Bachelor assignment: Suppression of coffee rings with electrowetting

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Summary

We investigated the relation between the flow speed inside droplets and the salt concentration diluted in the liquid of an AC electrowetted droplet. In another set of measurements we explored how the flow speed is related to the frequency of the applied voltage.The salt depency of this effect is a small part, but nevertheless it would be very usefull if the effects would be clear. This would mean that it would be possible to ajust the frequency on a droplet over time to account for evaporation and with that the increase of salt concentration. This way it might be possible to get a constant flow speed inside the droplet to make sure none of the particles deposit at the edges and a homogeneous spot is created. This would give several useful implications for processes where its important to have an homogeneous spot of the diluted solid. In theory every drop should have an eigenfrequency dependent on the size of the droplet. This experiment was done to see what size a drop has to be for a frequency to have a maximum flow speed. In the fourth set of measurements, the effects on different concentrations of particles inside the solution was investigated. Nine different solutions were made with different nanoparticle concentrations and the droplets were evaporated while measuring the contact angle. The last experiment was to evaporate droplets with different concentrations of nano particles with an applied voltage with constant frequency. The goal of this experiment was to see when the pinning of the contact line of the droplet was suppressed and at what concentration it cannot be suppressed.

In conclusion we did not observe any connections between the salt concentration and the flow speed inside a droplet. Instead a periodic change in flow speed was observed dependent on the applied frequency. This is related to the resonant frequencies of the droplet. It is also dependent on de size of the droplet. This means, even at a fixed frequency, the flow speed can change because of the change in size as the droplet evaporates.

Contents

1 Introduction

Both in nature and in lab environments, people often encounter liquids containing particles. That cup of coffee that might be in your hand right now is the quintessential liquid of this type - it is such a good example, that it has named the coffee ring effect. This effect, that causes these liquids to dry in a nonhomogenous way, is a problem. For some research applications, it would be better to have a homogenous dot instead of a ring. We have worked on a method to achieve this, using the instrument of electrowetting. Electrowetting with an alternating current is a very elegant way to keep the particles from depositing at the edge of the droplet, while simultaneously keeping the contact line from pinning. Our research goal is know how to control the shrinkage of the droplet. While the liquid of a droplet evaporates, the concentration of all soluted and suspended material increases. Therefore, we need to research the influence of solutions and suspensions on internal flow speed. The key questions are: "How does salt concentration affect electrowetting?" and "How does particle concentration affect electrowetting?" For practical applications, we need quantitave answers. To be able to do this we need a large amount of data. Our final key problem is "How do we automate the processing of results?".

2 Theoretical & Experimental aspects

V=voltage appied on the droplet	θ =the original contact angle without V
γ_{12}=the interfacial tension	θ_o =the original contact angle with V
d=he thickness of the dielectric layer	

2.1 Theory

In this section the basic theory of electrowetting will be explained. First the problem of a normal droplet on a surface will be explained (also known as the coffee ring effect). After this the basics of electrowetting are explained together with the solution to the coffe-ring problem.

2.1.1 Coffee ring effect

When you let a droplet of liquid containing particles dry, the particles will leave a dense ring along the perimeter of the droplet. These particles, which were originally homogenously distributed in the droplet, are deposited along the contact line of the droplet. During evaporation the fluid at the contact line evaporates, but the radius of the droplet cannot change because of the pinning effect. Therefore fluid must flow from the center to the edge of the droplet taking the particles with it and depositing them at the edges. At figure 1.b you can see the flow of an evaporating droplet. This effect is common wherever droplets with dispersed solids are dried. Though most of the times this effect isn't important in a(n industrial) process, some processes require a homogeneously distributed residue.

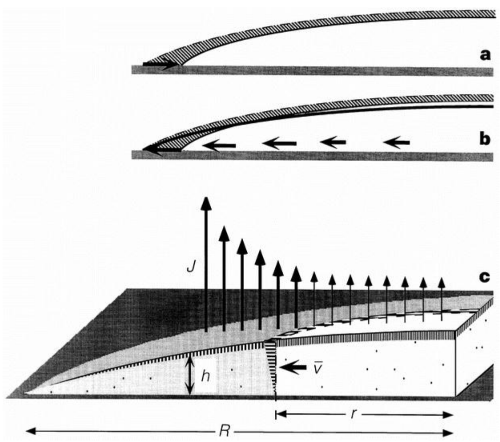


Figure 1: Outward flow during evaporation. With a being the result without flow, the droplet shrinks. (b), with (a) compensationg flow to the edges. And in (c), J the evaporation vapour, h the height of the drop and v the flow profile taken from ref:[1]

