Dielectrophoresis in thin liquid films

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Abstract
The goal of this project was to determine whether and to what extent the dynamics of thin liquid films is affected by surface charges present on a solid substrate. For this purpose we first studied the controlled deposition of surface charge patterns on insulating substrates such as glasses and polymers. Static charge patterns were created by dragging water droplets that were attached to a metallic needle along the substrate. The charge deposition was investigated for needles that were either grounded, insulated or set at a constant high electrical potential. All geometries were found to deposit static charges, although the droplet on an insulated needle only deposits charges over a finite distance. The measurements on the static charge distribution were conducted with an electrostatic voltmeter. This method provides an accurate measure for the deposited surface charge for broad lines and for slowly varying distributions.

Subsequently a thin liquid film of initially uniform thickness was spin-coated on the substrate. In response to the deposited static charges, the liquid film deformed and redistributed due to dielectrophoresis. We systematically measured the deformations by means of optical interferometry. In order to verify that the dominant redistribution mechanism was indeed dielectrophoresis, we developed a numerical model based on the lubrication approximation and electrostatic calculations. We studied the time dependency and the influence of the surface charge density on the liquid film and achieved good agreement between measurements and simulations. Furthermore the effect of the line width, initial film height, and two parallel lines on the behaviour of the liquid film were investigated with simulations.

Finally a start has been made to investigate the influence of static electricity on the stability and break-up of thin liquid films on partially wetting substrates.

Acknowledgement:
Hereby I want to thank everyone who has contributed to the success of this research. First of all I want to thank Anton Darhuber and Jos Zeegers for supervising my master project, for their encouragement, suggestions and corrections despite their busy schedules. I want to thank Christian Berendsen for his enthusiasm and cooperation in this project, for supervising me on a daily basis and for the good company and lots of good ideas he presented to me.

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Furthermore I want to thank Hein Castelijns, Michel Riepen and Ramin Badie for granting me the opportunity to perform experiments in the immersion lithography laboratory at ASML, for giving me a unique inside look at ASML and for their support in my master project.

Finally I want to thank all the inhabitants of Cascade for the enjoyable and interesting time I have spent at MTP the past year. A special thanks goes to all the people who made the ten o’clock coffee break a fun and interesting part of my daily work.
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1. Introduction

In the years between 1960 and 1980 there was much interest in the subject of static electricity. Several investigations were conducted where insulators were charged using a variety of methods. These charged insulators are commonly described as electrets. Studies have been conducted where the charges are applied by an electron beam \(^{[1]}\), by direct contact between electrode and substrate \(^{[2]}\) and by contact through a conductive liquid \(^{[3]}-[^{6}]\). In this last configuration a conducting liquid is applied between the electrode and the substrate to improve contact between the electrode and the substrate.

Another commonly used method to charge a substrate is by friction. Furthermore a water droplet can be used to charge a substrate by allowing the droplet to run over the substrate, thereby leaving charges behind \(^{[7]}\).

In the more recent publications the interest has shifted to dielectrophoresis where the influence of a charge pattern on a dielectric liquid is investigated. This effect can be used to generate micro lenses using two dielectric liquids between a bottom electrode and a patterned top electrode \(^{[8]}-[^{9}]\). The effect of dielectrophoresis can also be used to affect the stability of a liquid film by a surrounding electric field \(^{[10]}-[^{13}]\).

This research is initiated due to the interest of ASML to understand the break-up of thin water films in immersion lithography. The break-up of the water films can cause local temperature gradients on the wafers and this influences the accuracy of the lithography method used in the ASML machines to produce chips. Other applications are in roll-to-roll slot die coating. Due to the friction between the rolls and the web containing the coating, an inhomogeneous surface charge distribution can form on the web. This can result in the deformation of the liquid coating film and can eventually result in defects in the manufactured devices. Another possible application is the influence of static electricity on the directional colloidal crystallization \(^{[14]}\).

In this project static charges are deposited on an insulating substrate by dragging a water droplet over the substrate on a needle. The charges deposited on a substrate are measured with an electrostatic voltmeter. The theory and the experiments used to deposit and measure the charge distribution on the substrate are discussed in chapter 2.

The dielectrophoretic effects of static charges on a thin liquid film are investigated in chapter 3. The deformation and redistribution of the liquid film is investigated using both experiments and numerical simulations. Chapter 4 contains the conclusions and a discussion of the results. Some ideas for further research are given in chapter 5.
2. Measuring and depositing static charges

This chapter contains the measurements and theory needed to measure and deposit static charges. First the method to measure static charges is discussed. Secondly several de-charging methods are discussed. Then the charge deposition by dragging a droplet on a high voltage needle is explained as well as depositing charges by a moving contact line. Finally the stability of charge patterns is discussed.

2.1 Measuring static charges

The surface charges can be measured using an electrostatic voltmeter. This section explains how the electrostatic voltmeter is used to measure the surface charges. Furthermore, experiments are conducted to check this theoretical description.

2.1.1 Theory: the electrostatic voltmeter

The electrostatic voltmeter is a contactless method used to measure the surface charges on a substrate. The electrostatic voltmeter has an oscillating plate in the measuring probe. This plate is connected to a power supply. The voltage is controlled and using the field-nulling technique the surface charges can be determined. A schematic drawing of the measurement probe above the substrate is given in Figure 1.

![Schematic drawing of the electrostatic voltmeter above the substrate.](image)

The oscillating measuring probe is positioned above the substrate and measures the electric field in the air gap. The electrostatic voltmeter uses the voltage $V$ between probe and ground to reduce the electric field between the plate and the substrate to zero. The set voltage at which the measured electric field in the air gap is equal to zero is called the bias voltage. By using this procedure the surface charges on the substrate can be calculated from the bias voltage applied to the plate in the probe. The potential between the two plates can be calculated from the electric fields between them using:

$$V = d_1 E_1 + d_2 E_2$$  \(1\)

Where $d_1$ is the distance between the probe and the substrate and $d_2$ is the substrate thickness. The surface charge on the substrate can be calculated from the electric displacement.

$$D_2 - D_1 = \sigma$$ \(2\)

This electric displacement can be written as a combination of the electric field and the polarization according to:

$$D_1 = P_1 + \varepsilon_0 E_1$$ \(3\)
The polarization can be rewritten to have a part that reacts on a change in the internal field almost instantaneous and a part that reacts slowly. The instantaneous part can be characterized by the dielectric constant $\epsilon$.

$$P_1(t) = P_1(t) + P_2(t) = \epsilon_0(\epsilon - 1)E_1(t) + P_s$$  \hspace{1cm} (4)

In the air gap $P_2 = 0$, and $K = 1$ so combining equation (3) and (4) results in the following expression for the electric displacement.

$$D_1 = \epsilon_0E_1$$

$$D_2 = \epsilon\epsilon_0E_2 + P_s$$  \hspace{1cm} (5)

After rewriting equation (1) and using the expressions from equation (2) and (5) the electric field inside the air gap can be obtained which is given in equation (6)

$$E_1 = \frac{\frac{V-d_2}{d_1} \left( \frac{\epsilon - \epsilon_0}{\epsilon_0} \right)}{\epsilon d_1} = \frac{\frac{\epsilon_0E_1}{\epsilon\epsilon_0E_2 - P_s}}{\epsilon\epsilon_0E_2 + P_s}$$  \hspace{1cm} (6)

After some rewriting equation (6) reduces to equation (7)

$$E_1 = \frac{\frac{\epsilon_0E_1}{\epsilon\epsilon_0E_2 - P_s}}{d_2 + P_s}$$  \hspace{1cm} (7)

The voltage $V$ is then chosen to be such that the electric field inside the air gap ($E_1$) becomes zero. This voltage is the bias voltage $V_B$.

$$V_B = d_2 \left( \frac{\sigma - P_s}{\epsilon\epsilon_0} \right)$$  \hspace{1cm} (8)

Once this bias voltage is known the net surface charge can be calculated with the thickness and dielectric constant of the substrate.

$$\sigma - P_s = \epsilon\epsilon_0V_B/d_2$$  \hspace{1cm} (9)

Where $(\sigma - P_s)$ is the net surface charge density. This provides a non-contact method to measure the surface charges on a substrate. The output of the measurement probe is the bias voltage. The surface charges can then be calculated at each position using equation (9). For instance for a 1 mm substrate of polycarbonate ($\epsilon = 2.9$) the output voltage of the measurement probe should be divided by $3.90 \times 10^7$ [V/cm] to obtain the surface charge in C/m$^2$. For a 1 mm PMMA substrate, the conversion factor is $3.14 \times 10^7$. In each of the measurements the bias voltage of the electrostatic voltmeter is recorded and by using the conversion factor the surface charges are calculated.
2.1.2 Experimental set-up

For the experiments that are conducted in this project, two different configurations of the same set-up are used. The first configuration combines the XY-stage with the electrostatic voltmeter to measure static charge patterns. The second configuration uses a XY-stage and a water droplet to write static charges on an insulating substrate. In this section the configuration for measuring charges is described. First the experimental set-up is discussed together with the used components. Secondly the measurement method will be discussed.

2.1.2.1 Layout of the experimental set-up

The set-up consists of an XY-stage that is controlled by a computer. The XY-stage is used to control the movement of the substrate with respect to the needle or measuring probe. A photograph of the set-up containing the XY-stage is shown in Figure 2.

![Image of the experimental set-up](image)

*Figure 2: The TU/e measurement set-up containing the XY-stage and a bridge to mount the needle or measuring probe.*

The set-up can be used to measure the surface charge distribution on a substrate using an electrostatic voltmeter. The measuring probe scans the substrate by setting a trajectory for the XY-stage. In this manner the entire substrate can be scanned and the two dimensional charge distribution on the substrate can be determined from the measurement data. The measurement configuration of the set-up is given in Figure 3. A more detailed discussion of the experimental set-up is given in Appendix A. The manufacturers and model numbers of all used devices are given in Appendix A as well.
Figure 3: A picture (left) and schematic drawing (right) of the measuring probe mounted on the set-up.

The standard settings used for measuring the surface charge pattern are given in Table 1. These settings are used in all measurements unless stated otherwise.

Table 1: Standard settings for the measuring configuration of the set-up.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_m$</td>
<td>Speed of the measuring probe with respect to the substrate</td>
<td>5 mm/s</td>
</tr>
<tr>
<td>$t_m$</td>
<td>Time between two subsequent measurement points</td>
<td>25 ms</td>
</tr>
<tr>
<td>$h_m$</td>
<td>Distance between measuring probe and substrate</td>
<td>1.0 mm</td>
</tr>
</tbody>
</table>

These parameters result in a measurement point every 0.125 mm. In section 2.1.3.1, the resolution of the measurement probe will be discussed.

2.1.2.2 Measurement method

In this section the different measurement steps will be discussed, from the cleaning of the substrate to the display of the measured charges.

2.1.2.2.1 Cleaning the substrate

Before any measurement can be conducted the substrate is first cleaned and the charges are removed from the substrate. The substrate is cleaned to remove dust particles and possible traces of glue from the protective foil on the substrate. The cleaning of the substrate contains five consecutive steps:

1. Blowing nitrogen gas over the surface to remove dust particles
2. Washing the substrate by pouring deionized water over the surface
3. Drying the substrate by blowing with nitrogen gas
4. Removing remaining impurities and de-charging by pouring isopropanol over the surface
5. Drying the substrate by blowing with nitrogen gas

After these five steps the substrate is clean and most of the charges have been removed [16]. If the surface is already clean or when the substrate cannot resist the washing with isopropanol, the substrate can be de-charged by using an ionizer. The ionizer uses a high voltage (7 kV AC) to ionize the air molecules. These charged air molecules can then neutralize charges on the isolating substrate. After the de-charging steps the residual surface charge distribution is measured to assure the substrate is properly de-charged.
2.1.2.2.2 Measuring the surface charges

The surface charges are measured with an electrostatic voltmeter. The output signal of the electrostatic voltmeter is monitored and recorded using a computer. The output of the electrostatic voltmeter is the bias voltage necessary to decrease the electric field in the substrate to zero. This voltage can be translated to the surface charge at each position. A theoretical description of the method of the electrostatic voltmeter is given in section 2.1.1. The charges on the entire substrate can be measured by scanning the substrate with the measuring probe. The X- and Y-position are recorded together with the measured voltage at this point. The time and date are also logged.

The two-dimensional map of the bias voltage $V_{\text{bias}}(x,y)$ can be converted to the surface charge distribution using equation (9). A typical example of a surface charge distribution after dragging a droplet on a needle at high voltage is given in Figure 4. The two-dimensional surface charge distribution is displayed in both two and three-dimensional graphs where the height of the 3-D graph represents the surface charge density. Cross sections perpendicular to the droplet trajectory can also be made and an example of a cross section at a Y-position of 20 mm is shown in Figure 4b.

![Figure 4: The charge distribution can be displayed as a 2-D topography plot (a), a line plot (b) or as a 3-D color plot (c).](image-url)
2.1.3 Verification of the theory

In this section the theoretical model of the measuring probe (section 2.1.1) is tested against experiments. For this purpose the dependency on probe to substrate distance of the measured charges and the influence of an air gap between the grounded bottom plate and the substrate are investigated.

2.1.3.1 Dependency on probe to substrate distance

According to the theory the electrostatic voltmeter uses a method that is independent of the distance between the measuring probe and the substrate. This is applicable for a uniform surface charge on a substrate. Whether this also holds for surface charge patterns of finite with is tested by measuring a charged pattern with different probe to substrate distances. The charged pattern is a single horizontal line written with a droplet on a needle having an outer diameter of 6 mm. The measurements are conducted perpendicular to the written line. The substrate used in this measurement is polycarbonate and the geometry used is the same as in the schematic drawing in Figure 3. The measurements are displayed in Figure 5.

![Figure 5: Dependency of the measured surface charges on the probe to substrate distance.](image)

As can be seen in Figure 5, the surface charge at the center of the line can be determined accurately with a probe to substrate distance between 0.5 and 3 mm. However, the measurement at \( h = 0.5 \) mm shows distinct peaks at the positions \( \pm 2.8 \) mm. This effect will be discussed in section 4.2.2. Since the theory is developed for a homogeneous surface charge, the independency on probe to substrate distance no longer holds at the edges of the written line. This is also seen in Figure 5. The dependency on the distance \( h \) is smallest at the center of the written line which is expected since the edge effects are smallest there. The measurement indicates that the spatial resolution of the probe depends on the distance between the probe and the substrate with a minimum resolution of approximately 0.5 mm. This is consistent with the probe datasheet given in Appendix B.
2.1.3.2 Influence of an air gap between substrate and grounded bottom plate

In this section, the influence of an air gap between the bottom of the substrate and the grounded bottom plate is illustrated. First, surface charges are deposited on the substrate when the substrate bottom is on the grounded plate (no air gap). The electric potential due to the surface charges is then measured with different air gaps. The substrate is supported in the corners but the potential is measured at the center of the substrate. A picture of the geometry for these measurements is given in Figure 6.

Figure 6: The substrate is supported at the corners to control the air gap between substrate and grounded bottom plate.

The air gap dependency is also investigated by numerical simulations where the substrate is placed a distance above the grounded plate. An illustration of the simulation configuration is given in Figure 7. The resulting electric potential due to a surface charge of 20 µC/m² is given in Figure 8.

Figure 7: Configuration of the simulation for simulating the air gap dependency.
The measurement results from the electric potential in the simulations and the bias voltage of the electrostatic voltmeter in experiments 1 mm above the substrate are given in Figure 9. Both the experimental and simulation data are normalized using the potential and bias voltage measured when there is no air gap ($d_{air} = 0$ mm). The increase of the potential is similar for the experiments and the simulations for an air gap up to 5 mm. For larger air gaps, the experiments show that the potential reaches an asymptote that is not predicted by the simulations.

As can be seen in Figure 9, there is a dependency on the relative humidity. The green triangles and red circles are measurement conducted at an average temperature of 30°C and a relative humidity of about 21%. The black squares are the experimental results at an average temperature of 29°C and a relative humidity of about 34%. These humidity values are lower than the actual humidity in the room due to an error in the measurement devices. Therefore the relative humidity is approximately 20% higher. However for this measurement only the difference in relative humidity is important. From the experiments can be concluded that a higher relative humidity results in a decrease of the slope at which the potential increases with increasing air gap.

Figure 9: The air gap dependency of the electric potential measured by experiments and simulations.
The first part of the graph, up to an air gap of 5 mm, shows an increase in measured potential with increasing air gap. After these 5 mm the increase stagnates, which is not predicted by the simulations. In the measurements appears to be a jump at an air gap around 7 mm, this could be a result from the aluminum bridge hanging over the set-up to hold the measuring probe and the writing needle. The picture in Figure 6 shows the measuring probe above the substrate at an air gap of 15.7 mm. There is a relatively short distance from the substrate to the part of the set-up holding the measuring probe compared to the distance to the grounded bottom plate.

In order to investigate the effect of a grounded part above the substrate, simulations have been conducted with an extra grounded top plate 20 mm above the grounded bottom plate. The potential in the simulations is calculated one mm above the substrate. The simulation results are given in Figure 10a and the used simulation geometry is sketched in Figure 10b. The simulation shows a decrease in the measured electric potential from an air gap of 5 mm when an additional grounded top plate is introduced. This might explain the decrease in the measured potential in the experiments. However the aluminum bridge is not grounded completely and therefore it is possible that there is just a metal top plate containing mobile charges. Further research will be necessary to find the exact cause of the potential drop in the experiments.

