

Flexible strings of colloidal particles

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supervised by:

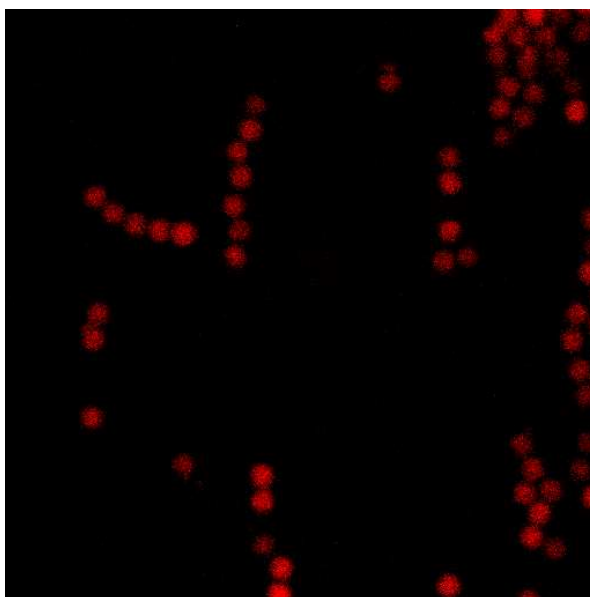
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Abstract

In this research we have synthesized cross-linked fluorescent PMMA particles and we used an high frequency AC-electrical field to align those particles in strings in polar solvents, which we fixated into flexible strings by heating. we investigated the detailed parameters under which the flexible strings can be obtained.



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1 Introduction

1.1 What are Colloids?

Colloids are particles dispersed in an continuous medium where the particles are small enough to experience Brownian motion through collusion with neighboring molecules of the continuous medium but large enough to be seen with normal light microscopy which means they range from around a few nanometer in size to few micrometer. The term colloid coming from $\kappa\omicron\lambda\lambda\alpha$ the ancient Greek word for glue, a term fist coined by Graham in 1861. The first person to observe the random motions of colloids was Robert Brown a Scottish botanist when he was observing pollen grains suspended in water with a light microscope.

Colloidal systems can be classified depending on the phase of the dispersed particles and the continuous medium, for example: foams(gas dispersed in liquid),liquid aerosols(water dispersed in gas for example fog),emulsions(liquids dispersed in liquid) and suspensions(solid particles dispersed in fluids for example blood,ink and milk). In this research we will only focus on a system where solid particles are suspended in a fluid.

1.2 Colloids as a model system

Colloidal particles are interesting as a model system because they are small enough to experience Brownian motion therefore they experience phase behavior similar to atoms and molecules but because they can still be seen by light microscopy they provide a easier way to mimic molecules at a visible scale. Colloidal interactions can be manipulated to great extents, which will cause them to experience a wide range of phase behaviors. When the colloidal particles are placed in a sufficiently polar solvent like water,most colloids absorb charged ions on their surface, this surface charge will attract oppositely charged ions that will form a diffuse cloud around the particles which together with the surface charge are called the "electric double layer", these ionic clouds will screen the coulomb interaction of the surface charge, reducing its range, this makes this interaction tunable by adjusting the salt concentration in the solvent. Their phase can also be manipulated with external fields to form 1D strings and rods, 2D sheets and 3D crystalline structures of colloidal particles depending on the strength

of the fields and the concentration of colloidal particles in the solvent. Specifically these one dimensional strings of colloids have been shown to be tunable in stiffness and can be used as a model for polymers. The tunability of these interactions makes colloids interesting for industrial applications.

1.3 Experimental goals/setup

In this research we will use a high frequency AC-electric field to create flexible strings of colloidal particles, heat those strings and analyze them by using confocal microscopy. The main difference between confocal microscopy and conventional light microscopy is the use of two pinholes, one of which is placed in front of the detector to remove out of focus light (this is also the origins of the name) and another one to create a pin-point source of laser, illumination only a small area of the sample, whereas with normal light microscopy the whole sample is illuminated. As only a small area is illuminated you can only observe a small part of the sample at a time however confocal microscopy allows for a resolution far greater than that of normal microscopy and when combined with fluorescent dye you can even re-solve micron sized particles at a single particle level. In most cases for research into colloids using confocal microscopy either sterically stabilized PMMA (Poly methyl methacrylate, also more commonly known as perspex) or inorganic silica particles have been used, mostly because it's easy to match their refractive indexes, preventing interference from light scattering. The high density of silica particles makes it considerably harder to match with the solvent, for the creation of flexible strings the concentration during the creation of the strings determines whether strings, rods or sheets will form, if the particles sediment too rapidly this will be harder to control therefore we will use PMMA particles in this project.

