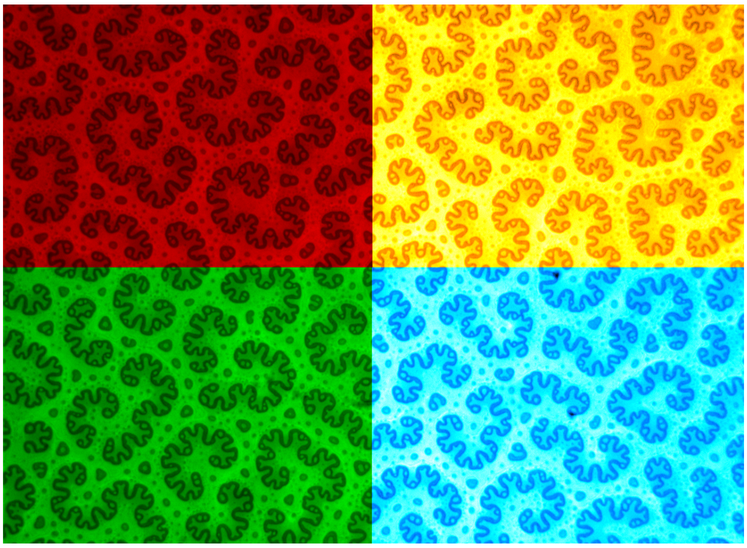
Wrinkling behaviour of critical ferrofluid droplets under external field

Thesis prepared for the Degree of Bachelor of Science



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Contents

1 Introduction

Magnetic fluids such as ferrofluids and their mixtures exhibit interesting phase phenomena under external magnetic fields. In this thesis, the wrinkling behaviour of ferrofluid rich phases under an external magnetic field has been studied.
It is already known how mixtures of ferrofluid, silicone oil and Lutidine behave under a perpendicular external magnetic field. Some compositions start to demix and form ferrofluid rich droplets [1]. These droplets can undergo certain deformation, starting with a simple shape transition into a dog-bone shape [2] to complex wrinkled forms [3].
These wrinkled ferrofluid droplets can be elongated by applying an oscillating lateral field. This work is about the elongation of these droplets and the relaxation back to the wrinkled state.
Therefore experiments from phase separation to wrinkling are reproduced. Afterwards there will be an experiment on the elongation and relaxation of wrinkled ferrofluid droplets.
This research aims to establish if the relaxation effect is energy or entropy driven. The results will be discussed with respect to known aspects of magnetic fields, and ferrofluids under magnetic fields to give a better understanding of the relaxation process.

2 Experiments

In this experiment the following aspects will be observed: the demixing of a critical ferrofluid mixture, the shape transition of the resulting structures, the wrinkling of the phase separation line and the behaviour of these structures under dynamic lateral magnetic field.