![Figure 10](image)

*Figure 10: The dependency of the measured electrical potential on the presence of a grounded top plate (a) and a schematic drawing of the simulated geometry.*

### 2.1.4 Discussion and conclusions

From the above can be concluded that the measuring probe measures the surface charges most accurately when the gradient in surface charges is small. The measurement probe can measure the surface charges at the center of a 6 mm wide written line with a probe to substrate distance between 0.5 and 3 mm. At the edges the measurement method becomes less reliable due to the limited spatial resolution of the probe.

Furthermore the effect of an air gap between the substrate and grounded bottom plate can triple the measured potential at an air gap of 1 mm compared to the case where no air gap exists. Therefore it is necessary to keep the bottom of the substrate on the grounded bottom plate to exclude the effects of an air gap on the measurements.

When the probe to substrate distance is small enough and no air gap is introduced, the electrostatic voltmeter can be used to measure static charges on an insulating substrate. The static charges at the center of a 2 mm line can be measured with a probe to substrate distance of 2 mm. A smaller probe to substrate distance will result in a more accurate measurement of the surface charge pattern, especially at the edges.
2.2 De-charging substrates

The effect of de-charging methods is investigated by writing a charge pattern on the PMMA substrate and checking the ability of the method to remove this pattern. Therefore the substrate is cleaned and a square pattern is written on the substrate using a voltage of $1.23\, \text{kV}$. The pattern is measured using the electrostatic voltmeter and then de-charged. The substrate is measured again after de-charging to see whether or not the charges are removed. Three different procedures will be considered:

- The five step method as described in section 2.1.2.2.1
- De-charging with the ionizer
- De-charging by pouring demineralized water over the substrate and drying with nitrogen

The last procedure is the same as the first three steps of the five step method. The surface charge distribution on the substrate containing the charged square pattern before de-charging is given in Figure 11.

The surface charges are calculated from the bias voltage of the electrostatic voltmeter using equation (9).

![Figure 11: The charged square pattern on the substrate before de-charging.](image)

2.2.1 The five step method

The five step method is used to de-charge the substrate and afterwards the surface charges on the substrate are measured again by the electrostatic voltmeter. The measurement after de-charging is given in Figure 12. As can be seen in Figure 12 most of the charges are removed. The remaining surface charge is reduced with a factor 30 and the pattern on the substrate is no longer visible. The remaining measured charges can be a result of the noise on the electrostatic voltmeter. These charges resemble a measured bias voltage of the order of $10\, \text{volts}$ and a transmitted voltage of order $10\, \text{millivolts}$ to the data acquisition module. The noise level of the probe is about $5 – 10\, \text{mV}$. 
2.2.2 Ionizer

The ionizer is used to de-charge the substrate by ionizing air molecules. The substrate is moved below the ionizer and the charges on the substrate are neutralized as a result from the charged air molecules. The measurement of the surface charges after using the ionizer are given in Figure 13. After de-charging with the ionizer, the remaining surface charges are less than 1 µC/m². The charge pattern is no longer visible just like with the 5-step de-charging method.
2.2.3 De-mineralized water

The third method to de-charge the substrate is by pouring de-mineralized water over the substrate. The substrate is then dried using nitrogen gas. This de-charging procedure consists of the first three steps of the 5-step method. The measurement of the surface charges on the substrate after de-charging with de-mineralized water is given in Figure 14. As can be seen in Figure 14 the square pattern is no longer visible. However, the method introduces charges that are even higher than before de-charging. Therefore this method is not useful to de-charge the substrate. The deposition of charges with water droplets is investigated in more detail in section 2.4.3.

![Figure 14: Measurement of the substrate after de-charging with de-mineralized water.](image)

2.2.4 Conclusion

From the measurements in this section can be concluded that the ionizer is the best way to de-charge the substrates. Another advantage of the ionizer is that this method can be used on every substrate.
2.3 Charge deposition by dragging a droplet at high voltage

2.3.1 Theory: Charge deposition

A conducting liquid contains ions that can move freely through the liquid. When this liquid is immersed between two electrodes and a charging voltage $V_c$ is applied between these electrodes, charge separation can occur at the solid surface due to ion absorption or proton dissociation and a charge double layer is formed. This double layer consists of a surface charge bound to the solid and a region of diffuse counter charge in the liquid. A schematic drawing of the charges in the liquid is given in Figure 15. According to Chudleigh [6], when the needle is moved relative to the substrate the contact line starts to move. However the charges are still bound to the substrate. Therefore a surface charge is left behind on the substrate that has the same sign as the sign of the charging voltage. A needle at positive charge will result in positive surface charges adsorbed on the substrate surface [6].

![Figure 15: Schematic drawing of the charge separation in a conducting liquid.](image)

The amount of charge deposited on the solid surface is determined by the location of the plane of charge separation. This location depends on the cohesive forces within the liquid and the adhesive forces at the solid liquid interface. At the molecular level this plane of charge separation depends on electrostatic and molecular forces operating on the ions in the liquid at the moment of separation. A quantitative estimate of the charge in the double layer can be obtained using the Gouy-Chapman theory [17].

2.3.2 Experimental set-up XY-stage

In this section the writing configuration of the experimental set-up with the XY-stage is discussed. The experimental set-up is discussed and the measuring method is explained.

2.3.2.1 Layout experimental set-up

The set-up explained in section 2.1.2 can be used to write charges by mounting a needle that is charged by a high voltage source. At the end of the needle the small water droplet bridges the gap between the needle and the substrate. The droplet between the needle and the substrate is conductive and therefore charge transport takes place through the droplet. When this droplet is then dragged over the substrate a line of charges is left behind. The applied voltage is controlled by the computer and the voltage applied at each position is recorded. The writing configuration is shown in Figure 16. The writing speed is set to 2.5 mm/s unless stated otherwise. Other standard settings for the writing configuration of the XY-stage set-up are given in Table 2. A more detailed discussion of the experimental set-up is given in Appendix A. The manufacturers and model numbers of all used devices are given in Appendix A as well.
2.3.2.2 Charge deposition method

After cleaning and de-charging the substrate, a surface charge distribution can be deposited at a specific location by dragging a water droplet attached to a needle over the surface. The metal needle is connected to a high voltage source and charged with a specific voltage. As a result a surface charge is deposited on the surface at positions where the droplet makes contact with the substrate. The amount of charge is related to the set voltage. The charge pattern can be controlled by the movement of the XY-stage. A series of (X,Y) coordinates is inserted in a text file and the XY-stage moves to these points subsequently. The text file contains three columns for the writing sequence. The first containing the X-coordinate, the second containing the Y-coordinate. The final column contains the voltage in kilovolts. An example of such an input file is given in Figure 17. The input file is displayed as well as the sequence that is run as a result.

Table 2: Standard settings for the writing configuration of the set-up.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_w$</td>
<td>Speed of the writing needle with respect to the substrate</td>
<td>2.5 mm/s</td>
</tr>
<tr>
<td>$d_{\text{needle}}$</td>
<td>Needle diameter</td>
<td>6.0 mm</td>
</tr>
<tr>
<td>$d_{\text{droplet}}$</td>
<td>Diameter of the water droplet between needle and substrate</td>
<td>6.0 mm</td>
</tr>
<tr>
<td>$h_w$</td>
<td>Distance between writing needle and substrate</td>
<td>0.5 mm</td>
</tr>
</tbody>
</table>

Figure 16: A picture (left) and schematic drawing (right) of the needle to write charges mounted on the set-up.

Figure 17: The input text file (left) and the resulting sequence of the XY-stage (right).
2.3.3 Calibration of the experimental setup

In this section the calibration of the high voltage source is discussed. The input voltage from the file is compared to the voltage on the needle. Furthermore the voltage on the needle and the final potential measured by the electrostatic voltmeter are compared. Finally the measured potential can be used to calculate the surface charge at each position of the substrate.

2.3.3.1 Input voltage versus needle voltage

Between the input voltage (voltage supplied by the DC power supply) that is delivered to the high voltage source to control the needle voltage and the actual display of the high voltage source (HV-source) is a conversion factor of approximately 1250. As a result the input is in volts whereas the output is in kilovolts. There is a difference between the display voltage of the HV-source and the voltage that is applied to the needle. To check this difference a measurement is conducted where the input voltage is set and the needle and output voltage are measured using a digital multimeter. The results from this measurement are displayed in Figure 18. Analysis shows that the input voltage is multiplied by a factor of $1.26 \times 10^3$ to obtain the needle voltage with zero offset within the error of the linear fit. There is a small offset between the display voltage and the voltage on the needle as well as a difference in slope of 0.03. The equation for the linear fit of the needle voltage and the display voltage as function of set voltage are given in equation (10).

\[
V_{\text{needle}}[\text{Volt}] = 1260 V_{\text{set}}[\text{Volt}]
\]

\[
V_{\text{display}}[\text{Volt}] = 1240 V_{\text{set}}[\text{Volt}] - 35
\] (10)

From the set voltage applied to the HV-source, the voltage on the needle can be calculated by multiplication with $1.26 \times 10^3$.

2.3.3.2 Dependency of the measured potential on the needle voltage

The measured potential as a result of a written line charge depends on the needle voltage. The voltage of the needle results in a charged water droplet that is dragged over the surface. As a result of this dragged droplet a surface charge is deposited on the substrate. This charge is measured by the electrostatic voltmeter and displayed as a bias voltage. The bias voltage is compared to the needle voltage for a polycarbonate substrate...
with a thickness of 0.75 and 0.175 mm. The dependency of the measured potential on the needle voltage is displayed in Figure 19. The error bars in the graph are the spread in written voltage over a cross section perpendicular to the direction of the line where charges were written.

![Figure 19: The written voltage on the polycarbonate substrate as a function of needle voltage.](image)

From Figure 19 can be concluded that there is a dependency of the measured bias voltage on the needle diameter but not on the substrate thickness. A thicker needle results in a lower measured voltage. The deposited surface charges are calculated from the measured bias voltage using a conversion factor. This factor will be discussed in detail in section 2.3.3.3. The deposited surface charges as function of the needle voltage are given in Figure 20.

![Figure 20: The deposited surface charge on a polycarbonate substrate as a function of needle voltage.](image)

The increase in slope of the deposited surface charge versus the needle voltage is expected for the 0.175 mm substrate, since a thinner substrate results in a lower distance from the charged water droplet to the ground and therefore in a higher electric field. The higher electric field results in more surface charges deposited at
the substrate. The magnitude of the deposited charges seems to saturate at $V_{\text{needle}} \approx 2.2$ kV. Further research is necessary to investigate the mechanism resulting in the saturation of the magnitude of the deposited charges and to find out why this happens at a needle voltage of about 2.2 kV.

### 2.3.3.3 Conversion of measured voltage to surface charge

The voltage measured by the electrostatic voltmeter has to be converted to a surface charge since the bias voltage of the electrostatic voltmeter depends on substrate properties like the thickness and dielectric constant. From the model presented in section 2.1.1 the net surface charge can be calculated from the bias voltage using the earlier derived equation (9).

$$\left(\sigma_t - P_s\right) = \varepsilon \varepsilon_0 V_B / d_1$$

The net surface charge depends linearly on the bias voltage. Therefore the surface charge can be calculated from the bias voltage by dividing with $\varepsilon \varepsilon_0 / d_1$. For a PMMA substrate having dielectric constant 3.6 and a thickness of 1 mm this results in the conversion factor:

$$\frac{d_1}{(\varepsilon \varepsilon_0)} = 3.14 \times 10^7$$

To check this theoretical value, a simulation of the surface charge dependency on the electric potential is conducted using Comsol Multiphysics 3.5a. Comsol is a software package to model physical problems using finite element analysis. In this case the electrostatic module is used to calculate the electric potential resulting from the surface charge. A description of Comsol and the steps taken to reach simulation results are given in Appendix C1.

The simulation is two dimensional and the geometry is visualized in Figure 21. On top of the PMMA substrate with a width of 70 mm, a surface charge is applied homogeneously over a line width of 6 mm. The aluminum bottom plate is grounded and has a width of 200 mm. The electric potential is calculated at the center, 1 mm above the PMMA surface.

![Figure 21: Simulated geometry for the dependency of the surface charge on the electric field.](image)

The electric potential measured directly above the center of the charged line is measured as function of the applied surface charge. The results from these simulations are given in Figure 22.
Figure 22: The electric potential 1 mm above the center of the charged line depending on the surface charge.

Figure 22 shows linear dependency between the surface charge and the measured electric potential. The slope of the fit through the data is $2.99 \times 10^7$ which is similar to the theoretical value of $3.14 \times 10^7$ calculated in equation (11). The theoretical conversion factor $3.14 \times 10^7$ will be used to calculate the surface charges from the measured electric potential.

### 2.3.4 Parameter variation

In this section the effect of different parameters on the deposition of static charges will be discussed. A number of different parameters are investigated where charges are deposited by dragging a water droplet on a needle set at high voltage. The investigated parameters are:

- Substrate material
- Writing speed

Furthermore the effects at the edge of a line of deposited charges are discussed in more detail.

#### 2.3.4.1 Influence of substrate material

In order to test the dependency of the charge deposition mechanism on substrate material, a variety of different surfaces are tested. The substrates are charged with a droplet dragged with a fixed needle voltage to write a line on each substrate. The bias voltage of the electrostatic voltmeter is then measured and the surface charge density is calculated. The different substrates and the possibility to deposit charges on the substrate are given in Table 3.
Table 3: Chargeability and the dielectric constant for different substrates.

<table>
<thead>
<tr>
<th>Material</th>
<th>Brand</th>
<th>Chargeable</th>
<th>Dielectric constant $\epsilon$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polycarbonate</td>
<td>Lexan 9030</td>
<td>Yes</td>
<td>2.9</td>
</tr>
<tr>
<td></td>
<td>Makrofol DE 1.1</td>
<td>Yes</td>
<td>2.9</td>
</tr>
<tr>
<td>PMMA</td>
<td>MargaCipta</td>
<td>Yes</td>
<td>3.6</td>
</tr>
<tr>
<td></td>
<td>Mitsubishi Rayon Shinkolite</td>
<td>Yes</td>
<td>3.6</td>
</tr>
<tr>
<td>PETG</td>
<td>Polyester</td>
<td>Yes</td>
<td>2.6</td>
</tr>
<tr>
<td>Polystyrene</td>
<td></td>
<td>Yes</td>
<td>2.7</td>
</tr>
<tr>
<td>D263 Glass</td>
<td>Schott</td>
<td>Yes</td>
<td>6.7</td>
</tr>
<tr>
<td>Glass</td>
<td>Corning 7095B-9</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>PTFE</td>
<td>Teflon</td>
<td>Yes</td>
<td>1.9</td>
</tr>
</tbody>
</table>

Table 3 shows that Corning Glass cannot be charged, possibly due to ions in the glass. The deposited charges are removed instantly due to the connectivity with ground, although the resistance could not be measured.

The deposited charge density can be calculated using the dielectric constant and the thickness of the substrate from the measured bias voltage of the electrostatic voltmeter (see section 2.3.3.3). Examples of charges deposited on the substrates PMMA, D263 glass and PETG are given in Figure 23. The PETG seems to be more difficult to charge than the PMMA and the D263 glass. The width of the written line depends on the size of the droplet dragged over the substrate and can therefore vary between measurements. The contact angle of the substrate can also have an influence. The contact angle of water on PMMA is about 68° [18], the static contact angle with PETG is about 73° [19]. The contact angle of water on D263 glass is lowest which could explain the wider line.

Figure 23: Deposited surface charges due to a droplet on a needle at 1.23 kV for PMMA (a), D263 glass (b) and PETG (c).
2.3.4.2 Effect of writing speed

The effect of the writing speed on the surface charge density is investigated by dragging the droplet over the PMMA substrate at different speeds while keeping the voltage on the needle constant. The charged line is written with a 6 mm needle supplied with a needle voltage of -1.25 kV. The results of these measurements are displayed in Figure 24. The cross section of the surface charge is plotted at a fixed line position (X) as function of Y, the coordinate direction normal to the line.

![Figure 24: Surface charge density after writing with different write speed.](image)

Figure 24 shows that the surface charge density on the substrate does not depend on the writing speed. The charge transfer process is thus independent of writing speed for speeds of the order mm/s. Furthermore, Figure 24 shows that there are shallow peaks at the edges of the written charges (best visible at writing speeds of 1, 1.5 and 4 mm/s). These peaks will be discussed in more detail in the next section.