2.1.2 Electrowetting

To get a homogeneously dried residue one can use electrowetting. Electrowetting is a technique which mainpulates the contact angle of a droplet with an electric current.[4]. By shaking the contact line of a droplet which is placed on a dielectric layer. The pinning of the contact line can be overcome. This in turn can suppress the coffee ring effect.[2]. In addition to the contact line oscillations, different flowpatters exist inside the droplet aswell. To apply the voltage a needle is inserted in the droplet and a voltage is applied between the needle and the dielectric layer. See figure 2. Applying this external voltage on the drop causes the contact angle to decrease.

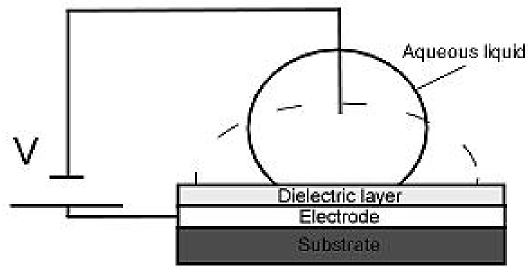


Figure 2: The basic principle of electrowetting

The equation which relates the contact angle to the applied potential (Equation: 1) is derived from the minimum free-energy requirement for thermodynamic equilibrium conditions. [3]

$$cos(\theta) = cos(\theta_o) + \frac{\epsilon V^2}{2\gamma_{12} d} \tag{1}$$

This effect does not solve the problem of pinning in a drop because the contact angle does change, but it just creates pinning at another point on the surface. To fix this problem we apply an AC current instead of a DC current. This alternating current makes the droplet oscillate. This oscillation prevents pinning of the contact line. Because the droplet can't pin on the surface the solid particles will not get deposited at the edges. This state is not always the case; if the frequency of the AC voltage is changed to a higher region it will eventually start to keep a single contact angle. The frequency is too fast for the droplet to physically change to the other contact angle and its surface will start to vibrate accordingly creating a flow inside the droplet which also prevents the solid particles from depositing at the perimeter of the drop. The actual origin of the flow inside the drop is still unknown, though some effects are found that do influence this flow. The first one is hysteresis on the substrate. The contact line of the drop moves a bit (around 10 μm and over 1kHz AC frequency) but due to hysteresis the contact line of the drop wont move the same way along this contact line. The second effect is the capillary waves on the droplet-surface which are due to the movement of the drop and the surface tension.

2.2 Experimental aspects

2.2.1 Setup

Setup 1
To study the electrowetting phenomena we used the setup shown in figure 3. We used a transparent substrate so that the droplet is observable from the bottom. To observe the drop over time, a high-speed camera was used. An objective was used with a magnification of x4 to enlarge the drop. The dielectric layer was made from SU8, which is capable of withstanding at least up to 200V and is a transparent material.

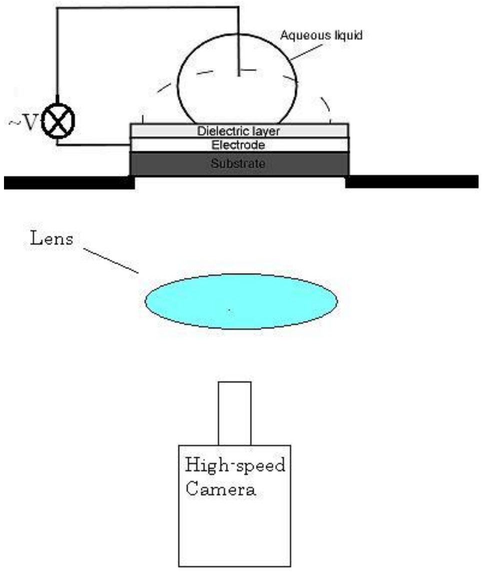


Figure 3: Experimental setup 1

Fluorescent particles where added to the liquid such that the flow can be visualized. These particles also form the coffee ring patterns. A mercury argon lamp was used with appropirate filters. The flow inside the droplets was recorded with a fast camera (photron SA3) and analyzed the results using computer programs.
Setup 2
The next subject of study was the contact angle of the droplet. To be able to track this we used a setup with a camera from the side. The camera was linked with a computer so we could track the contact angle of the drop. (figure 4)

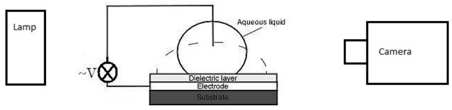


Figure 4: Experimental setup 2

3 Results

3.1 Measurements

In this section the experiments are explained together with the results. First experiments were done with salt solutions to get a better idea of the effects of salt on the flow speed inside the droplet. After that some experiments were done using solutions with fluorescent particles. In the second half of this section, the data processing will be explained together with any code that was used to analyze from the measured data.