2.1 Experimental setup

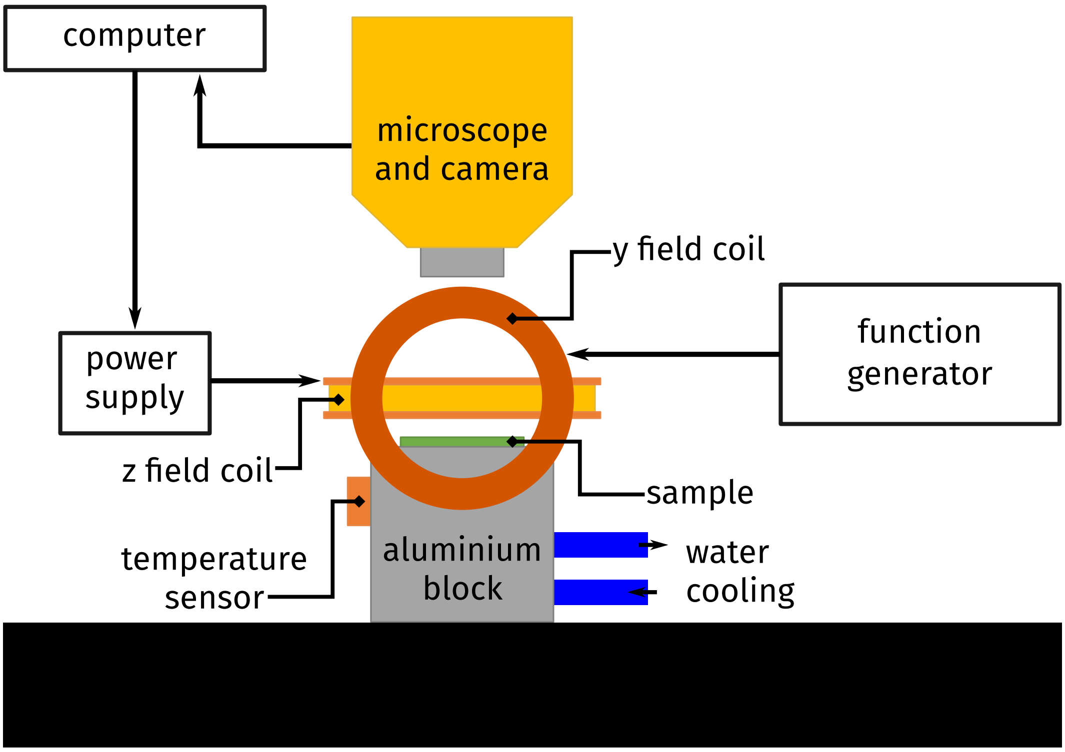


Figure 2.1: Experimental setup. The x field coil is not shown in this picture.

All observations are made with reflection optical microscopy using a Leica DMLP microscope.
After preparing a ternary mixture of ferrofluid, silicone oil and Lutidine (see 2.2), $4\mu l$ of the sample is put on a silicone wafer, which is then placed on a water cooled aluminium block under the microscope as seen in figure 2.1.
With the camera integrated in the microscope it is possible to focus on the surface

of the sample and observation can be made on the computer.
Further there are separate coils around the sample for applying a static or dynamic magnetic field in x-, y-, and z-direction. In the setup the z-direction is perpendicular to the sample's surface. The coils can be triggered separately and independent of each other.
The aluminium block is connected to a water cooling system, and an additional temperature sensor is applied to it, so the temperature can be checked during the experiment. The water cooling is necessary because the coils heat up during the experiment and therefore would heat up the aluminium block and the sample.
The power supply for the coil in z-direction is controlled either by a computer program (fieldcontrol written by Jonas Bugase) which will automatically increase the current continuously, or can be adjusted by hand, to get a constant value for the external field.
The x- and y-coils are powered by a function generator which will create an oscillating lateral field. Later, only the y-coil will be used, as the effects are stronger in y-direction. This is due to a slight mechanical instability in the setup which could not be fixed.
The measurements for the following experiments are recorded with the camera integrated in the microscope. These video files are processed later to obtain meaningful information on the relaxation.

2.2 Preparation of the samples

For the experiments the ester based ferrofluid APG 512 A from Ferrotec, silicone oil (Silicone DC 200) from Fluka and 2,6-Dimethylpyridine (Lutidine) 98% from Sigma-Aldrich are used. A composition of 3:1:1 (ferrofluid:Lutidine:silicone oil) is prepared, as this mixture will show all the effects explained on the following pages. To obtain this composition a sample of 100μl contains 60μl of ferrofluid, 20μl of silicone oil and 20μl of Lutidine. As the Lutidine evaporates, it is important to first pipette the silicone oil and the ferrofluid and at last the Lutidine. All components need to be mixed properly with a vibrating plate so they will become a homogeneous mixture.

2.3 Phase separation of the critical ferrofluid mixture

As already shown by Jonas Bugase [1], some specific compositions of mixtures of the ferrofluid are phase separating into a ferrofluid rich phase (or the minority phase) and a ferrofluid poor phase (or the majority phase) under an external magnetic field in z-direction. The ferrofluid rich phase forms dark droplets in contrast to the light ferrofluid poor phase. Further he found out that the droplets have a cylindrical shape, extending from bottom of the glass to the top. His experiment will be reproduced in the first step.
4μl of the sample are applied on the silicone wafer and placed under the microscope.

After focusing on the surface using reflectance microscopy, a homogeneous mixture can be observed. Now the program *fieldcontrol.tcl* is run, which slowly and linearly increases the current linear through the z-field coil and therefore the induced magnetic field.
At a value of about 1mT the sample starts to demix into a ferrofluid rich phase forming circular droplets and a silicone-Lutidine phase. Switching the field off destroys the droplets and a (nearly) homogeneous phase can be observed again.