2.3.4.3 Edge effects at lines of deposited charges

As can be seen in Figure 5 and Figure 24, charge peaks occur near the edges of the written line. These peaks could be an artifact of the measuring probe or reflect a non-uniform charge distribution on the line. In order to check the effect of the measurement probe, a measurement is conducted over a metal strip that has a known voltage of 1.25 kV. The measurement is given in Figure 25. In this measurement the measured charge distribution for the metal strip is compared with a distribution deposited with the droplet drag method at a similar voltage. Figure 25 shows a difference in behavior at the edges of the charged line. Whereas the metallic strip shows no difference between the charges at the center and at the edges, the written line shows peaks in the surface charge density at the edges. This means that the peaks at the edges of the written line are a result of the charge deposition method.
Simulations have been conducted to check whether the peaks at the edges of a surface charge also result in peaks in the electric potential just above the substrate. This is done since the electrostatic voltmeter measures the electric potential to calculate the surface charge distribution. Simulations with two different distributions \( \sigma_{1,2} \) are conducted. The first is a homogeneous charge distribution \( (\sigma_1) \). The second is a non-uniform distribution exhibiting peaks at the edges. Both charge distributions are plotted in Figure 26. The non-uniform charge distribution is symmetric around \( x = 0 \). The used expression for the uniform and non-uniform surface charge are given in equation (12)

\[
\begin{align*}
\sigma_1 &= \begin{cases} 
\sigma_0 & \text{for } 3 \text{ mm} < x < 3 \text{ mm} \\
0 & \text{else}
\end{cases} \\
\sigma_2 &= \sigma_1 + A exp \left(-\frac{(x-x_c)^2}{2w^2}\right) + A exp \left(-\frac{(x+x_c)^2}{2w^2}\right)
\end{align*}
\tag{12}
\]

The numerical values were chosen to as \( \sigma_0 = 5 \mu \text{C/m}^2 \), \( A = 5 \mu \text{C/m}^2 \), \( \pm x_c = 2.7 \text{ mm} \) is the center of the peaks and \( w = 0.3 \text{ mm} \), which is a measure for the width of the peaks.

Figure 26: Both surface charge distributions, symmetric Gaussian function and homogeneous distribution (left), and the resulting electric potential (right)
The resulting potential, determined from Comsol simulations as described in Appendix C1, at 0.2 mm above the charged line is displayed in the right graph of Figure 26. The potential shows shallow peaks near the position where the surface charge is higher. The electric potential for a uniform surface charge of $5 \ \mu C/m^2$ is also displayed. The geometry of the simulation is identical to that in section 2.3.3.3 and the simulation method is discussed in detail in appendix C1.

The right hand side of Figure 26 resembles the measured profile as given in Figure 25, which leads to the conclusion that the measured peaks by the electrostatic voltmeter are very probably the result of an inhomogeneous charge distribution and the surface charges at the edges of the line are higher than at the center. This means that the mechanism that deposits the surface charges is stronger at the edges of the droplet than in the bulk. In the experiments (Figure 25) an increase of surface charge at the edges of the surface charge distribution is measured of about 15 %. From the simulation results in Figure 26 can be concluded that an increase of the surface charge of 100 % at the edges results in about 7 % increase of the electric potential 1 mm above the substrate. Therefore the peaks in the surface charge distribution should be about 3 times the base charge $\sigma_0$ to explain the peaks at the edges of the surface charge distribution.

2.3.5 Discussion and conclusion

In this section the possibility to deposit charges in a specific pattern is investigated. It is found that an accurate pattern of charges can be written by dragging a droplet on a metallic needle that is connected to the high voltage source. The amount of charges that are deposited can be controlled by controlling the needle voltage. A calibration has been done that allows to predict the deposited charges resulting from a specific set voltage of the HV-source. Secondly, the influence of different substrates and the influence of different writing speeds have been investigated. It is found that some substrates can be charged easier than others whereas some substrates such as Corning glass cannot be charged at all. The writing speed does not have an influence on the deposited charges in the investigated range of writing speeds.

Finally the measurement with higher charge at the edges of a written line is investigated using both experiments and simulations. It is found that edge effects are probably not an artifact of the measurement probe but probably a result from the charge distribution. Kang [20] investigated the surface charge distribution in a liquid conducting droplet set at a specific voltage and found that the surface charge is highest at the edges. This is also observed in the experiments.

However these effects are not always measurable and further research will be necessary to investigate the reasons for these edge effects. One explanation could be the probe to substrate distance. For a higher probe to substrate distance the spatial resolution of the probe decreases and the peaks at the edges are no longer visible. A more accurate measurement device having a higher spatial resolution is necessary to measure the exact surface charge distribution.
2.4 Charge deposition by moving contact lines
In section 2.3 the deposition of charges by dragging a water droplet on a needle at high voltage were discussed. Surprisingly, charges are also deposited when no voltage is applied to the needle. In this section the charge deposition due to a moving contact line will be investigated. Therefore droplets on either a grounded or an insulated needle are dragged over the substrate and the resulting charges on the substrate are measured. The effect of dragging a droplet on a grounded needle on the charge deposition at higher speeds is investigated using a turntable. The measurements with the turntable were conducted at ASML in Veldhoven (NL).

2.4.1 Theory
When a deionized water droplet is dragged over a substrate, an electric double layer is formed at the interface between the solid substrate and the water droplet. As the droplet is dragged over the substrate, the negative ions are adsorbed on the substrate surface for most polymer materials. This adsorption occurs rapidly from the moment the droplet touches the interface. In the case where the droplet is dragged by a grounded needle, the deposited charges can be replenished and the deposition can proceed in a stationary fashion. In the case of an insulated needle, the negative charges are no longer replenished. Therefore the dragged droplet becomes more and more positive while depositing negative charges. As a result the amount of negative charges at the interface decreases and therefore also the deposited negative charge decreases. Eventually a reversing point is reached. The increase of accumulated positive charge will cause the adsorption of positive charges at the interface to dominate the adsorption of negative charges. From this point positive charges are deposited until the adsorption of negative charges becomes dominant again [21].

2.4.2 ASML turntable for high speed dragging
A turntable set-up from ASML is used to investigate charging effects with grounded needles at higher velocities. In this section the experimental set-up at ASML will be discussed and the measurement method used for the experiments with a grounded needle on the ASML turntable will be explained. The measurements with a grounded or insulated needle at low speeds ($v_{write} \leq 10 \text{ mm/s}$) are conducted with the XY-table. The experimental set-up and measurement method are identical to the set-up described in section 2.1.2 and section 2.3.2, except that the needle is no longer connected to the HV-source but to ground instead. For the case of the insulating needle, the needle is only connected to insulating parts.
2.4.2.1 Layout experimental set-up

The set-up contains a turntable driven by a computer to control the rotation angle and rotation speed. It has two high speed cameras taking images at a rate of 1000 frames per second and a concentric immersion needle providing water outflow and air suction. A photograph of the set-up is given in Figure 27.

![Figure 27: ASML turntable and high speed cameras.](image1)

The immersion needle is mounted on a series of translation and rotation stages such that the position in three directions and the tilt in two directions can be controlled. This is used to align the axis of the needle perpendicular to the substrate on the turntable. One camera is positioned below the substrate and views through the substrate to the immersion needle. The second camera is directed perpendicular to the substrate and views from the side to the needle. This second camera can record the contact angles between the droplet on the needle and the substrate. The immersion needle is given in Figure 28. Due to the constant inflow of water that is removed with the air flow there is a water flow in the droplet below the needle. There is also an air flow due to the air suction in the immersion needle.

![Figure 28: Picture of the immersion needle for ASML set-up (left) and schematic drawing (right).](image2)
2.4.2.2 Measurement method

The ASML turntable is used to investigate the effects of dragging a grounded droplet over a substrate at higher drag speeds. Therefore a series of PMMA wafers is used having different thickness. Just like in the previous case where a droplet on a needle at high voltage was dragged over the substrate a series of steps is followed to obtain the measurement results.

The first step is to de-charge the substrate with the ionizer. The part of the wafer that is of interest for the measurement is de-charged. Step two is to measure the remaining charges to validate that the de-charging procedure worked properly.

In step three the wafer is placed on the turntable and the needle and droplet are set in position. Then the turntable rotates with a set speed over a predetermined angle. In this step the charges are deposited due to the contact line movement.

Finally the applied surface charges are measured on the XY-stage, where the region of interest on the wafer is scanned in a similar way as for the case where the needle was set at high voltage. The resulting surface charge pattern can then be visualized in the same way as described in section 2.1.2.2.2.

2.4.3 Experiments

In this section the measurements for which the charge deposition occurs due to a moving contact line are discussed. At first the effect of a grounded or insulated needle at low drag speeds are discussed. In this case the needle is respectively connected to ground instead of to the high voltage source or a plastic needle is used. Secondly the effect of a droplet on a grounded needle on the charge deposition is investigated at higher speeds using the ASML set-up. Finally the dependency on sample history is investigated.

2.4.3.1 Grounded and insulated needle at low drag speeds

A measurement has been conducted using a grounded needle instead of a needle at a specified voltage. This means that a grounded droplet is dragged over the polycarbonate substrate on a 2 mm needle. The substrate gains a negative surface charge density at the positions where the droplet was dragged over the surface as can be seen in Figure 29. The writing speed \( v_{\text{write}} = 2.5 \text{ mm/s} \).

Figure 29: Surface charge distribution after dragging a grounded droplet.
The pattern of the dragged droplet is clearly visible. A surface charge density of approximately $-5 \, \mu\text{C/m}^2$ is observed at the positions where the droplet was dragged over the substrate. The substrate is equally charged over the length of the written pattern, since the droplet is connected to ground and therefore to an infinite source of negative charges. The same experiment has been done with an insulating needle. The written voltage is no longer uniform over the written distance and depends on the initial charges in the water reservoir of the needle. The amount of charges deposited decreases with increasing writing distance. This is displayed in Figure 30. Obviously while depositing charge, the amount of available free charge carriers in the water reservoir decreases.

Figure 30: Deposited surface charges after dragging with water droplet on insulated needle in 2-D (a) and 3-D (b).

As shown in Figure 30 the amount of deposited surface charges decreases until it is equal to zero. Then the droplet deposits some positive charges. This oscillation in the deposition of charges has also been observed by Yatsuzuka et al. [21].

2.4.3.2 Grounded needle at high speeds

The measurements in this section are conducted with the ASML turntable set-up. Unlike previous measurements conducted with the XY-stage where writing speeds reached only a few mm/s, measurements with the ASML setup can reach speeds of up to 100 mm/s. In this measurement the immersion needle is grounded and a PMMA wafer of 4 mm thickness is used as a substrate. In these measurements the turntable makes one half rotation to make sure the droplet is not dragged over the same substrate twice. A measurement with the electrostatic voltmeter is conducted after dragging the droplet over the surface with a specific speed. From these measurements a cross section is taken halfway the line, where the droplet was dragged over the substrate. The measured surface charge profiles for different rotation speeds and therefore different writing speed is given in Figure 31.
Figure 31: The surface charge deposited by a droplet on a grounded immersion needle for different rotation speeds.

Figure 31 shows that the charges deposited on the substrate increase with increasing writing speed. A linear fit of the data plotted on a semi logarithmic scale is given in Figure 32. The deposited surface charge can be calculated from the rotation speed as \( \sigma \left[ \mu \text{C/m}^2 \right] = -0.98 \log_{10}(v_{\text{write}}) - 2.0 \), where \( v \) is the rotation speed in mm/s. However further research is necessary to investigate the origin of this dependency.

Figure 32: Surface charge density vs. writing speed. The solid line corresponds to the fitted function.

As can be seen there is a quantitative difference between the deposited charges in this measurement compared to the measurements in section 2.3.4.2. This is probably due to the immersion needle that is used in the measurements with the ASML set-up. The immersion needle is used to stabilize the droplet attached to the needle and therefore making higher write speeds possible. The needle might influence the charge deposition mechanism since the water is constantly supplied and removed and there is an additional air flow around the needle.
2.4.3.3 Dependency on sample history

The measurements in this section are conducted at ASML with their setup which is described in section 2.4.2. With the measurements on the ASML turntable the dependency of charge deposition on sample history is investigated. A series of measurements is conducted starting with a clean and de-charged substrate (3.5 mm thick PMMA) that has no written charges on it. The results from these measurements are given in Figure 33.

- The first graph (Figure 33a) is a measurement of the written charges after dragging a grounded droplet over the substrate with a turntable speed of 107.8 mm/s. The deposited charges are calculated from the measured bias voltage of the electrostatic voltmeter.

- The substrate is de-charged and a horizontal line of surface charges is deposited with a needle voltage of 1.09 kV. The substrate is then positioned on the turntable and a droplet is dragged over the substrate on a grounded needle with a speed of 107.8 mm/s (same procedure as before). The resulting charges from these two steps are given in Figure 33b.

- The substrate is de-charged once again. The de-charged substrate is placed on the turntable and a droplet is dragged on a grounded needle. The resulting charges on the substrate are given in Figure 33c.

- The procedure used to obtain the graph in Figure 33c is repeated twice at later times to obtain Figure 33d and Figure 33e.

As can be seen in Figure 33, the effect of the written line is still visible even after de-charging several times and after waiting for more than 18 hours. In between each measurement when the substrate is de-charged with the ionizer the surface charges are measured. In these measurements the written line (10 μC/m²) is not visible. Therefore it can be concluded that charging a substrate with high voltages changes the electric properties of the substrate. Dragging a grounded droplet over the substrate results in lower surface charges at positions where the substrate was previously charged with high voltages.

The dependency on multiple charge deposition cycles without de-charging the substrate between cycles is also investigated. For this purpose a droplet on a grounded needle is dragged over a specific position of the substrate several times. But no difference in charge deposition is observed.

Figure 33: Series of measurements at 0, 56, 110, 140 and 1177 minutes to test the effect of sample history on the deposition of charges on the substrate.
2.4.4 Discussion and conclusion

From the experiments in this section can be concluded that there is a difference between dragging a droplet with a grounded or an insulating needle. When the droplet is dragged with a grounded needle, this means the droplet is connected to an infinite reservoir of free charges. When the droplet deposits charges on the substrate, these charges can be replenished. Therefore a constant amount of surface charges can be deposited over the parts of the substrate where the droplet was dragged. In the case of an insulated needle only the free charges in the droplet and water reservoir in the needle are available to be deposited on the substrate. The amount of surface charges deposited therefore depends on the initial charges in the droplet and on the amount of charges that are already deposited on the substrate. Therefore a decrease of the deposited charges is observed over the line where the droplet was dragged.

With the ASML set-up a dependency of the amount of deposited charges on the rotation speed of the turntable is found. The experiments show a logarithmic behavior where the deposited charges increase with increasing rotation speed. However further research will be necessary to validate and explain this dependency. Finally the effect of prior measurements is investigated. It is found that a large charge deposition can influence the charging behavior of the substrate even after the charges have been completely removed. This effect is found to last for at least 19 hours.
2.5 Charge stability

It is important to know how long the charges remain on the surface since any leakage of the charge can introduce uncertainties in the amount of charge when a liquid film is applied. Therefore a 2 mm charged line is written on a polycarbonate substrate (dielectric constant $k = 2.9$). The charges on the substrate are measured at different times using the electrostatic voltmeter. The surface charges are then calculated from the bias voltage. The time dependence of the static charges on the substrate is given in Figure 34. Figure 34 shows that the charges on the substrate remain constant for at least 45 minutes. Since a single measurement usually does not exceed 20 minutes, it is safe to say that the measured charges at the beginning of the measurement remain the same during the measurement.

Figure 34: Time dependency of the surface charges on a polycarbonate substrate.
3. Dielectrophoresis in thin liquid films

In this chapter the effects of static charges on thin liquid films will be discussed. First a theoretical description of dielectrophoresis in thin liquid films will be given. Then the experimental set-up and the measurement method will be explained. Thirdly the results from the conducted experiments and the simulations are discussed. Finally a discussion and conclusion of the main results will be given.

3.1 Theory

In this section a theoretical description of the main phenomena regarding dielectrophoresis related to this research will be given. First the basics of dielectrophoresis will be explained. Secondly an overview of the literature on dielectrophoresis in liquid films is given. After this the behaviour of a thin liquid film on a substrate containing charges is explained using a lubrication approximation adapted for this specific problem.

3.1.1 Dielectrophoresis

Dielectrophoresis \[^{[22]}\] is the translational motion of neutral matter caused by polarization effects in a nonuniform electric field. Any electric field, uniform or nonuniform, exerts a force on a charged body. A nonuniform field also exerts a force on a neutral body. In a uniform field, a charged particle is attracted to the electrode carrying the charge opposite to the charge of the particle. A neutral particle in the same field will become polarized. As a result the forces that the electrodes exert on the particle are equal and therefore the particle will remain in its original position. The two particles in a uniform field are schematically shown in Figure 35a.

![Figure 35: The behavior of a charged and a neutral particle in (a) a uniform and (b) a nonuniform field.](image)

The behavior of the charged and the neutral particle in a nonuniform field is illustrated in Figure 35b. The charged particle behaves the same as in a uniform field. It moves towards the electrode having a charge opposite to the charged particle. The neutral particle is polarized, which is identical to the uniform field case. However the particle does not remain at rest in a nonuniform field. This is due to the fact that the particle is neutral and therefore the magnitude of the negative charge is equal to the positive charge. But the fields are not equal on the positive and negative side of the particle. As a result there is a difference in the force exerted on the particle by the electric field on the two sides. The particle will thus start to move in the direction of the stronger field. The direction of motion is independent of the electrode polarity.
In the case of this project a line of surface charges generates the electric field and at the edges the electric field line density is highest. As a result the dielectric liquid starts to move towards the area with high field line density due to the dielectrophoresis effect. Most of the liquid comes from the areas outside the line of surface charges since the field line density is lowest at these positions. This effect is schematically drawn in Figure 36. The field lines are only visualized in the dielectric liquid.

