surface is more hydrophobic than at other places. This causes the drop to bounce more at specific points. Secondly, the initial fall height is not perfectly constant. Little vibrations in the table can cause the needle to drop or rise a little bit, changing the fall height of the experiment. Especially with the small heights used in these experiments this could cause a major error. Besides that, these vibrations cause the droplet to obtain or lose energy when falling. This was observed multiple times during the experiments.

Cleaning the surface was not done regularly during the measurements, due to the fear of damaging the substrates while cleaning them. Sometimes, that gave some trouble to the obtained data, because dirt or particles were visible on the video. To have a better performing substrate and better data, the cleaning procedure should be improved and followed during experiments.

In studying the restitution coefficients in 4.4, the conclusion is drawn that the cause for more linear energy loss at specific points, is because of the oscillations. When the oscillation is in sync with the bounce, less linear energy is lost. However, to prove this, the exact oscillation energy should be calculated, and compared with the linear energy.

In the quantitative research on steering droplets using a double gap electrode, multiple precautions have been done in order to draw a solid conclusion. However, one major aspect has not been introduced: wiring the two not-used electrodes to earth. Floating potentials could have influenced the measurements.

The inconclusive results in finding a relationship between critical voltage and the falling height is because of many reasons. The main reason is that there were not enough measurements to obtain a small error for the number of bounces per voltage.

Besides that, too few heights were used and the difference between the heights is so small, that the error is simply so big, that no unambiguous conclusion can be drawn from these experiments.

But it might not even be so realistic to try to find a relationship between the critical voltage and the falling height:
As discussed in chapter 4.4.1, the phase of oscillation of the droplet when it touches the surface, influences the linear energy loss. With an increase in height, there is more linear energy in the droplet. This suggests that a greater height also allows for a greater critical voltage. But when a droplet breaks off a needle, it starts oscillating, as shown in figure 5.2, started by the breaking. If the phase of the oscillation is at such a point that it is not 'in sync', i.e. the droplet wants to stretch in vertical direction, with the touchdown of the droplet, the droplet may lose more linear energy because of this. A droplet falling from a greater height might have more linear energy, but if it hits the surface in the wrong phase of the oscillation, it might lose more linear energy than a droplet falling from a smaller height hitting the surface at a more favorable point in the oscillation. Because in this latter case, linear energy is converted to not only electrical energy, but also into surface energy.

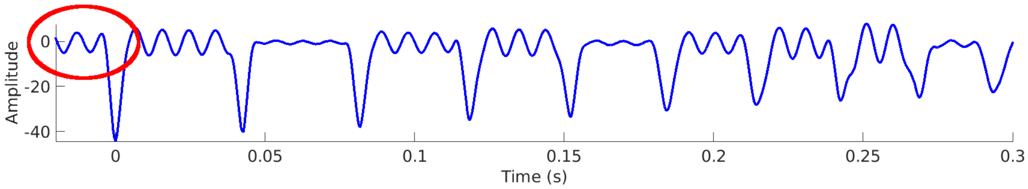

Figure 5.2: Legendre coefficient a_2

This suggests that a relationship between height and critical voltage might not so relevant at all. This because of the fact that height alone is not a parameter to vary in order to change the total energy loss. What might be more interesting and important to look at, is the total linear energy loss: the linear energy loss caused the difference in height in combination with the phase the oscillation is in right before it impacts the surface.

Those experiments are not suitable in order to prove the goals of this thesis. As discussed before, more experiments should be done per height, and more heights should be covered. Besides that, the degree of influence of the oscillation should be examined. Is the amount of linear energy that converts into surface energy instead of electrical energy indeed that big that it significantly influences the critical voltage?

Chapter 6

Conclusion

In this research the concepts of bouncing droplets on hydrophobic surfaces is combined with electrowetting. Firstly, in section 4.1, the behavior of droplets is discussed with influence, and without influence of electrowetting. When applying electrowetting, it is possible to reduce the number of bounces or even suppress the bouncing by trapping the droplet on the surface. Without electrowetting the droplet is able to bounce up to thirteen times on the superhydrophobic surface. With electrowetting this is reduced to one or zero.

In section 4.3, the influence of electrowetting on the droplet radius is investigated. As a droplet hits the surface the droplet spreads. The maximum radius the droplet reaches during the contact with the surface, depends on the initial fall height and the applied voltage. When the fall height is kept constant, a linear relationship between the maximum radius of the droplet and the voltage is observed.

Looking at the energies in section 4.2, it is observed that the unaccounted dissipation increases with the electrowetting voltage. This unaccounted dissipation is due to the loss of linear energy to electrical energy. With increasing voltage it is observed that the difference in kinetic energy before and after the first bounce increases with the voltage, as shown in figure 4.6. Most interestingly, this energy loss is related squarely to voltage, as predicted by the Electrowetting equation, equation 2.3.

Section 4.4 introduces the critical voltage, the voltage at which an impacting droplet is trapped. The critical voltage is influenced by many surface conditions and impacting height. In these experiments three voltages where used in order to find a relationship between critical voltage and fall height. From the number of bounces versus voltage, a linear extrapolation can be used to find the critical voltage per height. This relationship is shown in figure 4.11. The large error in this relationship is due to the unstable surfaces, discussed in section 4.6. However, what might be more interesting is the question if it is even possible to find a clear relationship between critical voltage and fall height. As shown in section 4.6 as well, the oscillation of the droplet influences the linear energy loss. When the droplet breaks off the needle, it starts oscillating in a horizontal en vertical direction described by the oscillation mode a_2. When the droplet hits the ground at the moment the droplet is fully squeezed in the horizontal direction and wants to expand in the vertical direction, a lot more energy is lost than the latter situation when the drop want to expand horizontally. This extra amount of energy loss might cause a droplet falling from a greater height to lose more energy than a droplet falling from a lower height, causing the critical voltage to be greater. It would be interesting to extend this research to find if this oscillation significantly influences the critical voltage.

The opportunity to steer a droplet by applying a voltage only to two out of four electrodes, is discussed in section 4.5. In this section the concept of electrowetting is extended to a two (or three) dimensional situation. It is observed that a droplet falling on the electrodes on which no voltage is applied, bounces towards to electrodes over which a voltage is applied. These findings are interesting, as they could be used to manipulate droplets, or to collect them after impact. It would be interesting to extend this research to droplets that are already charged before impact.

Finally, in the last section, section 4.6, there is a review of the fragility of the substrates. During the experiments the substrates were getting less hydrophobic when using electrowetting. Observed was that 79 experiments on the same spot of the substrate all had 10 to 15 bounces. When using electrowetting for 40 experiments, the surface was damaged that much, that afterwards, without electrowetting, only one bounce was observed. This decrease in hydrophobicity is due to damage of the nanoroughness of the substrate. This was observed using an Atomic Force Microscope (AFM).

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