3.1.1 Drop evaporation

First the effects of evaporation of droplets was measured to make sure there was accounted for any time effects during the experiments. This was done with the first setup with a solution with 1 mM salt and 200 nm fluorescent particles. With setup 1, a droplet was evaporated while tracking it with a high speed camera. With computer software the speed inside the droplet and the radius of the droplet was calculated over time.

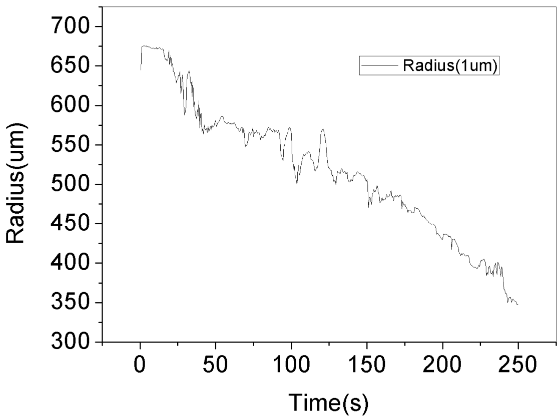


Figure 5: Flow speed and radius of an evaporating droplet

As shown the radius is going down over time due to evaporation. The radius does not reduce smoothly because of the pinning effect. It takes some time before there is enough stress on the contact line of the droplet to pull the radius down. As shown the effects of evaporating are significant on the flow speed, therefore any further experiments will be done with short windows of measurement to reduce influence on the data due to evaporation.

3.1.2 Salt dependence

To measure the salt dependence, we made five different solutions with different concentrations of salt (1M, 100mM, 10mM 1mM and 0.01mM). We used setup 1 to make movies of the droplets ($1u$L) with a high speed camera. To see the effect of different frequencies we used a function generator with a frequency sweep. To minimize the effect of evaporation the sweep was cut into three parts. First: 100Hz-1kHz, secondly: 1kHz-10kHz and third: 10kHz-100kHz. Each was conducted in 50s so the time steps can be transfered to the frequency.

The results can be seen in figures 6 to 10. As shown in the figures the flow speed fluctuates a lot which means that the sweep passes over the eigenfrequencies of the droplets. Note that when the frequency increases above about 10kHz, the speed slowly dies out.

For three of the sweeps, the expected eigenfrequencies have been calculated from the base radius. These can be found in tables 1 to 3.