1.4 Polymerization procedure

There are several ways to synthesize PMMA particles, for this research we will use the method of dispersion polymerization. Dispersion polymerization is defined as a polymerization reaction where the monomer is soluble in the solvent used for the reaction but the resulting polymer is not. As a result of that the polymer colloids will precipitate out of a homogeneous solution. A notable advantage of dispersion polymer-

ization over other ways of synthesis is that it allows the creation of micron size particles in one step.

In many researches the non-cross-linked version of PMMA is used because the synthesis of the non-cross-linked particles is easier, however uncross-linked PMMA particles have a couple of disadvantages, in most good solvents they swell considerably or can even fall apart and they are less resistant to both heating and dissolving, since we use heating as way to fixate the strings we chose to use cross-linked PMMA for this project. Research has shown its possible to disperse the particles in a polar or an apolar environment, however the method for dispersing the particles in a a-polar environment has been shown to be much lengthier and considerably more difficult. its also possible to transfer the PMMA particles from a polar environment to an apolar solvent using the surfactant span 85. A disadvantage of using a polar solvent is it is not possible to get a total refractive index match however the preparation takes less time and the created strings are more flexible.

2 Methodology and Theory

2.1 Chemicals

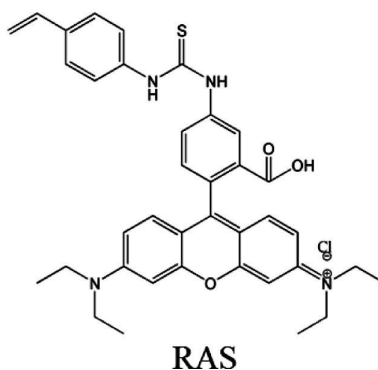


Figure 1: structure formula for RAS

For the synthesis we used the following chemicals: methyl methacrylate(MMA,Aldrich) as the monomer, azo-bis-isobutyronile(AIBN, Jansen Chimica) was used as the initiator , the fluorescent dye we used was N-(9-(2-carboxy-4-(3-(4-vinylphenyl)thioureido)phenyl)-6-(diethylamino)-3H-xanthen-3-ylidene)- N-ethylethanaminium chloride(RAS)(for the structure formula of RAS see figure), to prevent the particles from aggregating we used Polyvinylrolidone(PVP, K-90,Sigma) as a stabilizer, formamide(Baker,analytical grade) methanol and deionized water were used as solvents,Ethylene glycol dimethacrylate (EGDMA, Sigma-Aldrich) was used as cross-linker.

2.2 Synthesis steps

First we dissolved 2.5g of the monomer MMA, 0.0275g of the initiator AIBN and 1.015g of the stabilizer PVP in a mixture of the solvents (20.68mL of ethanol and 4.10mL of water). these chemicals were placed in a 250ml 3 necked flask equipped with a gas supply, a Teflon coated stir bar and a condenser. Next, this mixture was homogeneously dissolved, and nitrogen gas was bubbled through the reaction system for 30 min at room temperature. After that the flask was placed in a silicon oil bath which was kept at 55 °C for 30 minutes while being stirred at 100 rpm. On the other hand 23mg of the

dye(RAS), 0.507g of PVP and 24.3 μ L of the cross-linker(EGDMA) were dissolved in 2.05mL of water and 10.34mL of methanol, when the reaction started this solution was added dropwise to the flask at a constant rate for 2 hours. After this solution was added, the flask was maintained at 55 °C for 24 hours before cooling down.

2.3 Static light scattering measurements

After the particles were synthesized we used SLS(static light scattering) on a dilute suspension of the sample in methanol to measure the particle size and polydispersity(the polydispersity is the ratio between the standard deviation and the particle diameter), static light scattering is an optical technique that measures the intensity of scattered light as a function of the scattering angle which can be compared to the Mie solution for poly disperse particles with a homogeneous structure(the Mie solution to Maxwell's equations describes the scattering of light by spheres), from which certain properties of the particles can be derived. The resulting particle size was about 765nm and a polydispersity of about 5%, the resulting plot can be seen in figure 1.