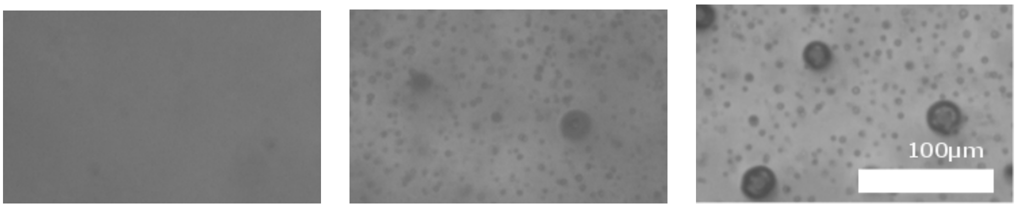


Figure 2.2: States of demixing of a critical ferrofluid mixture. On the left, there is a homogeneous phase. In the middle, a magnetic field was applied and the sample starts to demix. On the right the sample is phase separated; the ferrofluid has formed round droplets.

2.4 Shape transition

Increasing the external field further, the ferrofluid rich droplets deform into a bone shape at a z-field of about 3mT. This can be seen in figure 2.3.
When the droplets reaches a critical size, they become instable due to thermal fluctuations. On one hand, there is the line tension on the phase separation line. This attractive force wants to keep the round shape and therefore the smallest possible interface line. On the other hand, there is dipolar repulsion. So at a certain size of the droplet, the repulsive force becomes stronger than the line tension, and the droplet starts to elongate into a bone-shaped form.
This was first shown by P. Heinig et. al. [2].

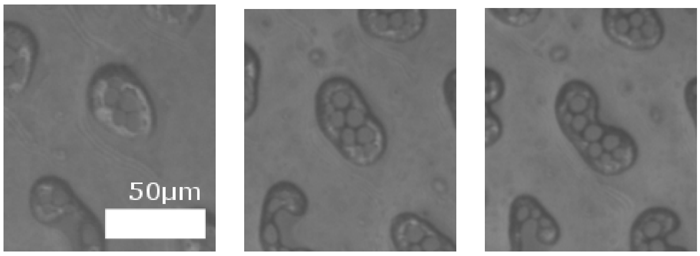


Figure 2.3: Shape transition of a ferrofluid droplet. On the left, there is a round droplet. The middle picture shows an oval shape of the same droplet. On the right, the droplet has elongated in the bone shape.

2.5 Wrinkling

Under further increasing external field the droplets deform into a labyrinth pattern. Their radius of curvature is around 100μm. At a field of about 4.5mT, the liquid/air interface of the ferrofluid rich phase starts to exhibit wrinkles independent of the curvature of the dog-bone deformed ferrofluid rich droplet. Here, there will be made a difference between the phase separation line on top and the bulk, which is the part of the phase that lies on the silicone wafer.
These wrinkles on the top have a radius of curvature of around 20μm and are therefore smaller than the wrinkles of the bulk. The wrinkling only occurs on a liquid/air interface.
For defining the wrinklenumber wr the path length $s - s'$ is needed which defines the length of a segment of the top, and the short cut length $|\boldsymbol{r}(s) - \boldsymbol{r}(s')|$ which is the distance between the ends of this segment. The wrinklenumber wr is then defined as

$$wr(s - s') = \ln\left(\frac{s - s'}{\langle|\boldsymbol{r}(s) - \boldsymbol{r}(s')|\rangle}\right) \tag{2.1}$$

Important to say is that the critical field for the small scale wrinkles lies above the critical field for the long range wrinkles.