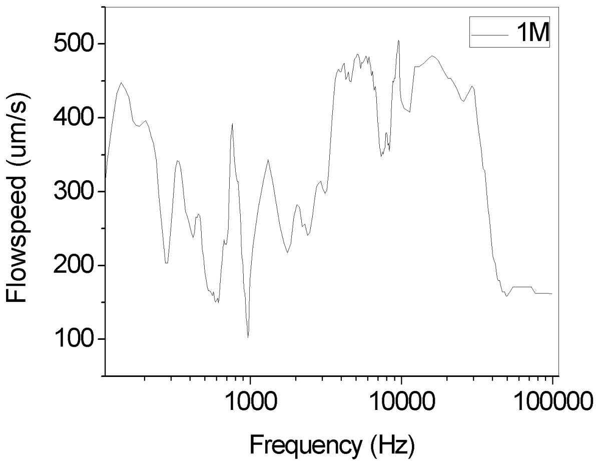


Figure 6: Frequency sweep of a droplet with 1M salt

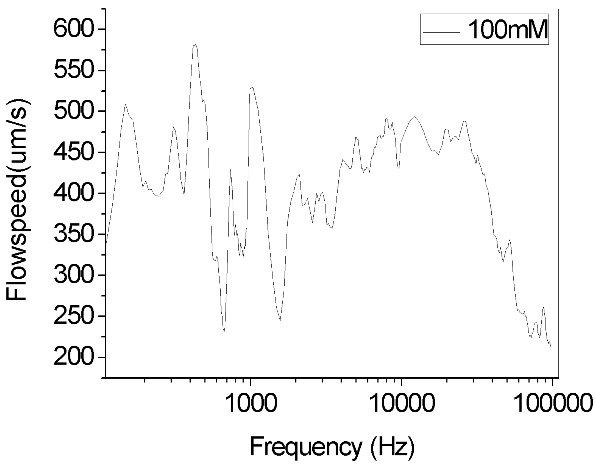


Figure 7: Frequency sweep of a droplet with 100mM salt

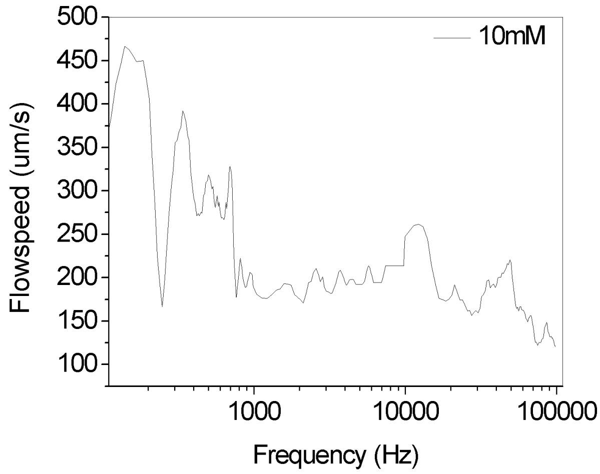


Figure 8: Frequency sweep of a droplet with 10mM salt

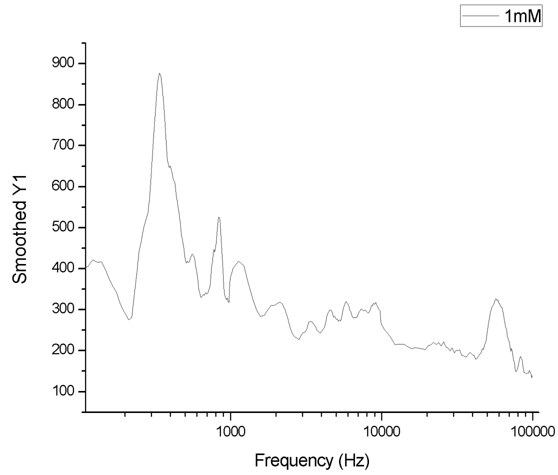


Figure 9: Frequency sweep of a droplet with 1mM salt

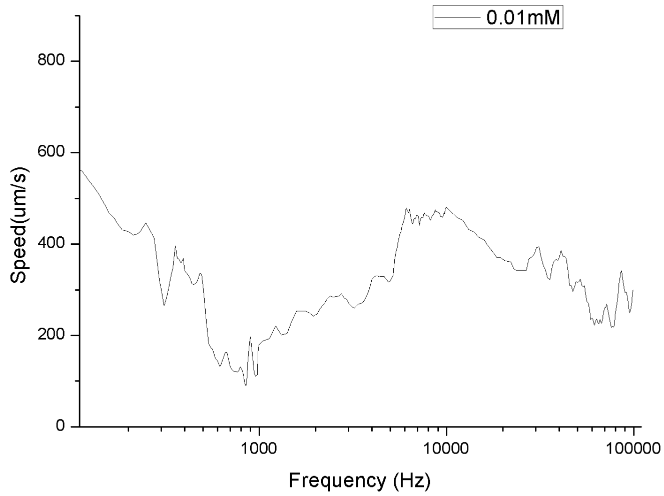


Figure 10: Frequency sweep of a droplet with 0.01mM salt

Table 1: 0.01mM

n	$f_{measured}(Hz)$	$f_{calculated}(Hz)$
2	104.5 ± 23.1	114.2 ± 10.3
4	356.5 ± 30.7	342.7 ± 30.8
6	662.5 ± 33.1	625.7 ± 56.3

Table 2: 100 mM

n	$f_{measured}(Hz)$	$f_{calculated}(Hz)$
2	149.5 ± 23.4	122.5 ± 11.0
4	311.5 ± 35.9	367.6 ± 33.1
6	599.5 ± 40.4	671.0 ± 60.4
8	1045 ± 114.1	1025.0 ± 92.3

Table 3: 1M

n	$f_{measured}(Hz)$	$f_{calculated}(Hz)$
2	140.5 ± 29.8	146.9 ± 13.2
4	455.5 ± 37.8	440.7 ± 39.7
6	761.5 ± 50.9	804.5 ± 72.4
8	1315 ± 118.4	1128.9 ± 110.6

We do not see any monotonic change in flow speed with the salt concentration. The flow speed fluctuates with frequency. This is related to the resonant frequencies of the drop. The peaks are not very apparent in all curves, because the contact line also has pinning due to evaporation. This affects the drop oscillations.