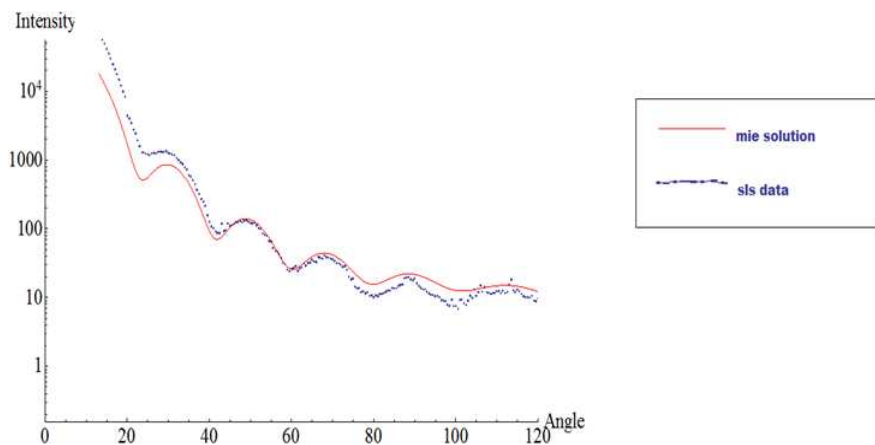


Figure 2: SLS measurement of PMMA particles with a diameter of 765nm and a polydispersity of 5%

2.4 Sample preparation

Next we took some of suspension to prepare a sample suitable for confocal measurement. To remove the remaining free PVP and second nucleations, we washed the suspension with methanol: We added methanol to the suspension in a 1:1 ratio and sonificated it for 10 minutes using a Branson 8510 sonicator, then, we centrifuged the suspension in a Eppendorf 5810 centrifuge for 20 minutes at 1500 rpm. Afterwards we removed the supernatant, and refilled the missing substance with methanol, we repeated this process 2 times with a rotation speed of 1500 rpm.

To prepare the sample for confocal measurement we had to transfer the particles from a solution of water and ethanol to formamide, as formamide has the closest refractive index out of the possible polar solvents. Therefore after we removed the supernatant of the suspension, we refilled the bottle with formamide and sonificated the mixture for about 10 minutes after which we centrifuged it for 30 minutes at 2000 rpm. After three cycles of rinse with formamide, we thought the solvent was totally swapped

2.5 Electric cells

During this research we used two different electric cells. Two 50/ μm diameter nickel alloy wires ran length wise on the opposite sides of the 1mm gap through a capillary (Vitrocom, U.K., 0.1x1mm) (for details, see figure 3). To prevent the positively charged particles of the sample from sticking to the negatively charged wall, we coated the cell with the polyelectrolyte PVP, by dissolving 1wt% Pvp in methanol which was put into the capillary and was dried afterwards by blowing nitrogen gas through the capillary. After the capillary was filled with the dispersion and closed by applying UV glue (Norland 65) to the ends of the capillary. Then we put the cell under a UV lamp for about 15 minutes, shielding the dispersion from the UV light with aluminium foil.

For the second cell (seen in figure 4) we parallelly placed 2 glass cover slips (130-160mm thick) on side of which were fully coated with a semi transparent conductive ITO layer (indium tin oxide), the thermocouple wires were connected, separated with spacers with various thickness, to the conductive sides of the cover slips fixated by UV glue and used silver paint to make a better electrical contact with the conductive layer. We used UV glue to attach the electric cell to a microscope

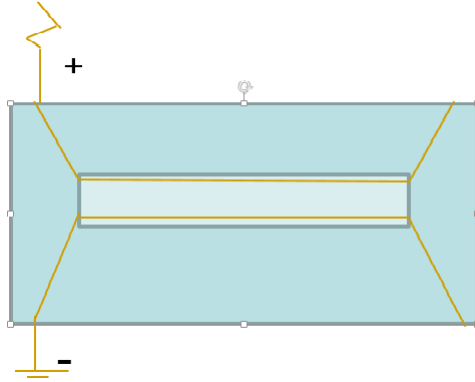


Figure 3: a schematic picture of a capillary cell

slide, subsequently we coated the walls in the same way as the first cells, before filling the space between the glasses with the dispersion and closing the sides with UV glue.