![Figure 36: Dielectrophoresis in a thin liquid film due to a positive surface charge (orange line).](image)

Due to the movement of the dielectric liquid a deformation develops at positions where the field line density is highest. These deformations are counteracted by surface tension effects and gravity. Eventually equilibrium will be reached between dielectrophoretic forces and surface tension and gravity forces.
3.1.2 Literature on dielectrophoresis in liquid films

In this section an overview of the literature regarding the effect of electric fields on liquid films will be given. Miccio et al. \cite{9} looked at the self-patterning of a PDMS liquid film due to dielectrophoretic effects. Therefore an x-cut Iron doped Lithium Niobate crystal is exposed to appropriately structured laser light. As a result there is a build-up of charge density in the crystal which results in dielectrophoretic deformations of the thin liquid film. It is shown that 1-D and 2-D patterning of PDMS gratings can be achieved.

Brown et al. \cite{10} have used dielectrophoretic forces to create a static periodic surface perturbation with a sinusoidal morphology on the surface of a thin layer of 1-decanol oil. This surface perturbation is observed when a voltage $V$ is applied between adjacent coplanar strip electrodes. It is found that the peak-to-peak amplitude $A$ of the wrinkle scales according to the functional form $A \propto V^2 \exp(-\alpha h/p)$ for a range of oil film thickness $h$ (between 15 and 50 µm) and electrode separations $p$ (160, 240 and 320 µm).

A model of a liquid in an electric field is discussed by Verma et al. \cite{11}. They modelled the patterning of a thin liquid film confined between two electrodes with an air gap using nonlinear 3D simulations. They studied the formation of fluid columns between the two electrodes as function of the applied electric field. A great variety of ordered structures can be produced by employing a topographically patterned electrode that produces a lateral variation and gradient of the electric field and causes a directed movement of the liquid toward the higher intensity of the field.

Lin et al. \cite{12} investigated the electric field induced dewetting at polymer/polymer interfaces. External electric fields were used to amplify interfacial fluctuations in the air/polymer/polymer system where one polymer dewets the other. For low electric fields, holes are generated heterogeneously in the top polymer layer (PS) which then dewets the liquid PMMA substrate. This process is only marginally modified by the electric field. If the electric field is large, the build-up of electrostatically amplified surface deformations results in the formation of columns that span from the PMMA to the upper electrode. The dominant driving force is the electric field.

Atta et al. \cite{13} have investigated the influence of electrostatic and chemical heterogeneity on electric-field-induced destabilization of thin liquid films using a numerical model. The effect of viscosity and surface tension on the film drainage time is observed for a homogeneous electric field. This results in random dewetting spots. Electrically heterogeneous fields, achieved by modelling electrodes with various periodic patterns, are explored to identify the effect on the drainage time and behaviour. Well controlled surface patterns are found on the application of periodic heterogeneity.
3.1.3 Lubrication approximation

The system considered in this project consists of a small layer of fluid on top of a surface that contains a charge density pattern at specific positions. In order to describe this system we start with the Navier Stokes equation and derive the lubrication approximation. From this we derive an expression for the pressure inside the liquid as a consequence of the charges on the bottom substrate. A schematic drawing of the thin liquid film on the substrate is given in Figure 37.

The liquid film is assumed to be an incompressible, Newtonian, thin liquid film.

\[ \rho \frac{\partial u}{\partial t} = -\nabla p + \mu \nabla^2 u \]
\[ \nabla \cdot u = 0 \]  \hspace{1cm} (13)

\( \mu \) is the viscosity of the liquid, \( \rho \) the density, \( u \) the velocity vector and \( p \) the pressure. The two equations are non-dimensionalized using the following definitions:

\[ (x, y, z) = \left( \frac{x}{L}, \frac{y}{L}, \frac{z}{H} \right) \]
\[ \bar{u}_x, \bar{u}_y, \bar{u}_z = \left( \frac{u_x}{U}, \frac{u_y}{U}, \frac{u_z}{V} \right) \]
\[ \bar{t} = \frac{t}{L/U} \]
\[ \bar{p} = \frac{p}{p_0} \]

The obtained continuity equation, omitting the bars is written in equation (15).

\[ \left( \frac{\partial \bar{u}_x}{\partial \bar{x}} + \frac{\partial \bar{u}_y}{\partial \bar{y}} + \frac{\partial \bar{u}_z}{\partial \bar{z}} \right) = 0 \]  \hspace{1cm} (15)

From equation (15) can be concluded that \( \frac{\bar{u}}{L} \approx \frac{V}{H} \) since all prefactors of the non-dimensionalized continuity equation should be of the same order of magnitude. The x-coefficient of the Navier Stokes equation becomes (omitting the bars):

\[ \rho \left( \frac{\partial^2 u_x}{\partial x^2} + \frac{\partial^2 u_x}{\partial y^2} + \frac{\partial^2 u_x}{\partial z^2} \right) = -\frac{\partial p}{\partial x} + \mu \left( \frac{\partial^2 u_x}{\partial y^2} + \frac{\partial^2 u_x}{\partial z^2} \right) \]  \hspace{1cm} (16)

Rewriting to obtain the Reynolds number at the beginning of the equation, results in equation (17).

\[ ReH \left( \frac{\partial u_x}{\partial t} + u_x \frac{\partial u_x}{\partial x} + u_y \frac{\partial u_x}{\partial y} + \frac{V}{H} u_z \frac{\partial u_x}{\partial z} \right) = -\frac{\rho_H \partial p}{\mu \partial x} + \frac{\rho_H}{\mu} \frac{\partial^2 u_x}{\partial y^2} + \frac{\rho_H}{\mu} \frac{\partial^2 u_x}{\partial z^2} + \frac{\rho_H}{\mu} \frac{\partial u_x}{\partial x} \]  \hspace{1cm} (17)

After multiplying by \( \varepsilon = H/L = V/U \) (from the continuity equation) the following equation is obtained.

\[ \varepsilon ReH \left( \frac{\partial u_x}{\partial t} + u_x \frac{\partial u_x}{\partial x} + u_y \frac{\partial u_x}{\partial y} + \frac{V}{H} u_z \frac{\partial u_x}{\partial z} \right) = -\frac{\rho_H \partial p}{\mu \partial x} + \varepsilon \frac{\partial^2 u_x}{\partial y^2} + \varepsilon \frac{\partial^2 u_x}{\partial z^2} + \varepsilon \frac{\partial u_x}{\partial x} \]  \hspace{1cm} (18)

\( p_0 \) is chosen to be equal to \( \mu U/H^2 \) to obtain equation (19).

\[ \varepsilon ReH \left( \frac{\partial u_x}{\partial t} + u_x \frac{\partial u_x}{\partial x} + u_y \frac{\partial u_x}{\partial y} + \frac{V}{H} u_z \frac{\partial u_x}{\partial z} \right) = -\frac{\varepsilon \partial p}{\mu \partial x} + \varepsilon \frac{\partial^2 u_x}{\partial y^2} + \varepsilon \frac{\partial^2 u_x}{\partial z^2} + \varepsilon \frac{\partial u_x}{\partial x} \]  \hspace{1cm} (19)
Since the discussed problem is a thin film, the height of the film is much smaller than the length \((H \ll L)\) and the velocity in z-direction is much smaller than in the x- and y-direction \((V \ll U)\). So \(\varepsilon \ll 1\) and for the x, y and z components of Navier Stokes the following equations can be obtained by neglecting terms of order \(\varepsilon\) and higher:

\[
\begin{align*}
x: & \quad 0 = -\frac{\partial p}{\partial x} + \frac{\partial^2 u_x}{\partial x^2} \\
y: & \quad 0 = -\frac{\partial p}{\partial y} + \frac{\partial^2 u_y}{\partial y^2} \\
z: & \quad 0 = \frac{\partial p}{\partial z}
\end{align*}
\]

Which in dimensional form can be written as equation (21):

\[
\begin{align*}
x: & \quad 0 = -\frac{1}{\mu} \frac{\partial p}{\partial x} + \frac{\partial^2 u_x}{\partial x^2} \\
y: & \quad 0 = -\frac{1}{\mu} \frac{\partial p}{\partial y} + \frac{\partial^2 u_y}{\partial y^2} \\
z: & \quad 0 = \frac{\partial p}{\partial z}
\end{align*}
\]

In order to determine the boundary conditions, a solid-liquid-air system is discussed. An inert and impenetrable bottom wall is assumed. This results in the following boundary condition at \(z = 0\):

\[
u_x = 0, \quad u_y = 0, \quad u_z = 0 \quad \text{at} \quad z = 0
\]

Furthermore no phase change and mass flux at the liquid air interface is assumed. The continuity equation is integrated in vertical direction to yield equation (23).

\[
\int_0^h \left(\frac{\partial u_x}{\partial x} + \frac{\partial u_y}{\partial y} + \frac{\partial u_z}{\partial z}\right) \, dz = 0
\]

\[
\int_0^h \frac{\partial u_z}{\partial z} \, dz + \int_0^h \frac{\partial u_y}{\partial y} \, dz + u_x(h) - u_x(0) = 0
\]

This expression can be rewritten using the boundary condition \(u_x(0) = 0\) and the Leibniz integration rule, resulting in equation (24).

\[
\frac{d}{dz} \int_0^h f(x, y, z) \, dz = \int_0^h \frac{\partial f}{\partial x} \, dz + \frac{\partial h}{\partial x} \int_0^h f(x, y, z = h) \, dz = \int_0^h f(x, y, z = h) \, dz + \frac{\partial h}{\partial x} \int_0^h \frac{\partial f}{\partial x} \, dz + \frac{\partial h}{\partial y} \int_0^h \frac{\partial f}{\partial y} \, dz + \frac{\partial h}{\partial z} \int_0^h \frac{\partial f}{\partial z} \, dz
\]

Applying this integration rule for the x- and y-integrals then results in equation (25).

\[
\frac{\partial}{\partial x} \int_0^h u_x \, dz - \frac{\partial h}{\partial x} u_x(h) + \frac{\partial}{\partial y} \int_0^h u_y \, dz - \frac{\partial h}{\partial y} u_y(h) + u_x(h) = 0
\]

The flow rates are defined as:

\[
Q_x \equiv \int_0^h u_x \, dz \\
Q_y \equiv \int_0^h u_y \, dz
\]

Using the expressions for the flow rates equation (27) is obtained

\[
u_x(z = h) - \frac{\partial h}{\partial x} u_x(z = h) - \frac{\partial h}{\partial y} u_y(z = h) = -\frac{\partial q_x}{\partial x} - \frac{\partial q_y}{\partial y}
\]

From the assumption of no mass flux through the boundary the following equation is obtained:

\[
\rho(\mathbf{u} \cdot \mathbf{n}_z - \mathbf{u}_{int} \cdot \mathbf{n}_z) = 0
\]
To obtain an expression for $u_{int}$ we define a function $F(x, y, z, t) \equiv z - h(x, y, t) = 0$, such that $F = 0$ defines the position of the liquid – air interface at all times. The function $F$ at two different times is schematically drawn in Figure 38.

![Figure 38: Schematic drawing of the function $F$ at two different times.](image)

The function is calculated for $t = t_1$ and $t = t_2$, which are an infinitesimal time step apart to obtain:

$$F(x_s(t_2), y(t_2), z_s(t_2), t_2) - F(x_s(t_1), y(t_1), z_s(t_1), t_1) = 0$$

(29)

This can be rewritten as:

$$F(x_s(t_2), y(t_2), z_s(t_2), t_2) - F(x_s(t_1), y(t_1), z_s(t_1), t_1) = F(x_s(t_1), y(t_1), z_s(t_1), t_2) - F(x_s(t_1), y(t_1), z_s(t_1), t_1)$$

(30)

Using the expression

$$\frac{F(x_s(t_2), y(t_2), z_s(t_2), t_2) - F(x_s(t_1), y(t_1), z_s(t_1), t_1)}{t_2 - t_1} = \frac{\partial F}{\partial t}$$

(31)

Equation (27) can be rewritten to equation (32).

$$(x_2 - x_1) \frac{\partial F}{\partial x} + (y_2 - y_1) \frac{\partial F}{\partial y} + (z_2 - z_1) \frac{\partial F}{\partial z} + (t_2 - t_1) \frac{\partial F}{\partial t} = 0$$

(32)

$u_{int}$ is defined as $\frac{r_s(t_2) - r_s(t_1)}{t_2 - t_1}$, consequently

$$\frac{\partial F}{\partial t} + u_{int} \cdot \nabla F = 0$$

(33)

The normal vector at the surface is defined as:

$$n_s = \frac{1}{|\nabla F|} \nabla F$$

(34)

From mass conservation equation (35) is obtained.

$$u \cdot n_s = u_{int} \cdot n_s = -\frac{1}{|\nabla F|} \frac{\partial F}{\partial t}$$

(35)

From the definition of the function $F$, the following expressions are obtained

$$\frac{\partial F}{\partial t} = -\frac{\partial h}{\partial t}$$

$$n_s = \frac{1}{|\nabla F|} \left( \frac{\partial F}{\partial x} \frac{\partial F}{\partial y} \right) = \frac{1}{|\nabla F|} \left( -\frac{\partial h}{\partial x} - \frac{\partial h}{\partial y}, 1 \right)$$

(36)

Combining equation (35) and equation (36) and using $u_{int} = (u_x, u_y, u_z)$ then results in

$$\frac{1}{|\nabla F|} \left( -u_x \frac{\partial h}{\partial x} - u_y \frac{\partial h}{\partial y} + u_z \right) = \frac{1}{|\nabla F|} \frac{\partial h}{\partial t}$$

(37)
Which reduces to equation (38):
\[
-u_x \frac{\partial h}{\partial x} - u_y \frac{\partial h}{\partial y} + u_z = \frac{\partial h}{\partial t} \quad \text{at} \quad z = h(x, y, t)
\] (38)

By combining equation (27) and equation (38) the following expression can be obtained
\[
\frac{\partial h}{\partial t} = -\frac{\partial u_x}{\partial x} - \frac{\partial u_y}{\partial y} \quad \text{(39)}
\n
The next step is to determine the fluxes $Q_x$ and $Q_y$. In order to do this the velocity profiles in the flow have to be determined. Therefore the stress conditions at a fluid-fluid interface are investigated. A schematic drawing of the interface is given in Figure 39.

![Figure 39: Schematic drawing of the fluid-fluid interface.](image)

Newton’s law for the fluid parcel $V(t)$ is given by
\[
\frac{d}{dt} \int_{V(t)} \rho \mathbf{u} \, dV = \sum \mathbf{F} = \mathbf{F}_{\text{body}} + \mathbf{F}_{\text{surface}} + \mathbf{F}_{\text{line}}
\] (40)

In this equation the body and surface forces also exist in the bulk material whereas the line forces are specific for the interface. In the limit where $L$ goes to zero the volume integrals vanish:
\[
\frac{d}{dt} \int_{V(t)} \rho \mathbf{u} \, dV \xrightarrow{L \to 0} 0
\] (41)

\[
\mathbf{F}_{\text{body}} = \int_{V(t)} \rho \mathbf{g} \, dV \xrightarrow{L \to 0} 0
\]

The contributions of the edges on the surface integral also vanish, which results in equation (42).
\[
\mathbf{F}_{\text{surface}} = \int_{S(t)} \overline{\mathbf{S}} \cdot \mathbf{n} \, dS \xrightarrow{L \to 0} \int_{S(t)} (\overline{\mathbf{S}}_2 - \overline{\mathbf{S}}_1) \cdot \mathbf{n}_s \, dS
\] (42)

The line integral for the line forces is a result from the surface tension that exerts an outward pull on the control volume.
\[
\mathbf{F}_{\text{line}} = \int_{\delta S(t)} \gamma \mathbf{m} \, dl
\] (43)

To write the line forces in a similar expression as the body surface force, the surface divergence theorem is used which is given in equation (45).
\[
\int_{\delta S(t)} \nabla_s \cdot \mathbf{a} \, dS = \int_{\delta S(t)} \mathbf{a} \cdot \mathbf{m} \, dl - \int_{S(t)} 2\kappa \mathbf{n} \cdot \mathbf{n}_s \, dS
\] (44)

Where $\mathbf{a} := \gamma \mathbf{c}$ and $\gamma$ is a constant vector, $2\kappa := -\nabla_s \cdot \mathbf{n}_s$ that takes into account the curvature of the control volume and $\nabla_s$ is the surface gradient. The curvature term is written in equation (45).
\[
-\nabla_s \cdot \mathbf{n}_s = \frac{\frac{\partial^2 h}{\partial x^2} \left[1 + \left(\frac{\partial h}{\partial y}\right)^2\right] \frac{\partial^2 h}{\partial y^2} + \frac{\partial^2 h}{\partial x^2} \left[1 + \left(\frac{\partial h}{\partial x}\right)^2\right] \frac{\partial^2 h}{\partial x \partial y} - 2 \frac{\partial h \partial h \partial^2 h}{\partial x \partial y \partial x \partial y}}{\left[1 + \left(\frac{\partial h}{\partial x}\right)^2 + \left(\frac{\partial h}{\partial y}\right)^2\right]^{3/2}}
\] (45)
From this an expression for the line force is obtained:

\[ F_{\text{line}} = \int_{S_{j}(t)} \mathbf{y} \cdot d\mathbf{l} = \int_{S_{j}(t)} (\nabla \mathbf{y} + 2\kappa \mathbf{n}) \cdot dS \]  

(46)

Inserting equation (42) and (45) in equation (40) results in equation (47).

\[ \int_{S_{j}(t)} \left[ (\mathbf{S}_2 - \mathbf{S}_1) \cdot \mathbf{n} + \nabla \mathbf{y} + 2\kappa \mathbf{n} \right] \cdot dS = 0 \]  

(47)

Since the control volume is arbitrary the integrand must vanish and the stress condition at a fluid-fluid interface is found.

\[ (\mathbf{S}_2 - \mathbf{S}_1) \cdot \mathbf{n} + \nabla \mathbf{y} + 2\kappa \mathbf{n} = 0 \]  

(48)

The stress tensor can be split in a normal and two tangential components using \( \mathbf{S} = p\mathbf{I} + \mathbf{T} \) and multiplication by \( \mathbf{n} \) and \( \mathbf{t} \) respectively.

\[ p_1 - p_2 + \mathbf{n} \cdot (\mathbf{T}_2 - \mathbf{T}_1) \cdot \mathbf{n} + 2\kappa \mathbf{y} = 0 \]

\[ \mathbf{t} \cdot (\mathbf{T}_2 - \mathbf{T}_1) \cdot \mathbf{n} + \mathbf{t} \cdot \nabla \mathbf{y} = 0 \]  

(49)

The stress conditions can be simplified for thin liquid films, which implies that the liquid-air interface is nearly flat, \( \frac{h}{L} = \varepsilon \ll 1 \), and that the vertical velocities are much smaller than the horizontal components. Therefore the interface slopes are small, \( \frac{\partial h}{\partial x} \sim \frac{h}{L} = \varepsilon \ll 1 \), and terms of order \( \varepsilon \) and higher are neglected.