3.1.3 Evaporation with nano particles

This experiment measures the contact angle and radius of an evaporating droplet.This way more can be understood about the process of an evaporating droplet on an SU8 surface. First DI water was studied which can be seen in figure 11. There are 3 phases seen during the evaporation of the droplet; the first where the radius is constant and the contact angle is decreasing, the second phase is with a constant contact angle and a decreasing radius and the last part where the contact angle is decreasing rapidly and the radius is slowly decreasing (in comparison to the contact angle) until the droplet is completly evaporated.

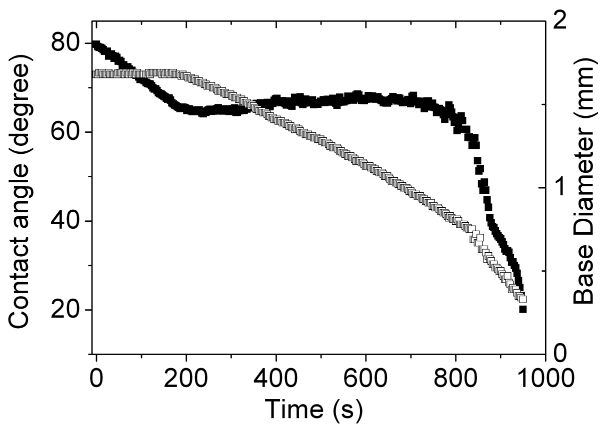


Figure 11: Contact angle and radius of an evaporating droplet of DI water

After this basic measurement the next step is to get a picture of what happens when we add different concentrations of nanoparticles to an evaporating droplet. The results are shown in figure 12. As the concentration of nanoparticles increases the evaporation time decreases. The second area of the curve (with the decreasing radius and constant contact angle) gets shorter when the particle concentration goes up. this is because the pinning force increases with the concentration of partical inside the droplet and the droplet will pin more easily.

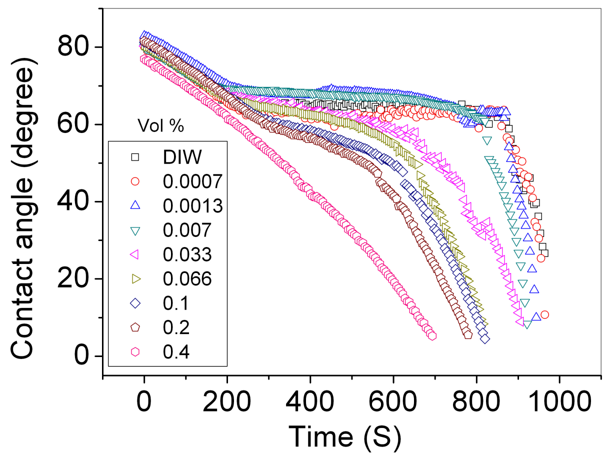
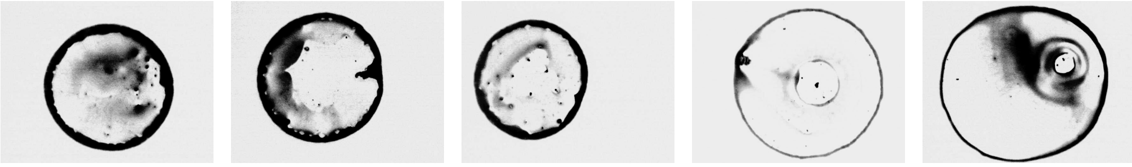


Figure 12: Contact angle of droplets with different concentration of nano particles (200nm)

3.1.4 Suppression of the coffee ring effect

With this experiment it was checked if particles in general had effect on the pinning process. To achieve this the concentration of fluorescent nanoparticles was varied from 0.005% up to 0.25% of te solution. The salt concentration in the solution was kept constant at 0.01mM. Also the applied voltage and frequency were constant at 120V and 10kHz. Of every solution we compared the residue that is left after evaporating without voltage with the one with voltage. A pipet which dispenses 1uL was used to keep a constant drop size. During the experiment it became clear that the needle had to be cleaned after every run because the particles deposit on the needle which has major impact on every measurement thereafter. The results can be viewed in figures 13 to 18 where the pictures A to C are the pictures without voltage and D to F are the pictures with voltage. The pinning process is not supressed with the concentrations 0.05%, 0.1% and 0.25%. The coffee rings formed after applying voltage is bigger than those whithout voltage, because by default electrowetting decreases the contact angle, which will actually enhance the pinning effect. The droplet oscillations in the mentioned cases cannot overcome the pinning forces. The concentrations 0.01% and 0.005% with voltage (figures 17 and 18 D to F) are clearly smaller then their counterparts without voltage (figures 17 and 18 A to C). So they are partially suppressed. A higher voltage might be required for complete suppression.