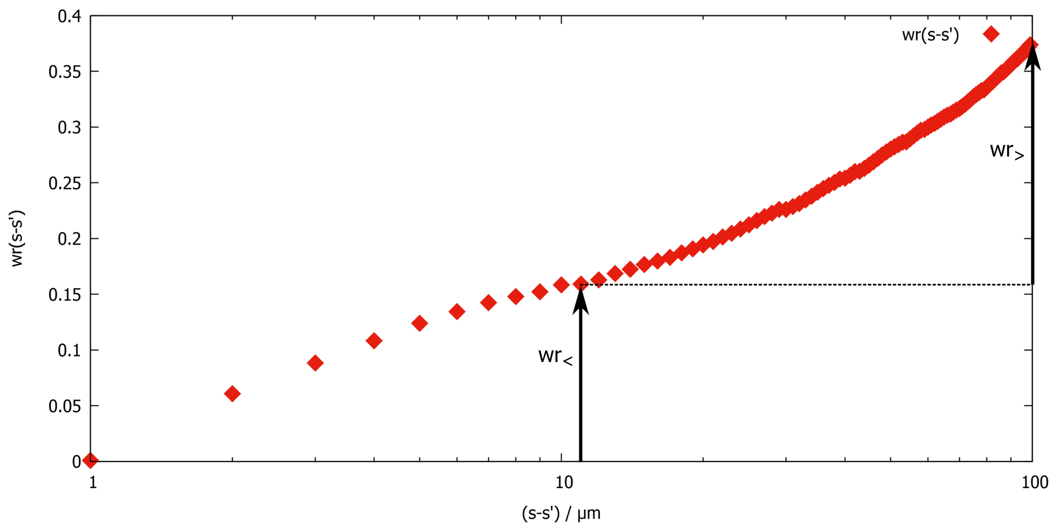


Figure 2.4: Wrinklenumber plotted against segment length. The external field has a value of 9.6mT. The total wrinklenumber can be written as a sum of $wr_<$ and $wr_>$.

The wrinklenumber increases with the length of the segment but reaches a saddle point at the typical path length of a small scale wrinkle which is of the order of 10μm. If the total length of the bulk is defined as the intermediate path length we can write the wrinklenumber as a sum of small and long scale wrinkles:

$$wr(S) = wr_< + wr_> \tag{2.2}$$

This is shown in figure 2.4.
These wrinklenumbers can be written as

$$wr_< = \ln\left(\frac{S}{B}\right) \tag{2.3}$$

$$wr_> = \ln\left(\frac{B}{|\boldsymbol{r}(S) - \boldsymbol{r}(0)|}\right) \tag{2.4}$$

where S equals the length of the top and B the length of the bulk. As this effect only appears at a liquid/air interface, one can think about the following:
The equilibrium lengths of top and bulk are different. The length of the top is bigger than the length of the bulk, but as they are not independent from each other, the top face has to wrinkle to stay in shape with the bulk, as it cannot become bigger than the bulk.
Research on this topic was first done by Natalia Wilke and Thomas Fischer [3].

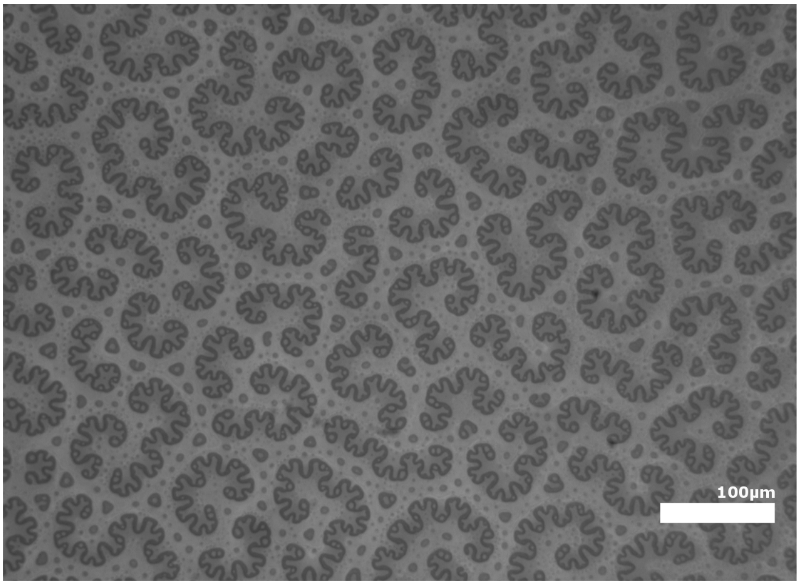


Figure 2.5: Wrinkled ferrofluid rich phase under external field.

3 Results

3.1 Elongation and Relaxation

In this thesis a closer look is taken at the wrinkled state of the minority phase to obtain an understanding of it. It was found out that the ferrofluid rich phase responds to an oscillating lateral field in x- and y-direction. It elongates in the direction of the lateral field and, after switching the lateral field off, it starts to wrinkle again. What is of interest is the time it takes for the phase separation line to relax back into its initial state.
Just like in the experiments before a sample is prepared as it is written in 2.5 and is exposed to a static external magnetic field in z-direction to obtain the demixed phases. After the wrinkled phase separation lines have formed, the external z-field is set to a constant value. The immediate consequence is that the minority phase stops growing and goes into an equilibrium state.
Now the lateral dynamic field in y-direction is switched on. For the purpose of elongation a sine wave is chosen on the function generator, with appropriate amplitude and frequency. When the oscillating magnetic field is applied to the sample, the wrinkled phase separation line starts to elongate in the direction of the lateral field. When the phase separation line has elongated, the lateral field (not the external z-field) is switched off again and a relaxation back into the wrinkled state can be observed. After the phase separation line has completely relaxed, the oscillating field is applied again to reproduce the effect.
This procedure is repeated for six different values of the external z-field. As the z-field increases, the lateral field needed adjustment. The higher the z-field, the higher the amplitude and frequency of the lateral field. The exact values of amplitude and frequency do not matter as they are only used to elongate the phase separation line. Measurements are made for z-field values of 6.4mT, 6.9mT, 7.5mT, 8.0mT, 8.5mT, 9.1mT and 9.6mT.