Furthermore, the viscous stresses in the gas phase are neglected since they are much smaller than in the liquid due to the smaller viscosity in the gas. As a result the viscous stress tensor in the gas phase can be neglected with respect to the viscous stress tensor in the liquid phase. This leads to \( \mathbf{T}_2 = 0 \). Finally the pressure in the gas is assumed to be constant because the hydrostatic pressure contribution in the gas phase can be neglected as a result of the low density in the gas phase compared to the liquid phase. Therefore \( p_2 = p_{\text{amb}} = \text{constant} \).

The definition for the components of the viscous stress tensor is given in equation (50).

\[ T_{ij} = \mu \left( \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right) \]  

(50)

The viscous stress tensor and the unit vectors are defined below, the tangential components are obtained by creating a vector that is tangential to the normal vector \( \mathbf{n} \).

\[ \mathbf{T} = \mu \begin{pmatrix} \frac{\partial u_x}{\partial x} + \frac{\partial u_y}{\partial y} & \frac{\partial u_x}{\partial x} + \frac{\partial u_z}{\partial z} & \frac{\partial u_y}{\partial x} + \frac{\partial u_z}{\partial z} \\ \frac{\partial u_y}{\partial x} & \frac{\partial u_y}{\partial y} + \frac{\partial u_z}{\partial z} & \frac{\partial u_y}{\partial x} + \frac{\partial u_z}{\partial z} \\ \frac{\partial u_z}{\partial x} & \frac{\partial u_z}{\partial y} & \frac{\partial u_z}{\partial z} + \frac{\partial u_x}{\partial x} \end{pmatrix} \]

\[ \mathbf{n} = \frac{1}{|\nabla P|} \begin{pmatrix} \frac{\partial P}{\partial x} \frac{\partial P}{\partial y} \frac{\partial P}{\partial z} \\ \frac{\partial P}{\partial x} & \frac{\partial P}{\partial y} & \frac{\partial P}{\partial z} \end{pmatrix} = \frac{1}{\sqrt{(\frac{\partial h}{\partial x})^2 + (\frac{\partial h}{\partial y})^2 + 1}} \begin{pmatrix} -\frac{\partial h}{\partial x} - \frac{\partial h}{\partial y} \\ 1 \end{pmatrix} \]  

(51)

\[ \mathbf{t}_1 = \frac{1}{\sqrt{1 + (\frac{\partial h}{\partial x})^2}} \begin{pmatrix} 1, 0, \frac{\partial h}{\partial x} \end{pmatrix} \]

\[ \mathbf{t}_2 = \frac{1}{\sqrt{1 + (\frac{\partial h}{\partial y})^2}} \begin{pmatrix} 0, 1, \frac{\partial h}{\partial y} \end{pmatrix} \]
From the definition an expression for \( \mathbf{n}_s \cdot \mathbf{T} \cdot \mathbf{n}_s \) is obtained in equation (52).

\[
\mathbf{n}_s \cdot \mathbf{T} \cdot \mathbf{n}_s = \frac{\mu}{(\frac{\partial h}{\partial x})^2 + (\frac{\partial h}{\partial y})^2 + 1} \left( -\frac{\partial h}{\partial x}, -\frac{\partial h}{\partial y}, 1 \right) \left( \begin{array}{c} \frac{\partial u_x}{\partial x} + \frac{\partial u_x}{\partial y} + \frac{\partial u_z}{\partial z} \\ \frac{\partial u_y}{\partial x} + \frac{\partial u_y}{\partial y} + \frac{\partial u_z}{\partial z} \\ 2 \frac{\partial u_z}{\partial y} \end{array} \right) \left( \begin{array}{c} -\frac{\partial h}{\partial x} \\ -\frac{\partial h}{\partial y} \\ 1 \end{array} \right) = \frac{\mu}{(\frac{\partial h}{\partial x})^2 + (\frac{\partial h}{\partial y})^2 + 1} \left( -\frac{\partial h}{\partial x}, -\frac{\partial h}{\partial y}, 1 \right) \left( \begin{array}{c} 2 \frac{\partial u_x}{\partial x} - \frac{\partial u_x}{\partial y} + \frac{\partial u_z}{\partial z} \\ 2 \frac{\partial u_y}{\partial x} - \frac{\partial u_y}{\partial y} + \frac{\partial u_z}{\partial z} \\ 2 \frac{\partial u_z}{\partial y} \end{array} \right) \left( \begin{array}{c} -\frac{\partial h}{\partial x} \\ -\frac{\partial h}{\partial y} \\ 1 \end{array} \right) \right)
\]

(52)

After calculating the inner product, nondimensionalizing and neglecting terms of order \( \varepsilon \) and higher equation (51) reduces to:

\[
\mathbf{n}_s \cdot \mathbf{T} \cdot \mathbf{n}_s = \frac{2\mu U}{L} \left( -\frac{\partial h}{\partial x} - \frac{\partial h}{\partial y} + \frac{\partial u_z}{\partial z} \right) - \frac{\gamma L}{\varepsilon} \left( \frac{\partial^2 h}{\partial x^2} + \frac{\partial^2 h}{\partial y^2} \right)
\]

(53)

This result is then implemented in the normal component of the stress condition (equation (49)) to obtain:

\[
p_1 = p_{amb} + 2\mu \left( -\frac{\partial h}{\partial x} - \frac{\partial h}{\partial y} + \frac{\partial u_z}{\partial z} \right) + 2k
\]

(54)

After simplification of the curvature term by nondimensionalizing and neglecting terms in order \( \varepsilon \) and higher this reduces to

\[
\frac{p_1}{p_0} = \frac{p_{amb}}{p_0} + 2\mu \left( -\frac{\partial h}{\partial x} - \frac{\partial h}{\partial y} + \frac{\partial u_z}{\partial z} \right) - \frac{\gamma L}{\varepsilon} \left( \frac{\partial^2 h}{\partial x^2} + \frac{\partial^2 h}{\partial y^2} \right)
\]

(55)

Rewriting by multiplying with \( p_0 \) then results in:

\[
p_1 = p_{amb} + 2\mu \frac{L^2}{\varepsilon} \left( -\frac{\partial h}{\partial x} - \frac{\partial h}{\partial y} + \frac{\partial u_z}{\partial z} \right) - \frac{\gamma L}{\varepsilon} \left( \frac{\partial^2 h}{\partial x^2} + \frac{\partial^2 h}{\partial y^2} \right)
\]

(56)

Where \( \frac{\gamma L}{\varepsilon} \) is the capillary number and from which we find that \( U \) is of order \( \varepsilon^2 \) since the aim is to investigate the surface tension effects on the pressure [34]. Therefore the second term on the right side is much smaller than the other terms (order \( \varepsilon^3 \)) and equation (56) reduces to:

\[
p_1(h) = p_{amb} - \frac{\gamma}{\varepsilon} \left( \frac{\partial^2 h}{\partial x^2} + \frac{\partial^2 h}{\partial y^2} \right)
\]

(57)

Now the tangential part of the stress condition is investigated.

\[
-\mathbf{t} \cdot \mathbf{T}_1 \cdot \mathbf{n}_s + \mathbf{t} \cdot \nabla \mathbf{y} = 0
\]

(58)

Where \( \nabla \mathbf{y} \) is defined as [35],

\[
\nabla \mathbf{y}_s = \frac{1}{(\frac{\partial h}{\partial x})^2 + (\frac{\partial h}{\partial y})^2 + 1} \left[ \begin{array}{c} 1 + \left( \frac{\partial h}{\partial y} \right)^2 \frac{\partial}{\partial x} - \frac{\partial h}{\partial y} \frac{\partial}{\partial y} \\ -\frac{\partial h}{\partial x} \frac{\partial}{\partial y} + \left( 1 + \left( \frac{\partial h}{\partial x} \right)^2 \frac{\partial}{\partial y} \right) \frac{\partial}{\partial x} \\ \frac{\partial h}{\partial x} + \frac{\partial h}{\partial y} \frac{\partial}{\partial y} \end{array} \right]
\]

(59)

At first the second term in equation (59) is investigated with both \( \mathbf{t}_1 \) and \( \mathbf{t}_2 \):

\[
\mathbf{t}_1 \cdot \nabla \mathbf{y}_s = \frac{1}{(\frac{\partial h}{\partial x})^2 + (\frac{\partial h}{\partial y})^2 + 1} \left[ 1 + \left( \frac{\partial h}{\partial y} \right)^2 \right] \frac{\partial}{\partial x} \frac{\partial h}{\partial y} + \left( 1 + \left( \frac{\partial h}{\partial x} \right)^2 \frac{\partial}{\partial y} \right) \frac{\partial}{\partial y} + \frac{\partial h}{\partial x} \frac{\partial}{\partial x} + \frac{\partial h}{\partial y} \frac{\partial}{\partial y}
\]

(60)

Once again, this term is nondimensionalized and terms of \( \varepsilon \) and higher are neglected to obtain:

\[
\mathbf{t}_1 \cdot \nabla \mathbf{y}_s = \frac{\partial}{\partial x}
\]

(61)
For the second tangential component a similar expression can be found:

\[
 t_2 \cdot \nabla_y = \frac{1}{\left( \frac{\partial h}{\partial x} \right)^2 + \left( \frac{\partial h}{\partial y} \right)^2 + 1} \left( 1 + \frac{\partial h}{\partial x} \right) \left( \frac{\partial h}{\partial x} \right) + \frac{\partial h}{\partial y} \frac{\partial h}{\partial y} + \left( \frac{\partial h}{\partial y} \right)^2 + y
\]  

(62)

This reduces to equation (63) after nondimensionalizing and neglecting terms of \( e \) and higher:

\[
 t_2 \cdot \nabla_y = \frac{\partial y}{\partial y}
\]  

(63)

Finally the term \( t \cdot \mathbf{T}_1 \cdot n_s \) is evaluated.

\[
 t_1 \cdot \mathbf{T}_1 \cdot n_s = \mu \left[ 1, 0, \frac{\partial h}{\partial x} \right] \cdot \left[ -\frac{2 \partial h}{\partial x} \frac{\partial u_x}{\partial x} - \frac{\partial h}{\partial y} \frac{\partial u_x}{\partial y} - \frac{\partial h}{\partial x} \frac{\partial u_y}{\partial x} + \frac{\partial u_y}{\partial y} \frac{\partial u_x}{\partial y} + \frac{\partial u_x}{\partial y} \right] + \ldots
\]  

(64)

This is also nondimensionalized and terms of \( e \) and higher are neglected to obtain:

\[
 t_1 \cdot \mathbf{T}_1 \cdot n_s = \mu \frac{\partial u_x}{\partial x}
\]  

(65)

The same method is used to find an expression for \( t_2 \cdot \mathbf{T}_1 \cdot n_s \) which becomes:

\[
 t_2 \cdot \mathbf{T}_1 \cdot n_s = \mu \frac{\partial u_y}{\partial y}
\]  

(66)

From the above the tangential components at the interface reduces to

\[
 \mu \frac{\partial u_x}{\partial x} = \frac{\partial y}{\partial x} \quad \text{and} \quad \mu \frac{\partial u_y}{\partial y} = \frac{\partial y}{\partial y} \quad \text{at} \quad z = h
\]  

(67)

From the Navier Stokes equation, the expressions for the pressure are derived in equation (21). From which can be concluded that the pressure is independent of \( z \). And the following expressions are obtained for the velocities:

\[
 u_x = \frac{1}{\mu} \frac{\partial}{\partial x} \left( \frac{x^2}{2} + z f_1(x, y, t) + g_1(x, y, t) \right)
\]

\[
 u_y = \frac{1}{\mu} \frac{\partial}{\partial y} \left( \frac{x^2}{2} + z f_2(x, y, t) + g_2(x, y, t) \right)
\]  

(68)

By application of the boundary conditions at the solid-liquid (\( z = 0 \)) and liquid-liquid interface (\( z = h \)) the velocity profile becomes:

\[
 u_x = \frac{1}{\mu} \frac{\partial}{\partial x} \left( \frac{x^2}{2} - h z \right) + z \frac{\partial y}{\partial x}
\]

\[
 u_y = \frac{1}{\mu} \frac{\partial}{\partial y} \left( \frac{x^2}{2} - h z \right) + \frac{\partial y}{\partial y}
\]  

(69)

From equation (69) the fluxes can be calculated to be:

\[
 Q_x = \int_0^h \frac{1}{\mu} \frac{\partial}{\partial x} \left( \frac{x^2}{2} - h z \right) + z \frac{\partial y}{\partial x} \ dx = \left[ \frac{1}{\mu} \frac{\partial}{\partial x} \left( \frac{x^3}{6} - h z \frac{x^2}{2} \right) \right]_0^h = \frac{1}{\mu} \frac{\partial}{\partial x} \left( \frac{h^3}{6} - \frac{h^3}{2} + \frac{h^3}{2} \right)
\]

\[
 Q_y = \int_0^h \frac{1}{\mu} \frac{\partial}{\partial y} \left( \frac{x^2}{2} - h z \right) + \frac{\partial y}{\partial y} \ dx = \left[ \frac{1}{\mu} \frac{\partial}{\partial y} \left( \frac{x^3}{6} - h z \frac{x^2}{2} \right) \right]_0^h = \frac{1}{\mu} \frac{\partial}{\partial y} \left( \frac{h^3}{6} - \frac{h^3}{2} + \frac{h^3}{2} \right)
\]  

(70)
Rewriting equation (71) then results in:

\[ Q_x = -\frac{h^3}{3\mu} \frac{\partial p}{\partial x} - \frac{h^3}{2\mu} \frac{\partial v}{\partial x} \]

\[ Q_y = -\frac{h^3}{3\mu} \frac{\partial p}{\partial y} + \frac{h^3}{2\mu} \frac{\partial v}{\partial y} \]  

(71)

These results are inserted in equation (40) to obtain the lubrication approximation:

\[ \frac{\partial h}{\partial t} + \frac{\partial}{\partial x} \left( \frac{h^3}{2\mu} \frac{\partial v}{\partial x} - \frac{h^3}{3\mu} \frac{\partial v}{\partial x} \right) + \frac{\partial}{\partial y} \left( \frac{h^3}{2\mu} \frac{\partial v}{\partial y} - \frac{h^3}{3\mu} \frac{\partial v}{\partial y} \right) = 0 \]  

(72)

For a one dimensional case and assuming the surface tension of the liquid to be constant, equation (72) can be simplified to:

\[ 3\mu \frac{\partial h}{\partial t} = \frac{\partial}{\partial x} \left( h^3 \frac{\partial p}{\partial x} \right) \]  

(73)

3.1.4 Derivation of electric force terms

In section 3.1.3 the lubrication approximation was derived. Now the electrical terms need to be included. To do this an extra component is added to the stress condition in equation (49) in the form of the Maxwell stress tensor. However this component is not coupled to any of the other components in the stress condition and the electric contribution is derived separately and later inserted in the final equation.

A series of assumptions is made in the derivation.