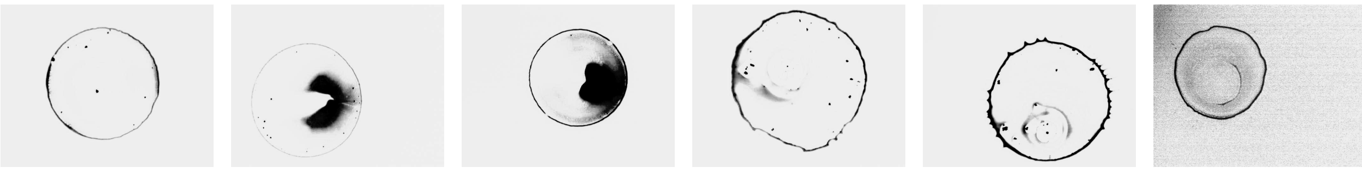


(A) (B) (C) (D) (E)

Figure 13: 0.25% nano particles solution

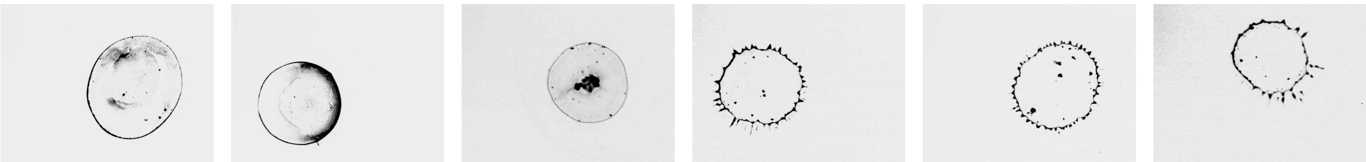
(A) (B) (NA) (D) (E)

Figure 14: 0.1% nano particles solution



(A) (B) (C) (D) (E) (F)

Figure 15: 0.05% nano particles solution

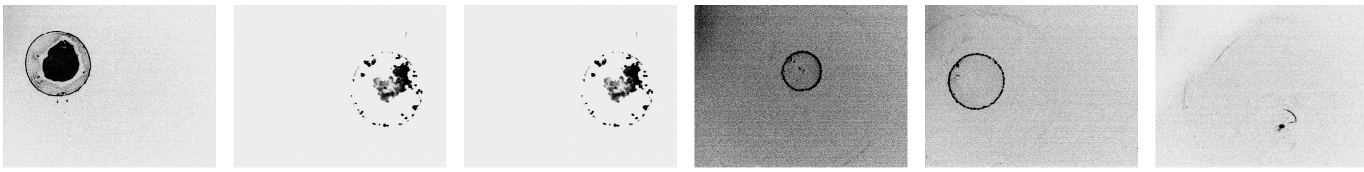


(A) (B) (C) (D) (E) (F)

Figure 16: 0.025% nano particles solution

(A) (B) (C) (D) (E) (F)

Figure 17: 0.01% nano particles solution



(A) (B) (C) (D) (E) (F)

Figure 18: 0.005% nano particles solution

3.2 Data processing

To obtain this data, both ImageJ and Matlab were used. Since ImageJ loads all data in the computer memory first, it can process image sequences very fast. However, the amount of data it can process at a time is limited by the physical memory available. Most of the work that had to be done was very repetitive, so using macros was necessary. In the following sections, the macros written for this research will be explained. The code can be found in appendix ....

The greater part of our raw data were image sequences; from this, we had to find average particle velocity and droplet size. Initially, the way to do this was to manually clarify an image sequence in ImageJ, fine-tune ParticleTracker_ to track a decent amount of particles and to use the m-file FloProfile_5 to calculate an average velocity. Using the line tool in ImageJ, the radius of droplets was measured. This all was a lot of manual work that we wanted to automate so that we could process more data.