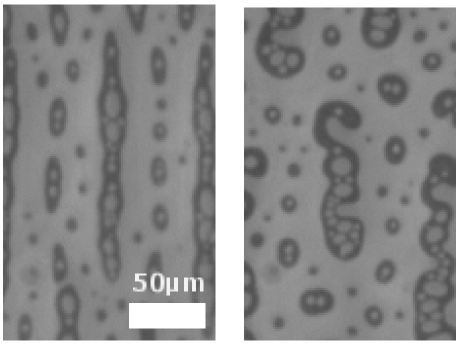
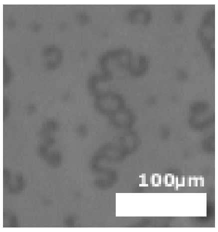


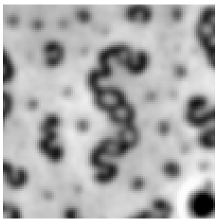
Figure 3.1: Ferrofluid rich phase during relaxation process. On the left is the elongated phase separation line right after switching off the lateral field. On the right the phase separation line has completely relaxed after 2.7 seconds.

3.2 Data processing

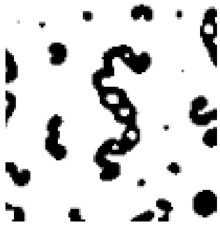
In attempt to gain information on the relaxation times, the videos from the measurements need to be processed using ImageJ. First, a background correction has to be made using a bandpass filter. This is necessary because the background is not illuminated even. The bandpass cancels that gradient and one obtains an even background. After doing so the data is converted into binary pictures of black minority phase on white background, and then the edges of the phase separation line are gained by using a gradient filter.
Now there are many such phase separation lines in the processed videos. It is obvious that not every single one can be described. It was observed that the same elongated relaxing wrinkles were dissipating out of focus or breaking during the relaxation process. Only separated single wrinkled phase separation lines that do not break into pieces can be described properly.
To separate such phases from the data, the Python program *select_snake.py* (written by Florian Maier) is used, which will cut out a small space of the whole picture, and also removes smaller droplets that do not belong to the selected one. After having selected a specific phase separation line, its outline is set to a thickness of only one pixel by using ImageJ again, as the following programs only work with one pixel thickness. The pictures are skeletonized to obtain this one pixel thick edge. At last the pictures are inverted as the following programs need white lines on black background to work.
Now the pictures can be converted into actual data points using the programs *cut_appendices.py*, *get_coordinates_ordered.py* and *wrinkle.py*. The first two programs cleans the phase separation line from any appendix and get the coordinates in a logical order. What is important is that *wrinkle.py* can compute certain properties of the line like the wrinklenumber wr of the phase separation line (wr is explained in 2.5). The program will print the data in a *.txt* file, so one can directly plot the data with gnuplot.
Sometimes these programs need to be run more than once, because there are cases it calculates a negative wrinklenumber. Running the programs again will fix that, but will also give more noise. During the data processing it became clear that two runnings are enough to get an amount of points to work with. Structures that do not give enough data points are sorted out due to too much noise.



(a) raw data

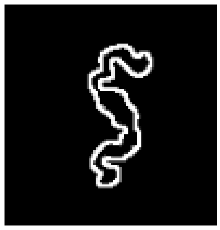


(b) after bandpass filter



(c) made binary

(d) after gradient filter



(e) after *select_snake.py*

Figure 3.2: Example for the different processing steps using ImageJ and *select_snake.py*. The skeletonized figure is not shown here due to printing resolution properties.