1. The bulk charge density of the liquid is zero
2. The surface charge density at the liquid – air interface is zero
3. The surface charge density at the liquid – solid interface varies gradually (on a length scale larger than the height of the air gap)
4. Magnetic fields and conduction currents are absent
5. The liquid is a simple dielectric with constant and uniform relative permittivity

The third assumption is necessary to use the lubrication approximation. In the case that the magnetic terms are absent, the Maxwell stress tensor is given by equation (74):

\[ S_{\text{el}}^{\text{el}} = \varepsilon \varepsilon_0 \left( \mathbf{E} \mathbf{E} - \frac{1}{2} \varepsilon^2 \mathbf{E} \right) \]  

(74)

Where \( \mathbf{E} \) is the electric field vector, \( \mathbf{E} \) the unity tensor and \( \varepsilon \) the dielectric constant of the medium. The electric body force density is given by the divergence of the Maxwell stress tensor.

\[ f^{\text{el}} = \nabla \cdot S^{\text{el}} \]  

(75)

Therefore an expression for the individual components can be obtained as written in equation (76)

\[ f_{i}^{\text{el}} = \frac{\partial}{\partial x_i} \left[ \varepsilon \varepsilon_0 \left( E_i E_j - \frac{1}{2} E^2 \delta_{ij} \right) \right] = \varepsilon \varepsilon_0 \left[ E_i \frac{\partial}{\partial x_j} (\varepsilon E_j) + E_j \frac{\partial}{\partial x_i} (\varepsilon E_i) - \frac{\varepsilon}{2} \frac{\partial}{\partial x_i} (E^2) \right] \]  

(76)

The total electric body force then becomes

\[ f^{\text{el}} = \varepsilon \varepsilon_0 \left[ 0 + \mathbf{E} \cdot \nabla \mathbf{E} - \frac{1}{2} \nabla E^2 \right] = -\varepsilon \varepsilon_0 \mathbf{E} \times (\nabla \times \mathbf{E}) = 0 \]  

(77)

In equation (77) three equations where used:

\( -\mathbf{E} \times (\nabla \times \mathbf{E}) = -\frac{1}{2} \nabla (E^2) \)  

(78)

\[ \nabla \cdot \mathbf{D} = \nabla \cdot (\varepsilon \mathbf{E}) = \rho^{\text{el}} = 0 \]  

(79)

\[ \nabla \times \mathbf{E} = -\frac{\partial \mathbf{D}}{\partial t} = 0 \]  

(80)
In equations (79) and (80) respectively assumptions 1 and 4 are used. From equation (77) can be concluded that there is no electric bulk force. The stress condition at the liquid – air interface is given in equation (81)

\[
\left(\mathbf{S}_2^{\text{tot}} - \mathbf{S}_1^{\text{tot}}\right) \cdot \mathbf{n}_z + \nabla \psi + 2\kappa \mathbf{n}_z = 0
\]  

Equation (81) is split into a normal and a tangential component in the same way as in equation (49). The contribution of the Maxwell stress tensor to the shear condition is given by:

\[
\mathbf{t} \cdot \left(\mathbf{F}_1^{el} - \mathbf{T}_a^{el}\right) \cdot \mathbf{n}_z
\]

\[
\mathbf{t} \cdot \left[\varepsilon_0 \left(\mathbf{E}_1 \mathbf{E}_1 - \frac{1}{2} \mathbf{E}_1^2 \mathbf{E}\right) - \varepsilon_0 \left(\mathbf{E}_a \mathbf{E}_a - \frac{1}{2} \mathbf{E}_a^2 \mathbf{E}\right)\right] \cdot \mathbf{n}_z = \mathbf{t} \cdot \left[\varepsilon_0 \varepsilon_0 (\mathbf{E}_1 \mathbf{E}_1 - \frac{1}{2} \mathbf{E}_1^2 \mathbf{E}) - \varepsilon_0 (\mathbf{E}_a \mathbf{E}_a - \frac{1}{2} \mathbf{E}_a^2 \mathbf{E})\right] \cdot \mathbf{n}_z
\]

Where \(\varepsilon_1\) and \(\varepsilon_a\) are respectively the dielectric constant of the liquid and of the air. The equality in equation (82) holds since the inner product between the tangential and normal unit vector is always equal to zero \((\mathbf{t} \cdot \mathbf{n}_z = 0)\). Due to continuity of the tangential component of the electric field \((E_\| = E_{\text{at}})\) equation (83) can be rewritten as:

\[
\varepsilon_0 E_\| (E_\| E_\|) - \varepsilon_0 E_0 (E_\| E_\| - E_\| E_\|) = \varepsilon_0 E_\| (D_\| - D_\|) = 0
\]

Because the surface charge density is zero at the liquid – air interface (by assumption 2). Therefore the tangential component of the stress condition is unaffected by the electric stresses. The contribution of the Maxwell stress tensor on the normal component of the stress condition is given in equation (85).

\[
\mathbf{n}_z \cdot \left(\mathbf{S}_1^{el} - \mathbf{S}_a^{el}\right) \cdot \mathbf{n}_z = \mathbf{n}_z \cdot \left[\varepsilon_0 \left(\mathbf{E}_1 \mathbf{E}_1 - \frac{1}{2} \mathbf{E}_1^2 \mathbf{E}\right) - \varepsilon_0 \left(\mathbf{E}_a \mathbf{E}_a - \frac{1}{2} \mathbf{E}_a^2 \mathbf{E}\right)\right] \cdot \mathbf{n}_z
\]

After rewriting equation (85) and using that \(E_\| = E_\|^2 + E_{\text{at}}^2\), equation (86) is obtained.

\[
\varepsilon_0 \left((\mathbf{n}_z \cdot \mathbf{E}_1)^2 - \frac{1}{2} \mathbf{E}_1^2 \mathbf{E}\right) - \varepsilon_0 \left((\mathbf{n}_z \cdot \mathbf{E}_a)^2 - \frac{1}{2} \mathbf{E}_a^2 \mathbf{E}\right) = \frac{1}{2} \varepsilon_0 (E_\|^2 - E_{\text{at}}^2) - \frac{1}{2} \varepsilon_0 (E_\|^2 - E_{\text{at}}^2) = \frac{1}{2} \varepsilon_0 (E_\|^2 - E_{\text{at}}^2) - \frac{1}{2} \varepsilon_0 (E_\|^2 - E_{\text{at}}^2)
\]

The last term in equation (86) is zero since there are no charges at the liquid – air interface (assumption 2) and therefore \(D_\| - D_{\text{at}} = 0\). Equation (86) is rewritten using \(\nabla \psi = E\) to obtain equation (87).

\[
\mathbf{n}_z \cdot \left(\mathbf{S}_1^{el} - \mathbf{S}_a^{el}\right) \cdot \mathbf{n}_z = \frac{1}{2} \varepsilon_0 [\nabla (\psi_\| \cdot \mathbf{n}_z)^2 - \varepsilon_4 (\nabla \psi_\| \cdot \mathbf{n}_z)^2]
\]

This is the contribution of the electric components to the normal component of the stress condition. To investigate the importance of the different terms, the terms are nondimensionalized and all terms of order \(\varepsilon (= H/L)\) and higher are neglected.

\[
\nabla \psi \cdot \mathbf{n}_z = \frac{1}{\sqrt{\left(\frac{\partial \psi}{\partial x}\right)^2 + \left(\frac{\partial \psi}{\partial y}\right)^2 + 1}} \left( - \frac{\partial \psi}{\partial x} - \frac{\partial \psi}{\partial y} \frac{\partial \psi}{\partial y} + \frac{\partial \psi}{\partial z}\right)
\]

Where \(\psi\) is the electric potential. In the root, the third term is dominant since it scales with \(1\) whereas the first two terms scale with \(\varepsilon^2\). The dimensionless form of the term in brackets is given in equation (89).

\[
\begin{pmatrix}
- \frac{\partial \psi}{\partial x} - \frac{\partial \psi}{\partial y} \frac{\partial \psi}{\partial y} + \frac{\partial \psi}{\partial z}\end{pmatrix} = \frac{\psi_0}{H} \left( - \frac{\partial \psi}{\partial x} - \frac{\partial \psi}{\partial y} \frac{\partial \psi}{\partial y} + \frac{\partial \psi}{\partial z}\right)
\]
The third term in brackets is of order 1 whereas the first to terms scale with order \( \varepsilon^2 \). As a result the terms in equation (87) can be approximated as:

\[
\mathbf{n}_s \cdot \left( \hat{\mathbf{S}}_s^{el} - \hat{\mathbf{S}}_s^{el} \right) \cdot \mathbf{n}_s = \frac{1}{2} \varepsilon_0 \left[ \varepsilon_1 \left( \frac{\partial \Phi}{\partial z} \right)^2 - \varepsilon_s \left( \frac{\partial \Phi}{\partial z} \right)^2 \right]
\]  

(90)

As can be seen in equation (91), only the first derivative of the potential in the liquid and in the air are necessary to compute the effects of surface charges on a thin liquid film. Therefore the next step is to compute the potential resulting from the surface charges on a substrate. The geometry used for the calculation is given in Figure 40. The top and bottom plate are connected to ground and therefore the potential at the top plate and at the bottom of the substrate are equal to zero.

Figure 40: Schematic drawing of the geometry to calculate the potential in the solid – liquid – air system.

The potential \( \psi \) is piecewise linear since \( \nabla^2 \psi = 0 \) in the absence of bulk charges (assumption 1). This results in the following expressions for the potential in each part of the system:

\[
\begin{align*}
\psi_s &= c_1 + c_2 z \\
\psi_l &= c_3 + c_4 z \\
\psi_a &= c_5 + c_6 z
\end{align*}
\]  

(91)

The constants \( c_4 \) and \( c_6 \) are most interesting since they are equal to \( \frac{\partial \psi_1}{\partial z} \) and \( \frac{\partial \psi_a}{\partial z} \) of equation (90) respectively. By inserting the known boundary conditions \( \psi = 0 \) at \( z = D \) and \( z = -d \), equation (91) can be rewritten to equation (92).

\[
\begin{align*}
\psi_s &= c_2(z + d) \\
\psi_l &= c_3 + c_4 z \\
\psi_a &= c_6(z - D)
\end{align*}
\]  

(92)

There are also 4 boundary conditions at the interfaces:

- The continuity condition of the potential at the liquid – air and at the solid – liquid boundary.
- The continuity condition of the first derivative of the potential at the liquid – air boundary, since there are no surface charges at this boundary (assumption 2).
- A jump in the first derivative of the potential at the solid – liquid boundary due to the surface charges on this boundary.

These boundaries can also be written in formulas:

\[
\begin{align*}
\psi_s &= \psi_l & \text{at } (z = 0) & \quad (93.1) \\
\psi_l &= \psi_a & \text{at } (z = h) & \quad (93.2) \\
\varepsilon_l \frac{\partial \psi_l}{\partial z} - \varepsilon_s \frac{\partial \psi_s}{\partial z} &= \frac{\sigma}{\varepsilon_0} & \text{at } (z = 0) & \quad (93.3) \\
\varepsilon_a \frac{\partial \psi_a}{\partial z} - \varepsilon_l \frac{\partial \psi_l}{\partial z} &= 0 & \text{at } (z = h) & \quad (93.4)
\end{align*}
\]
After applying these boundary conditions to the equations from equation (92), the following equations are obtained:

\[ c_2d = c_3 \]  \hspace{1cm} (94.1)

\[ c_3 + c_4h = c_a(h - D) \]  \hspace{1cm} (94.2)

\[ \varepsilon_c c_4 - \varepsilon_a c_2 = \frac{\sigma}{\varepsilon_a} \]  \hspace{1cm} (94.3)

\[ \varepsilon_a c_6 - \varepsilon_c c_4 = 0 \]  \hspace{1cm} (94.4)

With the expressions in equation (94) there are 4 equations with 4 unknown which can be solved. This results in the following expressions for \( c_6 \) and \( c_4 \).

\[ c_6 = \frac{c_1 c_4}{c_a} \]  \hspace{1cm} (95.1)

\[ c_4 = \frac{\sigma}{\varepsilon_a d} \left( \frac{2 h - \varepsilon_a c_a (h - D)}{d} \right) \]  \hspace{1cm} (95.2)

These results can be used to simulate the behavior of a thin liquid film when the surface charges on the substrates are known. The pressure term for this problem consists of three terms; the capillary pressure as derived in equation (57), a hydrostatic pressure term due to gravity and an electric contribution that is derived in equation (90). This pressure term is used in the calculation of the time derivative of the film thickness which is derived in equation (73). Therefore the governing equations for this problem that are implemented in Comsol Multiphysics are:

\[ p = -\gamma \frac{\partial^2 h}{\partial x^2} + \rho gh + \varepsilon_a (\varepsilon c_4^2 - \varepsilon_a c)^2 \]  \hspace{1cm} (96.1)

\[ 3\mu \frac{\partial h}{\partial t} = \frac{a}{h^3} \left( h^2 \frac{\partial p}{\partial x} \right) \]  \hspace{1cm} (96.2)
3.2 Experimental set-up
In this section the experimental set-up to deposit the thin liquid films and the set-up to measure the film thickness are discussed. Furthermore the measurement method is discussed in which the steps from a charge pattern to a measurement of the deformed film are explained.

3.2.1 Layout of the experimental set-up
The liquid film is spin coated on the substrates with a model CEE200 spin coater from Brewer Science. A picture of the spin coater is given in Figure 41. The spin time and speed can be controlled which influences the final film thickness of the spin coated film.

![Picture of the Brewer Science spin coater](image)

*Figure 41: Picture of the Brewer Science spin coater used to apply the thin films on the substrates.*

After spin coating the thin liquid film, the film deformations are measured by means of optical interferometry using an upright Olympus BX51 microscope. The microscope is connected to a computer with a Pike 145B camera from AVT. The interference pattern can then be saved on the computer and analyzed at a later time. A schematic drawing of the set-up to measure the film deformations is given in Figure 42.

![Schematic drawing of the set-up](image)

*Figure 42: Schematic drawing of the set-up to measure film deformations in the thin liquid film.*

As shown in Figure 42 the 0.75 mm thick polycarbonate substrate is placed on top of a grounded plate. A grounded piece of ITO glass (i.e. glass with a conductive coating of indium tin oxide) is positioned above the substrate. This is done to make sure the electrical boundary conditions are well-controlled and surroundings
of the substrate are identical in each measurement and the charges influencing the liquid film (squalane) are only the charges on the substrate. The spacing between the aluminum bottom plate and the grounded ITO glass is always 1.5 mm. The light source used by the microscope has a wavelength of 650 nm and the objective has a magnification of 2.5 times. The scale of the recorded microscope pictures are calibrated with a calibration sample. This sample has squares of 200µm and is given in Figure 43. The calibration factor is determined to be 234 pixels / mm.

![Figure 43: Recording of the calibration sample with the microscope.](image)

### 3.2.2 Measurement method

For each measurement of the deformation of a thin liquid film above a charge pattern a series of steps is conducted. These steps include applying the surface charge pattern, spin coating a liquid film and measuring the film deformations. The first step is to write a charge pattern and to measure the written charges. These steps are explained in detail in chapter 2 and will therefore not be discussed here.

#### 3.2.2.1 Applying a thin liquid film

After writing a charge pattern and measuring this pattern, a thin liquid film is spin coated on the substrate. In this research a thin layer of squalane (Aldrich, 234311) is deposited on the (Makrofol) polycarbonate substrate. The spin coater has an initialization step and a second step in which the film is actually spin coated to form the thin liquid film. First, a thick layer of squalane is deposited on the substrate manually. The thickness of this layer is of the order of several hundreds of micrometers. Then the first spin coating step is started in which the spin coater rotates at 500 rpm for 5 seconds with an acceleration of 500 rpm/s. This step is to distribute the squalane over the substrate and to get rid of excess amounts of squalane. Then the speed increases to 3000 rpm with an acceleration of 1000 rpm/s and the film is spin coated for a set time (15 seconds unless stated otherwise). After these steps the film has a thickness of the order of 5 µm depending on the spin time.

#### 3.2.2.2 Measuring the interference picture

The next step is to measure the interference pattern of the thin liquid film to determine the height profile. In this step the microscope set-up is used to create a picture of the interference pattern at a given time after spin coating. It is also possible to make a series of pictures to investigate the time evolution of the deformations. From the interference pattern the height profile can be calculated since the fringes have a known height difference between two subsequent fringes (black to white line). This fringe to fringe height difference can be calculated from the wavelength of the light source and the refractive index of the liquid which is given in equation (97).
\[ \Delta h = \frac{\lambda}{4n_{\text{squalane}}} = \frac{650}{4 \times 1.452} = 112 \text{ nm} \] (97)

An example of an interference spectrum measured by the microscope set-up is given in Figure 44. The initial film height of this film is 4 µm which is obtained after spin coating for 15 seconds.

3.2.2.3 Calculating the height profile

The final step is to calculate the height profile from the interference image. As found in section 3.2.2.2 the height difference between a black and a white line is 112 nm. The error due to the bandwidth of the light source is about 2 nm. The height profile can be obtained from the interference image by finding the locations of the centers of the fringes. In order to use this technique, the film height at one position has to be known. The initial thickness after spin coating is measured and is used as the height of the film at a location as far from the written line as possible. The minima and maxima are visible in the interference spectrum since the fringe next to the maximum or minimum connects with itself on both sides of the extreme point. With this data the height profile can be constructed from the locations of the fringes. The positions of the fringes are determined manually and the X- and Y-positions of these fringes are used to calculate the height profile. An example of a height profile obtained in this way is given in Figure 45. The height profile is taken at a horizontal cross section of the interference picture in Figure 44 indicated with the red line.

Figure 44: Interference image of an initially 4 µm thick squalane film above a line of surface charges of 22 µC/m².

Figure 45: Height profile obtained from the interference image in Figure 44.
3.3 Systematic parameter variation

In this chapter the effect of different parameters on the film deformation is given. The time behavior of the deformation will be discussed first. Then the effect of the film thickness, applied surface charge and line width will be discussed. The parameters are varied in both experiments and simulations. For the simulations a Comsol Multiphysics model is used that is discussed in detail in Appendix C.2.