ParticleTracker_ (v1.5), an ImageJ java plugin written by Guy Levy of ETH Zurich was provided to us, but the extensive graphic user interface was not very practical for mass processing. However, the source code was distributed along with the program. After learning basic Java, we have limited the output to our purposes and allowed for command line input. We have also added functionalty to pass through an index number to append to the file name. This customised version is now called ParticleTrackerData2_.

3.2.1 ImageJ droplet tracking macros

Clarify_, MassProcess_, MassTracker_ and SweepTracker_ are all prepatory files for particle tracking with the ParticleTracker plugin. The last two incluide tracking using the more macro-friendly ParticleTrackerData2_. EdgeSampler_is used to periodically get images wherein the edge of the bubble is clearly visible.

Most image stacks require some clarification before ParticleTracker_ can track a decent number of particles. Background illumination, constant bright spots and lack of proper contrast are the major problems that need to be dealt with first. The first will be dealt with later in this section, as it is quite tricky; the second and third will be adressed here.

Constant background specks and spots are caused by reflections, the needle, dirt and/or luminous particles from previously dried drops. For the purpose of particle tracking they can easily be removed by calculating the minimum intensity of the image stack, and substracting the calculated image from the stack. This is not the method used in the programs, because using the average intensity has some other advantages.

The proper contrast to find moving particles is easily solved by enhancing contrast, but there are minor problems at the edge of the circle. Since many particles gather there, it is a lot brighter on average. This tends to make moving particles indistinguisable at increased contrast. For image sequences in which the drop size doesn't significantly decrease (which is true for most of the processed image batches), the aforementioned problem can be solved by substracting the average intensity. The average intensity incluides all constant spots as well as overly bright particle conglomerates.

Clarify_ requires an opened image stack, which it processes by substracting background illumination, calculating the average, substracting that average, and increasing the contrast. Clarify_ is a very basic macro that just saves a couple of mouse clicks and grants you full visual confirmation. The same method of clarification is used in the other files.

MassProcess_ asks for a folder and processes (as Clarify_ does) all avi files in that folder, which is saves in a new folder.

MassTracker_ asks for a folder and if that folder has been processed, and runs all the avi files through ParticleTrackerData2_, outputting the trajectory files.

SweepTracker_ processes one (unopened) avi file in batches. It is designed for large files that cannot be opened at once. It can be used in two ways: either it can sample at a set interval (which can even overlap, depending on the sample width and number of measurements), or it processes long portions of the file in smaller chunks. This is where the index numbers passed through ParticleTrackerData2_ come in, as this macro creates many trajectory files from a single avi.

Getting a clear image of moving particles is one thing; getting a clear image of the edge is quite another. The easiest way to automatically find the radius of the droplet is to fit a circle over the outermost intense pixels. To do this, a threshold value is needed. This is problematic when a portion of the circle is not clearly visible (i.e. about as intense as background illumination).

Using AutoSubstract2_, the background illumination can be greatly reduced. However, this does provide a new inaccuracy in the radius: because that macro shields a blurred form resembling the droplet from being reduced in intensity, a small circle of shielded background illumination *might* form around the real circle. With a single threshold value, this cannot be easily distinguished from a dimly lit edge.

EdgeSampler_ uses the minimal intensity over a number of frames to filter out motion. Assuming a low number of frames, this will mean that particles have moved, but the edge has not. From the open file,EdgeSampler_ takes small sets of frames at regular intervals and filters out motion and background illumination. The resultant files are saved, as they will be processed in Matlab to find the radii.

3.2.2 ImageJ general macros

For many digital processing applications, background illumination is inconvenient at best. This can often be countered by increasing contrast, but when the desired information in the image is as bright as the background, one needs a different approach. With a stack of subsequent images, there is a way to distinguish areas with movement from areas without movement: this can be done by calculating the standard deviation projection (i.e. the σ for each pixel in the set of images). By blurring this, the general shape of the droplet becomes clear. When the background illumination is substracted, this shape can be shielded and your image will be clearer. A second obstacle in ImageJ is the way Brightness and Contrast works. B&C can only translate the image histogram linearly: when changing brightness, all pixels simply get a value added, and when changing contrast, all pixels get their values multiplied by a constant. For better visibility, a nonlinear contrast function like what is used in the professional Photoshop software is vital. To do this in ImageJ with a small calculation time was a challenge that was solved by using a predifined curve. The important information is between the intensities of 30 and 100 (on a scale from 0 to 255), and anything between 20 and 150 should be distinguishable as well. The nonlinear operations available are exponents .5 and 2. Neither suit the stated demands, but 1.5 (the product of the square root and the original image) does. See image

AutoSubstract_ substracts a constant value from all pixels. This value is found by looking at squares in the corners of the image (or the minimum intensity projection of the image) and finding the maximum intensity that is below a standard deviation threshold (this program is built to substract background, which is typically uniform and therefore has a low standard deviation).