3.3 Relaxation time

After obtaining analysable data, the wrinklenumber is plotted against the framenumber n_f using gnuplot. The wrinklenumber was already explained in (2.5). As a relaxation was observed this number is expected to converge against a constant value. As frames is not a good unit, the framenumber has to be devided by the framerate which is 21 frames per second to get the time in seconds.

$$t = \frac{n_f}{21} s$$

Now the wrinklenumber can be plotted against the time. As expected, the wrinklenumber converges, as it can bee seen in figure 3.3.
In the next step the relaxation time τ is specified. τ is defined by the time it takes until the system has reached a value of $\frac{1}{e}$ of its start value. By eye the following function is fit to the data points:

$$s(t) = a + b \cdot tanh\left(\frac{(t-t_s)\cdot 21}{\tau}\right)$$

Parameters a (y displacement), b (amplitude) and t_s (x displacement) are chosen as they best fit the data, $\frac{1}{\tau}$ defines the curvature of the function.
This function serves the first idea of an exponential relaxation behaviour and still fits for increasing field.

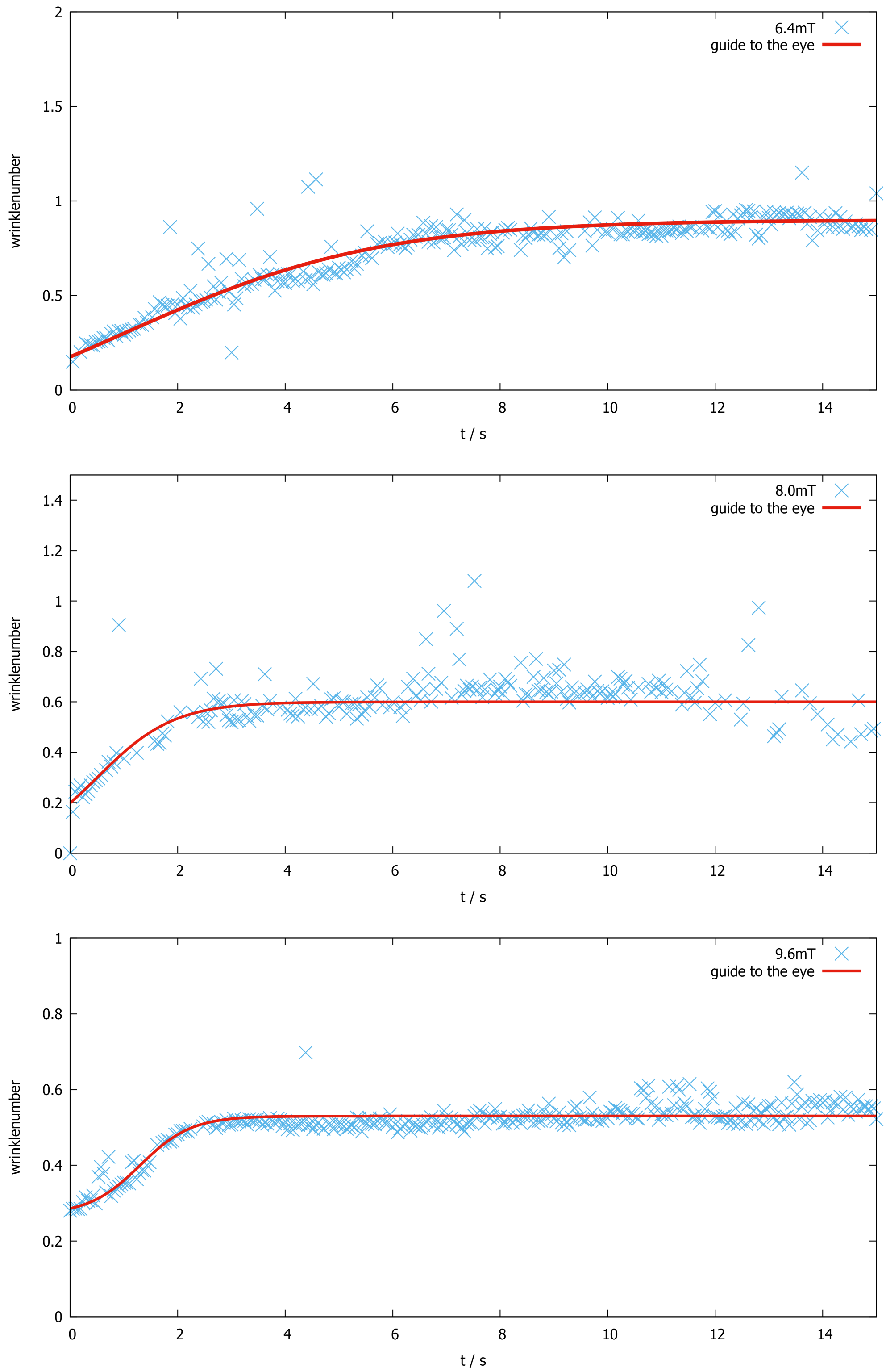


Figure 3.3: Examples for data points and fitted graphs for the relaxation time. Wrinklenumber is plotted against the time. The external field increases from top to bottom of the page.