3.3.1 Values of the used constants

The expressions used to simulate the behavior of the thin film were given in section 3.1.3 in equation (96).

\[ p = -\gamma \frac{\partial^2 h}{\partial x^2} + \rho g h + \epsilon_0 (\epsilon_i \epsilon_a^2 - \epsilon_a \epsilon_{e_0}^2) \]  
\[ 3\mu \frac{\partial h}{\partial t} = \frac{\partial}{\partial x} \left( h \frac{3}{2} \frac{\partial p}{\partial x} \right) \]  

The constants \( c_2 \) and \( c_4 \) were given in equation (95).

\[ c_6 = \frac{c_2}{\epsilon_a} \]  
\[ c_4 = \frac{\epsilon_0}{\epsilon_{e_0}^2} \frac{\epsilon_0}{\epsilon_a^2} \frac{\epsilon_{e_0}^2}{\epsilon_a^2} (\frac{\partial h}{\partial x}) \]  

There are a lot of parameters in these equations which are listed in Table 4. These values are used in each simulation unless stated otherwise.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Name</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \gamma )</td>
<td>Surface tension</td>
<td>0.0282</td>
<td>N/m</td>
</tr>
<tr>
<td>( \epsilon_0 )</td>
<td>Dielectric constant of vacuum</td>
<td>8.854 x 10^{-12}</td>
<td>C^2/Nm^2</td>
</tr>
<tr>
<td>( \epsilon_a )</td>
<td>Dielectric constant of the air</td>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>( \epsilon_l )</td>
<td>Dielectric constant of the liquid</td>
<td>2.105</td>
<td>-</td>
</tr>
<tr>
<td>( \epsilon_s )</td>
<td>Dielectric constant of the substrate</td>
<td>2.9</td>
<td>-</td>
</tr>
<tr>
<td>( d )</td>
<td>Thickness of the substrate</td>
<td>0.75 x 10^{-3}</td>
<td>m</td>
</tr>
<tr>
<td>( D )</td>
<td>Distance of the air gap</td>
<td>0.75 x 10^{-3}</td>
<td>m</td>
</tr>
<tr>
<td>( \mu )</td>
<td>Viscosity</td>
<td>0.0205</td>
<td>Ns/m^2</td>
</tr>
<tr>
<td>( \rho )</td>
<td>Density</td>
<td>805</td>
<td>kg/m^3 s^2</td>
</tr>
<tr>
<td>( h_0 )</td>
<td>Initial film height</td>
<td>4 x 10^{-6}</td>
<td>m</td>
</tr>
</tbody>
</table>

The surface charge distribution used in the simulations is designed to resemble the experimental results. The total surface charge on the substrate is kept constant. The exact shape of the surface charge distribution is difficult to measure due to the limited spatial resolution of the measurement probe. Therefore several surface charge distributions are investigated in simulations to see the effect of different distributions. 3 different simulated surface charge distributions are given in Figure 46. The measured surface charges (with a 1 mm probe to substrate distance) are shown in Figure 46 as well. The resulting deformations of the liquid film after 900 seconds are shown in Figure 47.
Figure 46: The measured surface charge distribution by the electrostatic voltmeter (□) and 3 simulated distributions.

Figure 47: Film deformations due to the surface charge distributions from Figure 46.

Figure 47 shows that the distribution $\sigma_p$ results in a very similar profile of the thin liquid film as measured in the experiments. However the surface charge distribution looks very different then the measured surface charge distribution. This is due to the spatial resolution of the probe. The probe is unable to measure a sharp peak such as in the peaked distribution of Figure 46 and instead measures an average over a specific distance. This averaging depends on the type of probe and on the probe to substrate distance as discussed in section 2.1.3.1.
The peaked distribution consists of three parts which are given in equation (98).

\[ \sigma_p = \sigma_0 + \sigma_1 + \sigma_2 + \sigma_3 \]

\[ \sigma_1 = \sigma_{\text{max}} \exp \left( \frac{(x-x_0)^2}{w_{\text{peak}}^2} \right) * (x > x_c) \]

\[ \sigma_2 = \sigma_{\text{slope}} \exp \left( \frac{(x-x_c)}{w_{\text{slope}}} \right) * (x \leq x_c) \]

\[ \sigma_3 = (\sigma_{\text{max}} - \sigma_0 - \sigma_{\text{slope}}) \exp \left( \frac{(x-x_c)^2}{w_{\text{peak}}^2} \right) * (x \leq x_c) \]

The constants in equation (98) are given in Table 5. This charge distribution is used in all the simulations unless stated otherwise.

**Table 5:** The values of the constants used to create the surface charge distribution in the simulations

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Name</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\sigma_0)</td>
<td>Base surface charge</td>
<td>(17 \times 10^{-6})</td>
<td>C/m²</td>
</tr>
<tr>
<td>(\sigma_{\text{max}})</td>
<td>Maximum surface charge of the peak</td>
<td>(58 \times 10^{-6})</td>
<td>C/m²</td>
</tr>
<tr>
<td>(\sigma_{\text{slope}})</td>
<td>Maximum surface charge of the slope</td>
<td>(4 \times 10^{-6})</td>
<td>C/m²</td>
</tr>
<tr>
<td>(x_c)</td>
<td>position of the peak</td>
<td>(0.8 \times 10^{-3})</td>
<td>m</td>
</tr>
<tr>
<td>(w_{\text{peak}})</td>
<td>Width of the peak</td>
<td>(0.05 \times 10^{-3})</td>
<td>m</td>
</tr>
<tr>
<td>(w_{\text{slope}})</td>
<td>Width of the slope</td>
<td>(0.2 \times 10^{-3})</td>
<td>m</td>
</tr>
</tbody>
</table>

### 3.3.2 Time development of the film deformation

The deformation of the thin liquid is time dependent and the deformation increases until equilibrium is obtained between the forces that increase the deformation (the electric forces) and the forces that decrease the deformation (gravity and surface tension). The time to equilibrium is influenced by the viscosity of the fluid. A more viscous fluid will take more time to reach equilibrium than a less viscous one. The behavior of a 4 µm squalane film above a 17 µC/m² line having a width of 2 mm is investigated as function of time. Therefore the film is spin coated on the substrate and a series of measurements of the film height is obtained from the recorded fringe patterns. The height profile at 6 different times is given in Figure 48. The first image is taken 29s after spin coating and the last is taken almost 30 minutes after spin coating. Figure 48 shows that two peaks are formed at the edges of the deformation with dips just outside the peaks. It also shows that a center dip is formed at early times but this dip is eventually filled. Furthermore there is an slight asymmetry in the peak height.
Simulations were also conducted using the surface charge pattern as described in section 3.3.1. The time development for both experiment and simulation are given in Figure 49 for comparison.

Figure 49 shows that the simulations predict a similar behavior as observed with experiments. The peaks are at about the same location. The formation of the outer dips is predicted and the initial dip at the center is also visible. Furthermore the simulations also predict the filling of the center dip at later times. The main difference between the experiments and the simulation is the time. In experiments the peak is formed faster and the maximum height is reached earlier than in the simulations. Another difference is the maximum depth of the dips which are deeper in experiments than in the simulations.
Characteristic features to investigate are the behavior of the maximum peak height and the maximum depth of the dip. The depth of the dip is particularly interesting since a very thin film can result in film rupture at the dip position.

The deformation of the liquid film due to the 2 mm wide line of charges (17 μC/m²) is repeated three times to check the reproducibility of the measurement results. The maximum relative height of the peak can be calculated from equation (99).

\[ h_{r,max} = \frac{h_{peak} - h_0}{h_0} \]  

(99)

The maximum relative height of the peak is investigated as well as the maximum relative depth of the dip.

The time dependent relative height of the peak for these three measurements and for the simulation is given in Figure 50.

In Figure 50 the error bars are a result from the possible error in counting the fringes. For low thickness and therefore low numbers of fringes this error is limited to one fringe. For peaks consisting of more than 15 fringes this error increases to two fringes. And for even peaks higher than 25 fringes this error increases to three fringes.

There is a clear increase of the maximum height visible for the first 300 seconds. After this time the increase in maximum film height stagnates and eventually becomes constant. This effect can also be seen in Figure 48 which shows that after about 200 seconds the peak stops growing. There is still transport of fluid from outside the charged area towards this area, but this is used to fill the centre dip instead of increasing the peak height. Another effect that stagnates the growth of the peak is the leaking of fluid over the edges of the substrate which will be discussed in section 3.3.3.

The simulations also predict an increase of the maximum film deformation with time. The slope of the simulation results is very close to the slope of the experimental data but the increase in peak height stagnates at later times (about 1000 seconds). This difference in time behaviour is also observed in Figure 49. This difference could be a result from the assumptions made in the model, or from the definition of the start of the experiment. In this case the time starts when the spin coating of the thin film is complete. However the deformations in the liquid film might already start during spin coating. This cannot
be checked with the current set-up. In order to check this, the film thickness profile should be measurable in the spin coater during spin coating.

Another cause of the difference could be that the measurement probe does not measure the amount of deposited charges accurately since the spatial accuracy of the measurement probe is of order 0.5 mm. A wider line of charges should give more accurate values of the deposited surface charges. With this measurement a more accurate surface charge distribution can be created to use in the simulations.

The maximum depth of the dip next to the line is also measured and given in Figure 51. The maximum relative depth of the dip is calculated at the dip position as:

$$d_{r,max} = \frac{h_0 - h_{dip}}{h_0}$$

The depths of the three measurements are measured as well as the depth of the dip in the simulations.

![Figure 51: Time dependency of the maximum relative depth of the dip in experiments and simulations.](image)

Figure 51 shows that the simulations predict the same time development as the experiments since the slope of the experimental data (is almost identical to the slope of the simulation. A fit is made through the data points of measurement 3 (green) having a slope of 0.35 whereas the fit of the simulation data (blue) has a slope of 0.33. There is a difference in offset between the simulation and the experiments. This might also be a result of the definition of the starting time.
3.3.3 Film thickness

In this section the influence of the film thickness on the deformation of the liquid film is investigated. Lower film thicknesses can be obtained by spin coating longer with the same speed.

3.3.3.1 Spin time dependency of film thickness

First the dependency of the film thickness on the spin time is investigated. From theory can be found that the film thickness scales with one over the square root of the spin time for large spin times \( h = \frac{h_0}{(1 + \frac{\rho \omega^2}{3\eta} t)^{1/2}} \) (101).

The thickness of the squalane film is measured at the center of the substrate during spin coating using spectral interference \([31]\) to investigate this dependence on spin time. The results from this measurement are given in Figure 52. The measurement is repeated 6 times where the spin coater is stopped at 3, 5, 10, 15, 20 and 30 seconds. The film thickness is measured for at least 100 seconds to investigate the time dependency of the film thickness while and after spin coating.

![Figure 52: The dependency of the film thickness on spin time.](image)

As shown in Figure 52 the film thickness decreases slightly when the spin coater is stopped. This is a result of the low viscosity of the squalane. Due to the low viscosity the liquid leaks over the edges of the substrate and hereby decreases the film thickness over time. In this measurement the effect of both the spin coating and of the squalane leaking is visible since the film height still decays after spin coating has stopped. The film thickness at 180 seconds is obtained from this measurement and given in Figure 53. This film height is then used as the initial film height without deformation for the deformation measurements. The error bars in Figure 53 are due to the error made in extrapolating the data and in reading the value of the film thickness at 180 seconds.
Figure 53: Log-log plot of the film thickness as function of the spin time at 180 seconds.

The slope of the line in Figure 53 is equal to 0.5, this is equal to the theoretical value of equation (102) for high spin times. From the measurements the initial height is found to scale as $h \sim t^{-0.5}$ for spin times higher than 10 seconds. For lower spin times the initial film height deviates from the line, which is also predicted by the theory.
3.3.3.2 Deformation dependency on initial film thickness

The dependency of the deformation on the initial film thickness is investigated by simulations. Therefore a series of simulations is conducted where the initial film thickness is varied. The other parameters such as surface charge and line width are kept constant. The surface charge applied for this simulation is $17 \, \mu C/m^2$. The results from this simulation are given in Figure 54.

As shown in Figure 54 the relative depth of the dip increases with increasing initial film height for short times after spin coating. For longer times (after 100 seconds) the maximum relative depth of the dip becomes almost independent on the initial film thickness. In graph (b) and (c) of Figure 54 the profile after 10000 seconds is visualized for the case where $h_0 = 0.5 \, \mu m$ and $h_0 = 10.0 \, \mu m$ respectively. As shown in the height profiles in graph (b) and (c) there is a large difference between the two film deformations. In the case of a low initial film thickness ($0.5 \, \mu m$) the surface charges result in two peaks (one at each edge of the surface charges) but in the case of high initial film thickness ($10.0 \, \mu m$) the film deformation results in one broad peak at the center of the charged line. This is probably due to the larger amounts of fluid that can be transported for a thicker film resulting in a higher and broader peak.
3.3.4 Applied surface charges

The next parameter to investigate is the surface charge. A series of measurements is conducted where the amount of surface charge deposited on the substrate is varied. For this measurement a 4 µm squalane film is spin coated on the polycarbonate substrate. The surface charge is deposited with a needle having a width of 2.0 mm and the film deformation is measured as function of the time since spin coating. Furthermore simulations are conducted using the surface charge distribution as in section 3.3.1 scaled with the surface charge. The relative height of the peak and the relative depth of the dip from measurements and simulations are given in Figure 55 and Figure 56 respectively.

**Figure 55:** Relative height of the peak as a function of the time since spin coating for different surface charge densities. The symbols denote experimental data and the dashed lines represent numerical simulations.

**Figure 56:** Relative depth of the dip as a function of the time since spin coating for different surface charge densities. The symbols denote experimental data and the dashed lines represent numerical simulations.
As shown in Figure 55, there is an increase in the deformation height with increasing surface charge. This is to be expected since an increase of the surface charge increases the electric field. This increases the dielectrophoretic effect that creates the deformation resulting in a higher maximum deformation. The maximum deformation is measured at the peak maximum, which is at the edges of the line. The simulations predict a similar behavior as the experiments and the height of the peak predicted by the simulations is almost identical to the experiments. The measurement and simulation for the 11.5 µC/m² are very different however. The reason for this difference is not known and further research is necessary to investigate this effect. The similarity between the simulation and experiments becomes smaller for low surface charges. This is partly due to the fact that for low surface charges only a couple of fringes appear in the fringe images. Since only the black and white lines in the fringe image are investigated this results in large uncertainties. To improve the experimental results for low surface charges the gray scale of the fringe image should be investigated. Figure 56 shows that the depth of the dip is slightly lower in the simulations (except at 30 µC/m²) but the trend of the experimental data is very well represented. This could once again be a result of the definition of starting time \( t_0 \).

The error bars in Figure 55 and Figure 56 are a result of the accuracy when counting the fringes just like before. This error becomes bigger with a larger deformation since more fringes appear in the interference images.

### 3.3.5 Line width

The effect of different line width is investigated with simulations. Therefore the horizontal base of the surface charge is extended by varying the position of the peak \( x_c \). All other parameters are kept constant. The deformation is measured as function of the time after spin coating.

Figure 57: Film thickness profiles at different times and several values of the width of the charged line (1, 1.5, 2, 2.5, 3 and 5 mm).
Figure 57 shows that for a line width below 1.5 mm one single peak is formed at the center of the surface charge distribution. Higher line widths result in the formation of two peaks instead of one central peak within the simulated time. This is partly due to the limited simulated time, which does not allow for the equilibrium solution to be reached. The broadest line (5.0 mm) requires more time to form one central peak since the distance between the two peaks is larger and therefore it takes more time to merge these two peaks. This effect is also visible in the height of the central peak. The maximum deformation height decreases with increasing line width.

3.3.6 Two parallel lines

In this section the effect of two parallel lines is investigated. The goal is to achieve a dip that is as deep as possible within a certain time by varying the distance between the two parallel lines. The motivation is to induce film rupture on a partially wetting substrate. However, as a first step we study completely wetting substrates. Simulations are conducted using an altered form of the surface charge distribution of section 3.3.1. The surface charge is mirrored around the YZ-plane. An example of the surface charge distribution is given in Figure 58. The distance L is varied resulting in different spacing between the two surface charge distributions (the simulation is symmetrical around zero).

The film deformations for 5 different gap widths 2L between the two parallel lines are given in Figure 59. The gap width is varied between 0 and 5 mm in steps of 1 mm. Figure 59 shows that the depth of the center dip can be influenced by the distance between the two charge distributions. For very low gap width a peak appears between the two charge distributions and for very high gap width the film deformation due to each surface charge have hardly any effect on each other. In between is a maximum in the depth of the dip for a gap width of approximately 1 mm. The film reaches a film height five times lower than the initial film height within $10^4$ seconds. The depth can be further increased with a higher surface charge density as shown in section 3.3.4.
Figure 59: Film thickness profiles for different times and several values of the line spacing 2L.
3.4 Discussion and conclusion

In this section the deformation of a thin liquid film over a charge distribution is investigated both experimentally and with simulations. The deformation depends on the amount of surface charge, the line width, the initial film thickness and is time dependent.

The shape of the film deformation depends on the initial film thickness. For high initial film thickness a single broad peak is formed whereas for a low initial film height two sharp peaks appear in the film at the edges of the surface charge distribution. After 30 seconds the relative depth of the dip no longer depends on the initial film thickness but for lower times a thicker film will result in a deeper relative depth of the dip in the film.