AutoSubstract2_ is built for image stacks. It finds the shielding image described above, normalises it to 1.2 times the substraction constant found in AutoSubstract_ and substracts this from the original stack.

Nonlinear_Contrast uses the 1.5 exponent on all pixel values (by duplicating and multipling the image with the square root of itself), and defines the maximum intensity at source pixel value 162.

Nonlinear_Contrast2 is a slightly heavier version of Nonlinear_Contrast, as it duplicates the base image and then promotes both clones to 32 bit, where Nonlinear_Contrast only promotes one of them. The advantage is a more visually attractive result, because the intensities over 162(source) now scale from 240 to 255 in the result. This is done by scaling and adding the square of the source image.

Many high-speed camera movies are good for processing, but too slow to watch manually. Speeding things up can be done by brute force, i.e. using a program that shows all frames at a higher framerate or skips a number of frames from the source file. However, this takes a lot of computing resources and is suceptable to latency. Secondly, this approach does not solve the problem in a second viewing. A better approach is to do this in steps: first create a smaller set of frames from the source, and then view it.

AviSampler_ simply opens an avi file frame by frame, at a given frequency. It then saves the frame as an image, and in the end opens all saved images as an image stack.

Other minor macros written for ImageJ to facilitate this research project:

MassInvert_ is a macro that asks for a folder with .jpg images in it, and then creates a subfolder in which it places inverted (and somewhat contrasted) copies of those images.

Save_Contrast applies the Nonlinear_Contrast macro and then saves the result in a subfolder of the opened image stack.

3.2.3 Matlab processing

Using a slightly automated version of FloProfile_5 by Dileep Mampallil, the flow speeds of the tracked particles have been computed. The radii have been computed with a set of m-files from Burak Eral, modified to use a gaussian window to correct the error AutoSubstract2_ has introduced. To correct for noise (random noise or remains of other droples), the following filtering function was written:

schoon.m assumes that the majority of the points that might be on the edge that it receives as input are correct. By comparing all point locations with their average and standard deviation, minor noise in the center and at the edges can be filtered out. The m-file actively searches for remains of other droplets by looking for concentrations of dots that are far outside the circle of standard deviation around the center.

4 Discussion and Conclusion

The effects of electrowetting on a droplet were investigated by conducting electrowetting measurements with alternating current. First the internal flow speed was measured during electrowetting. This was done at different concentrations of salt. However, no influence due to the salt concentration was observed. The flow speed does fluctuate and peak at certain frequencies. This could be related to the resonant frequencies of a droplet. Secondly the pinning of the contact line of a droplet was observed. During the observations three phases were found during evaporation. With greater particle concentration, the pinning effect was shown to be stronger. Because of the increased pinning the droplets will start to leave coffee rings. During the investigation it became clear that electrowetting can be used to suppress the coffee ring effect. This was studied as a function of the particle density. With increased particle concentrations (above 0.025% diluted 200nm particles) the coffee ring can not be suppressed because the particle density is to high. At lower particle densities the coffee ring effect will start to be suppressed and at low enough concentrations the pinning is fully suppressed. Electrowetting force at the contact line depends on the applied voltage. Increasing the voltage (on a suitable substrate) can help in fully supressing the coffee ring effect at higher particle concentrations. Future research can be done on the effect of particle size.

5 References

References

[1] R.D. Deegan, O. Bakajin, T.F. Dupont, G. Huber, S.R. Nagel, and T.A. Witten. Capillary flow as the cause of ring stains from dried liquid drops. *Nature*, 389:827–829, 1997.

[2] M.H.G. Duits H.B. Eral, D. Mampallil and F. Mugele. Web, 2011. softmatter.

[3] Kwan Hyoung Kang. How electrostatic fields change contact angle in electrowetting. Web, 2002. http://pubs.acs.org/doi/pdf/10.1021/la0263615.

[4] Frieder Mugele and Jean-Christophe Baret. Electrowetting: from basics to applications. Web, 2005. http://doc.utwente.nl/54091/1/electrowetting.pdf.