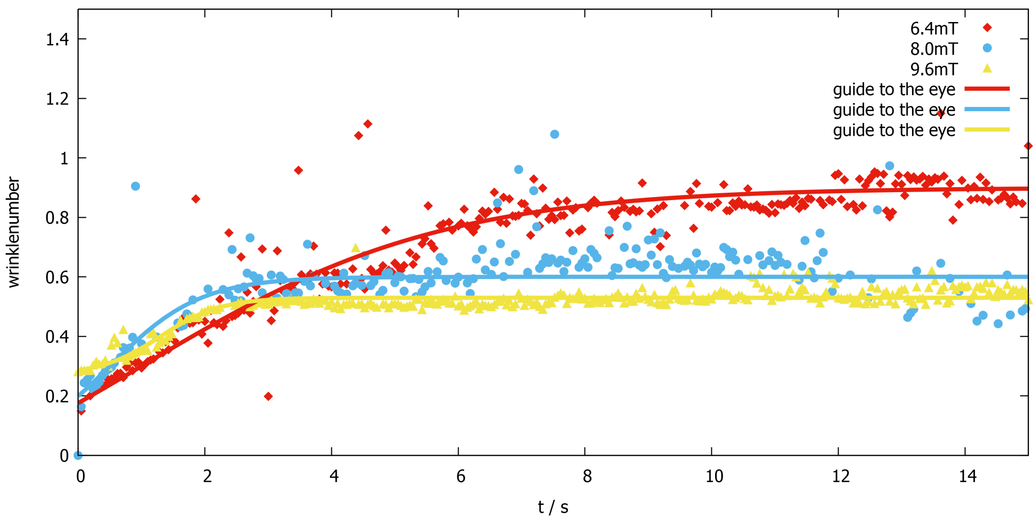


Figure 3.4: Comparison of relaxation times of low (red), middle (blue) and high (yellow) external fields.
$\tau_{red} = 4.76$s, $\tau_{blue} = 1.43$s, $\tau_{yellow} = 0.95$s

The curvature of the graphs increases with the increasing external field. Therefore the relaxation time decreases with increasing external z-field, which corresponds with the observations made during the experiment.
In the next step the relaxation times are plotted against the magnetic field H. The function

$$f(x) = \frac{a}{x^2} \tag{3.1}$$

is fitted to the data points.
The value of the fitting parameter computed by gnuplot is given by

$$a = 301.85 \pm 28.45 \tag{3.2}$$

Taking a look at these results, one comes to the conclusion that

$$\underline{\underline{\tau \propto \frac{1}{H^2}}} \tag{3.3}$$

The results can be seen in figure 3.5.

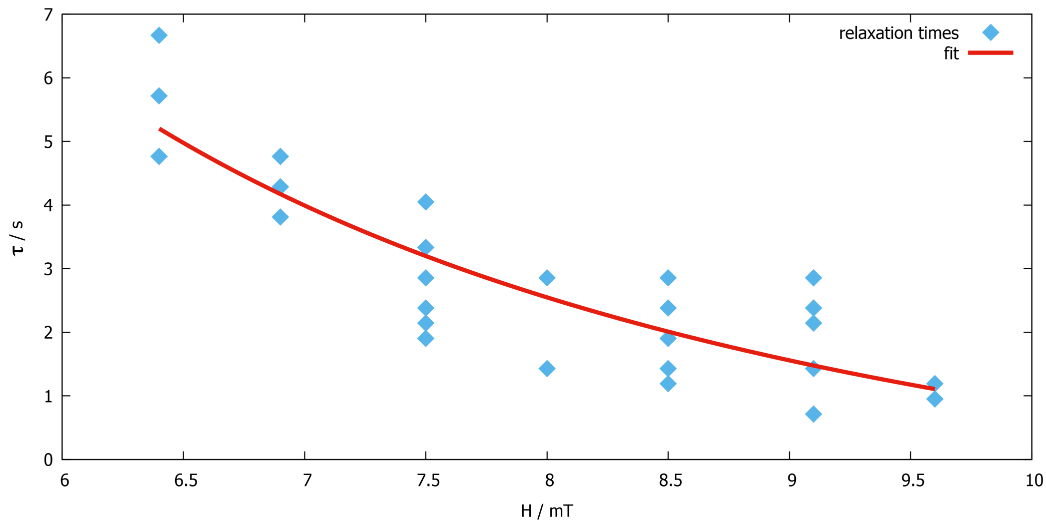


Figure 3.5: Relaxation time vs. external field. The relaxation time decreases with the square of the increasing magnetic field.