The dependence on surface charge is a lot stronger. This is because the surface charge is the driving force in generating the deformation. Without surface charges, there is no gradient in the electric field and no gradient in the density of the electric field lines and therefore no driving force to generate the deformation. A higher surface charge thus results in a higher relative peak height and a deeper relative dip.

The line width influences the time it takes for the two initial peaks at the edges of the line of surface charges to merge into one central peak. The further the two peaks are apart, the longer it takes them to merge and form one central peak. The distance also influences the width of the peak. A smaller line of charges results in a sharper peaked deformation.

Finally two parallel lines are investigated and the distance between them is varied. For large gap widths (more than 3 mm), the deformations due to the two surface charge distributions hardly affect each other. For very low gap width, the two peaks merge to one peak at the position in between the two charge distributions. A minimum of the film thickness is found between the two charge distributions when the gap width is approximately equal to 1 mm.

All experiments are compared to simulations using a Comsol Multiphysics model, which predicts quite accurately the behavior of the deformation. The differences between the experiments and simulations are mainly the time for the deformation to reach a specific height or depth. Parameters that could influence this time are the viscosity that influences the time scale and the surface tension that counteracts the deformation. Since both parameters are literature values these can be slightly different in the experiments.
4. Conclusions and recommendations

4.1 Measuring static charges
When the probe to substrate distance is small enough and no air gap is introduced, the electrostatic voltmeter can be used to measure static charges on an insulating substrate. The accuracy of the measurement depends on the probe to substrate distance. A smaller distance will result in a more accurate measurement of the surface charge distribution. The measuring probe measures the surface charges most accurate when the gradient in surface charges is small. The measurement probe can measure the surface charges at the center of a 6 mm wide written line with a probe to substrate distance between 0.5 and 3 mm. At the edges the measurement method becomes less reliable due to the limited spatial resolution of the probe.

To obtain an even better measurement of the surface charge distribution a different measurement technique is necessary. One of the possible techniques to improve the spatial resolution might be by using an AFM to measure the surface charge density.[32]

4.2 Depositing static charges
In this research, the possibility to deposit charges in a specific pattern is investigated. It is found that charge pattern can be written by dragging a droplet on a metallic needle that is connected to a high voltage source. The amount of charges that are deposited can be controlled by controlling the needle voltage. The amount of charges deposited on the substrate depends on the kind of substrate, the substrate thickness and the charging voltage of the needle.

The effect of dragging a droplet on a grounded or insulated needle is investigated and it can be concluded that there is a difference between dragging a droplet with a grounded or an insulating needle. When the droplet is dragged with a grounded needle, this means the droplet is connected to an infinite reservoir of free charges. When the droplet deposits charges on the substrate, these charges can be replenished. Therefore a constant amount of surface charges can be deposited over the parts of the substrate where the droplet was dragged. In the case of an insulated needle only the free charges in the droplet and water reservoir in the needle are available to be deposited on the substrate. The amount of surface charges deposited therefore depends on the initial charges in the droplet and on the amount of charges that are already deposited on the substrate. Therefore a decrease of the deposited charges is observed over the line where the droplet was dragged.

With the ASML set-up, a dependency of the amount of deposited charges on the rotation speed of the turntable is found. The experiments show a power law behavior where the deposited charges increase with increasing rotation speed. However further research will be necessary to validate and understand this dependency.

Finally the effect of prior measurements is investigated. It is found that a large charge deposition can influence the charging behavior of the substrate even after the charges are completely removed. This effect is found to last for at least 19 hours.
4.3 Influence of static charges on thin liquid films

The deformation of a thin liquid film above a non-uniform charge distribution is investigated both experimentally and with simulations. The deformation depends on the amount of surface charge, the line width, the initial film thickness and is time dependent.

The shape of the film deformation depends on the initial film thickness. For high initial film thickness a single broad peak is formed whereas for a low initial film thickness two sharp peaks appear in the film at the edges of the surface charge distribution. The dependence on surface charge is a lot stronger. This is because the surface charge is the driving force in generating the deformation. Without surface charges, there is no gradient in the electric field and no gradient in the density of the electric field lines and therefore no driving force to generate the deformation. A higher surface charge thus results in a higher relative peak height and a deeper relative dip.

The line width influences the time it takes for the two initial peaks at the edges of the line of surface charges to merge into one central peak. The further the two peaks are apart, the longer it takes them to merge and form one central peak. The distance also influences the width of the peak. A smaller line of charges results in a sharper peaked deformation.

Finally two parallel lines are investigated and the distance between them is varied. For large gap widths, the deformations due to the two surface charge distributions hardly affect each other. For very low gap width the two deformations merge to one deformation having a peak at the position between the two charge distributions. A minimum of the film thickness is found between the two charge distributions where the gap width is approximately equal to 1 mm.

All experiments are compared to simulations using a Comsol Multiphysics model, which predicts quite accurately the behavior of the deformation. The differences between the experiments and simulations are mainly the time for the deformation to reach a specific height or depth. Parameters that could influence this time are the viscosity that influences the time scale and the surface tension that counteracts the deformation. Since both parameters are literature values these can be slightly different in the experiments.

An example of a specific surface charge distribution on a thin liquid film is given in Figure 60. The left graph shows the surface charge distribution and the right shows a picture of the deformed film.

![Figure 60: Example of a surface charge distribution and the resulting deformation in a thin liquid film.](image)
5. Further research

One of the interesting possibilities for further research is the effect of static electricity on liquids on a partially wetting substrate. The break-up of a thin liquid film due to an inhomogeneous charge distribution can be investigated. In this project a start of this investigation is made. However due to a lack of time no quantitative study of the effect was performed. Nonetheless some promising results were found which will be discussed in this section.

For the measurements a D263 glass substrate is used with a coating of Octyltrichlorosilane (OTS)\textsuperscript{[33]}. Squalane is used as the liquid. Due to the OTS coating the glass substrate becomes partially wetting for squalane (receding contact angle of about 30°). Therefore the liquid dewets from the edges of the substrate to the center. Without any surface charges, the liquid eventually forms a droplet in the center. The dewetting of a 2.9 µm squalane film without static charges is visualized in Figure 61.

![Figure 61: Dewetting of squalane on OTS coated D263 glass substrate before depositing surface charges.](image)

After cleaning the substrate with chloroform to remove the squalane and removing the charges with the ionizerm, a charge pattern containing four squares is deposited. A 2 mm needle at 500 Volt is used to drag a water droplet over the substrate. After writing, the charges are measured and the resulting surface charge distribution is given in Figure 62.
After depositing the surface charges a 2.9 µm film of squalane is spin coated and the dewetting of the squalane is monitored. The dewetting is visualized in Figure 63. The deposited charge pattern is visible and in the top right square the break up inside the square is visible. This break up might be the result of the charge pattern. Furthermore it is observed that the dewetting is slowed and at most positions even stopped at the edges of the written charged lines.

Figure 62: The resulting charge distribution after writing 4 squares.

Figure 63: Dewetting of squalane on D263 glass after depositing charge pattern of Figure 62.
After this measurement the squalane is removed with chloroform and the charges on the substrate are neutralized using the ionizer. Then a new thin film of squalane is spin coated on the substrate and the dewetting is monitored again. Astonishingly this resulted in the same dewetting phenomena as observed when the surface charge pattern containing the four squares was written on the substrate. This indicated the surface charges have influenced the surface of the substrate, possibly damaging the OTS coating. However after removing the squalane and washing with water and isopropanol the coating seems renewed. The dewetting behavior is found to be identical to the dewetting before charges were deposited on the substrate. This means that the seemingly irreversible change in the dewetting behavior after depositing a charged line can be reversed by washing with water and isopropanol. These effects might be related to the effects discussed in section 2.4.3.3.

A second measurement series is conducted with a 2.9 µm squalane film and a higher charging voltage to amplify the dielectric effects. A higher charging voltage should result in higher deformations and deeper dips near the charged line. This will reduce the time to break up and hopefully shows the break-up of the film near the deposited lines of surface charges. However, the squalane dewets from the edges too fast. The final drop pattern on the D263 glass substrate is shown in Figure 64 along with the charge geometry. The transparent red line in the background of the picture represents the locations where the droplet was dragged over the substrate on a needle at 1 kV. Over the transparent black line the droplet was dragged with a needle voltage of 0 kV.

Figure 64 shows the formation of droplets on the locations where surface charges are deposited. The break-up also occurred between two of the charged lines but this happened too fast to record in a picture. Further research will be necessary to investigate the break up due to the static charges and to see if the break-up always occurs near the edges of the written lines.
6. References


Appendix A: Detailed measurement set-up

Before each measurement the substrate is de-charged with the ionizer. For the measurements presented in this report an MEB antistatic bar of Simco is used with a 7 kV AC power supply of the type A2A7S. The set-up for measuring the surface charges is schematically given in Figure 65 and the set-up for writing charges is given in Figure 66.

The devices used in the experimental set-up to measure the surface charges and to write the charges are given in Table 6. The manufacturer and the model numbers of the devices are given as well as the numbers used in Figure 65 and Figure 66.
Table 6: The brand and type of the devices used in the measurement set-up.

<table>
<thead>
<tr>
<th>Nr.</th>
<th>Device</th>
<th>Brand</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Probe electrostatic voltmeter</td>
<td>Monroe Electronics</td>
<td>Isoprobe® Model 1017A-EH</td>
</tr>
<tr>
<td>2</td>
<td>Electrostatic voltmeter</td>
<td>Monroe Electronics</td>
<td>Isoprobe® Model 244</td>
</tr>
<tr>
<td>3</td>
<td>Data acquisition module</td>
<td>National Instruments</td>
<td>BNC-2110 (card: PCI-6250)</td>
</tr>
<tr>
<td>4</td>
<td>Stepper motor controller</td>
<td>Standa</td>
<td>8SMCl-USBhF</td>
</tr>
<tr>
<td>5</td>
<td>High voltage source</td>
<td>Fug Elektronik GMDB</td>
<td>HCN14-12500</td>
</tr>
<tr>
<td>6</td>
<td>DC power supply</td>
<td>Agilent</td>
<td>6614C</td>
</tr>
</tbody>
</table>
Appendix B: Probe datasheet 1017A-EH

The spatial resolution of the measurement probe depends on the aperture of the probe. In the case of this research the 1017A-EH probe is used having a 0.5 mm aperture. The spatial resolution is limited by this aperture and the distance between the probe and the measured substrate. Curve 3 in Figure 67 shows that at a probe to substrate distance of 0.5 mm the smallest line where the top value can be measured with 99% resolution is about 1.5 mm. This means that lines thinner than 1.5 mm result in a lower value measured by the electrostatic voltmeter.

---

**ISOProbe® Electrostatic Voltmeter Probe Performance**

<table>
<thead>
<tr>
<th>Probe</th>
<th>Used With</th>
<th>Special Features</th>
<th>10% to 90% Step Response</th>
<th>Noise Referred to Input</th>
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<td>1017AE or AS</td>
<td>244A</td>
<td>General Measurement</td>
<td>&lt;2.5ms to 1V</td>
<td>&lt;0.2Vrms or 20p-p</td>
</tr>
<tr>
<td>1017A-EH</td>
<td>244A</td>
<td>High Resolution</td>
<td>&lt;2.5ms to 1V (typ.)</td>
<td>&lt;2.0Vrms (typ.)</td>
</tr>
<tr>
<td>1017AE or ASL</td>
<td>244A</td>
<td>High Gain</td>
<td>&lt;2.5ms to 1V (typ.)</td>
<td>0.4Vrms</td>
</tr>
<tr>
<td>1017T</td>
<td>244A</td>
<td>Transparent</td>
<td>3.0ms</td>
<td>80Vrms</td>
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<tr>
<td>1017EJ</td>
<td>244A</td>
<td>Silk Aperature</td>
<td>(Special Purpose)</td>
<td></td>
</tr>
<tr>
<td>1017AE or ASL</td>
<td>244AL</td>
<td>Low Noise</td>
<td>&lt;3ms to 10V</td>
<td>20mVrms (typ.)</td>
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<tr>
<td>1018E or B</td>
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<td>1018AEH</td>
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</table>

**Typical Performance Characteristics**

- **Figure 67:** Datasheet probe 1017A-EH.
Appendix C: Comsol Multiphysics

Comsol Multiphysics is a software package to model physical problems using finite element analysis. Comsol contains a series of modules where each module covers a specific region of physical problems. There is also a multiphysics option that allows the coupling of several modules to simulate more complicated problems.

C1: Electrostatic simulations

For electric field calculations, the electrostatics part of the electromagnetics module is used. This part is used to simulate electrostatics in dielectric materials. First a geometry must be specified, which consists of an aluminium bottom plate, the PMMA substrate and a surface charge. The rest of the domain is filled with air. The geometry is given in Figure 68. This is a close up of the interesting region. In the model, the aluminium plate has a length of 200 mm and the substrate has a length of 70 mm. These are also the dimensions of the experimental setup. The line of surface charge \( \sigma \) is 6 mm wide and the height of the simulated region is 90 mm. The simulation is 2-dimensional.

![Figure 68: Simulated geometry for the dependency of the surface charge on the electric field.](image)

After creating the geometry the materials and boundary conditions are specified. For each domain the material is specified by three parameters; the space charge density \( \rho \) (in this configuration for all materials equal to 0), the thickness (1m) and the relative permeability \( \epsilon \). The applied boundary conditions are:

- The boundaries of the aluminum plate and the outside edges of the specified geometry are grounded.
- At the interface between air and PMMA a continuity boundary condition is implemented in the region where \( \sigma = 0 \).
- At the line on top of the PMMA substrate a surface charge is specified.

The next step is to create a mesh. This mesh consists of triangles that specify the points where the governing equations are calculated. The mesh is finer at the region of high field gradients and coarser at positions that are less important. The used mesh for this problem is given in Figure 69.
Figure 69: The mesh used in the simulation to simulate the dependency of the electric potential on the surface charge.

In this case the region around the applied surface charge is most interesting and therefore the mesh is finer in this region. The effect of an even finer mesh is investigated and there are no significant differences between the mesh in Figure 69 and a finer one.

When the geometry, the boundary conditions and the mesh are specified, the simulation can calculate the electric potential or the magnitude of the electric field at each point of the mesh. These parameters are calculated from the first Maxwell equation in matter in potential form.

\[-\nabla \varepsilon \varepsilon_0 \nabla V = \rho_f \tag{C1}\]

The calculated electric potential is given in Figure 70. It is also possible to calculate the electric potential at a horizontal line. The calculated electric potential as function of the X-position is given in Figure 71.
Figure 70: The calculated electric potential above a line with surface charge 5 μC/m².

Figure 71: The calculated electric potential on a horizontal line 1 mm above the PMMA substrate.
C2: Film deformation simulations

In this section the simulations used to calculate film deformations due to static charges on the substrate are discussed. Unlike the electrostatic simulations in the previous section, the simulations with the film deformation are time dependent. Furthermore due to the use of the lubrication approximation these simulations are 1-dimensional. The geometry used for these simulations is therefore only a line at a specific height for each segment. The initial condition corresponds to a constant initial film thickness, typically in the range 2 – 5 µm.

Before simulations can be started the governing equations of the system should be implemented. Therefore the results from the lubrication approximation with electric components derived in section 3.1.3 are inserted in a Comsol model. Therefore the PDE module is used with the partial differential equations in general form. The general equation is given in equation (C2).

\[ e_a \frac{\partial^2 u}{\partial t^2} + d_a \frac{\partial u}{\partial t} + \nabla \cdot \Gamma = F \]  

(C2)

In the case of this simulation two coupled PDE's are used to simulate the behavior of the film above a known surface charge distribution. The two equations are rewritten in the form of equation (B1) resulting in the parameters given in Table 7. The first equation is the equation that influences the film height \( h \) due to the change in pressure \( p \) whereas the second equation calculates the pressure difference due to the new height profile.

Table 7: Equations for the height \( h \) and the pressure \( p \) in a liquid film above a surface charge distribution.

<table>
<thead>
<tr>
<th>Equation for hh</th>
<th>[ \frac{\partial h}{\partial x} ]</th>
<th>( p - pgh - \epsilon_0 (\epsilon_1 c_4^2 - \epsilon_0 c_6^2)/2 )</th>
<th>( h )</th>
<th>( p )</th>
<th>( h )</th>
<th>( p )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equation for pp</td>
<td>[ -h^3 \frac{\partial p}{\partial x} ]</td>
<td>( 0 )</td>
<td>( 0 )</td>
<td>( 3\mu )</td>
<td>( 0 )</td>
<td></td>
</tr>
</tbody>
</table>

In each time step the two equations are solved for the pressure and height at each segment of the line. The elements of the line have quadratic basis functions. Finally there are also boundary and initial conditions in the model. For both boundaries a Neumann boundary condition is used which represents a symmetry condition which is given in equation (C3).

\[ \frac{\partial h}{\partial x} = 0, \quad \frac{\partial p}{\partial x} = 0 \quad \text{at } x = 0 \text{ and outer boundary} \]  

(C3)

The initial conditions are given in equation (C4).

\[ h(t_0) = h_0 \]  

\[ p(t_0) = 0 \]  

(C4.1)  

(C4.2)

From the simulations a time dependent solution or a solution at a specific time can be obtained for a layer of fluid above a known surface charge distribution.