4 Discussion

There are a few things that are already known about magnetic fields and ferrofluid rich droplets under such fields.

The energy density w_m of the magnetic field is given by

$$w_m = \frac{1}{2}HB \tag{4.1}$$

Using $B = \mu_0(H + M)$ one obtains

$$w_m = \frac{1}{2}\mu_0 H^2(1 + \chi_{eff}(\boldsymbol{r})) \tag{4.2}$$

μ_0 is the magnetic field constant/permeability and χ_{eff} the magnetic susceptibility. The energy density of the magnetic field is proportional to H^2. [4]

The force on the phase separation line is given by [2]

$$\boldsymbol{F} = \frac{\partial w_m}{\partial \boldsymbol{r}(s)} \tag{4.3}$$

Taking a look at (4.2) one can assume

$$\boldsymbol{F} \propto \mu_0 H^2 \tag{4.4}$$

This force on the phase separation line causes the minority phase to contract. The velocity $\boldsymbol{v}$ of this movement follows

$$\boldsymbol{v} = \int_P \underline{\underline{\boldsymbol{O}}}(s, s') \cdot \boldsymbol{F}(s') ds' \tag{4.5}$$

P is the phase separation line of our minority phase, $\underline{\underline{\boldsymbol{O}}}$ is a non-local second rank tensor.
Assuming that

$$\underline{\underline{\boldsymbol{O}}} \propto \frac{1}{\eta} \tag{4.6}$$

where η is the viscosity of our mixture, and using (4.5) and (4.6) one comes to the conclusion

$$\boldsymbol{v} \propto \frac{\mu_0 H^2}{\eta} \tag{4.7}$$

The following function was fitted to the data points to find out the relaxation time:

$$s(t) = a + b \cdot \tanh\left(\frac{(t - t_s) \cdot 21}{\tau}\right) \tag{4.8}$$

With this τ can be described as

$$\begin{aligned} \tau &= \int_{s(0)}^{\frac{s(0)}{e}} \mathrm{d}t \\ &= \int_{s(0)}^{\frac{s(0)}{e}} \frac{\mathrm{d}t}{\mathrm{d}s'} \mathrm{d}s' \end{aligned}$$

Using

$$\frac{\mathrm{d}t}{\mathrm{d}s} = \left(\frac{\mathrm{d}s}{\mathrm{d}t}\right)^{-1} = v(t)^{-1} \tag{4.9}$$

one obtains for the relaxation time

$$\tau = \int_{s(0)}^{\frac{s(0)}{e}} \frac{1}{v(t)} \mathrm{d}s' \tag{4.10}$$

With (4.7) follows

$$\underline{\underline{\tau \propto \frac{\eta}{\mu_0 H^2}}} \tag{4.11}$$

This is a good result as it corresponds with (3.3). Therefore the relaxation can be assumed as an energy driven effect.

5 Conclusion

In this thesis, experiments on a critical ferrofluid-silicone-Lutidine mixture were conducted. it was observed that the mixture can undergo a phase separation under an external magnetic field into round ferrofluid rich droplets as well as a shape transition of these round droplets into a bone shape.
Further observations were made on how these ferrofluid rich phase wrinkles under higher external fields, and that their bottom and top show independent wrinkling behaviour due to their interface properties.
In order to contribute to the understanding of this critical mixture experiments on the relaxation of the phase separation line were performed. An applied oscillating field caused the wrinkled droplets to elongate. After the external field was switched off the droplets relaxed back into the wrinkled state. It was found out that the time it takes to relax back scales with the square of the external magnetic field.
This result corresponds well with what is already known about energetic effects in magnetic fields.

Bibliography

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Erklärung

Hiermit bestätige ich, dass ich die vorliegende Arbeit selbst verfasst, nur die angegebene Literatur als Hilfsmittel verwendet habe und alle wörtlich oder sinngemäß übernommenen Äußerungen anderer Autoren gekennzeichnet habe. Außerden versichere ich, dass ich die Arbeit zu keinem früheren Zeitpunkt bereits zur Erlangung eines akademischen Grades eingereicht habe.

Bayreuth, 23. Mai 2017 ______________________________

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