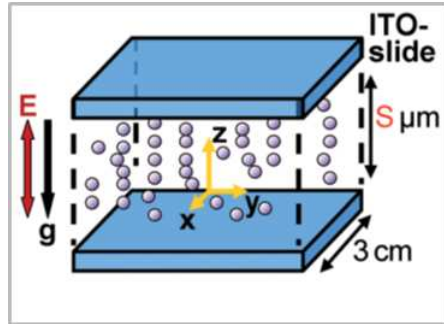


Figure 4: a schematic picture of an ITO-coated cell [5]

2.6 Theory

When colloidal particles in a colloidal suspension have a sufficiently different dielectric constant compared to the suspension fluid, applying an electrical field will cause the colloidal particles to have a dipole moment, and dipole interactions between the particles can radically change the phase of fluid. With our experimental setup (neglecting vanderwaals interactions because the particles are sterically stabilized) the interaction potential between PMMA particles in a solvent that is

a close refractive-index match can be approximated as a pair potential that is a combination of a hard-core repulsion and a coulomb potential due to electrical charge of the double layer. when you combine these two interactions you get the Yukawa pair-potential, that is described as follows [3].

$$\frac{u_{Yukawa}}{K_b T}(r_{ij}) = \begin{cases} \frac{\phi \exp(-\kappa(r_{ij}-\sigma))}{r_{ij}/\sigma}, & \text{if } r_{ij} > \sigma. \\ \infty, & \text{if } r_{ij} < \sigma. \end{cases} \quad (1)$$

with

$$\kappa = \sqrt{8\pi\lambda_B c}$$

$$\lambda_B = \frac{e^2}{4\pi\epsilon_0\epsilon_m K_B T}$$

Where K_b is the Boltzmann's constant, T the temperature, r_{ij} the separation length between the 2 particles, σ the particle diameter, ϵ_0 the vacuum permittivity and ϵ_m the dielectric constant of the solvent,

$$\phi = \frac{Z^2 \lambda_B}{\sigma(1 + \kappa\sigma/2)^2} \quad (2)$$

is the potential when the two particles make contact ($r_{ij} = \sigma$) where $2c$ is the number density of the monovalent salt in the solvent, κ is the inverse debye screening length, λ_B is the Bjerrum length.

If salt is added to the solvent that will increase κ through c , which in turn increases the rate the potential decays with r_{ij} , as the interaction is repulsive this will allow the particles to get closer to each other(see figure 6) .

After turning on the electric field the particles acquire a dipole moment and there will be a dipole contribution to the interaction potential. Therefore in the approximation that the particles are perfect dipoles the contribution of the dipole interaction becomes

$$\frac{u_{dipole}}{K_b T} = \gamma(\sigma r_{ij})^3(1 - 3\cos^2 \theta_{ij}) \quad (3)$$

$$\gamma = \frac{\mathbf{p}^2}{2\pi\epsilon_0\epsilon_m K_B T}$$

where θ_{ij} is the angle between the direction of r_{ij} and the direction of the electrical field, γ is a dimensionless factor

$$\mathbf{p} = \frac{\pi}{2}\beta\epsilon_0\epsilon_m\sigma^3(E_{dip} + E_{external}) \quad (4)$$

is the induced dipole moment, β is a dimensionless factor $\beta = \frac{\epsilon_p - \epsilon_m}{\epsilon_p + \epsilon_m}$ that is dependent on the dielectric strengths of the medium and the

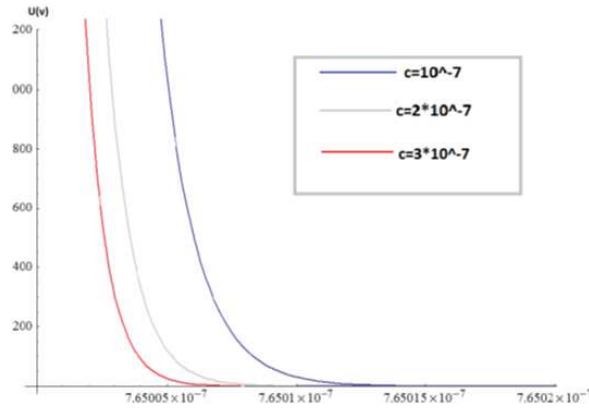


Figure 5: potential as a function of r_{ij} with various salt concentrations and other variables held constant

particles(ε_p). looking back at eq3, because r_{ij}, σ and γ are all positive by definition it follows that this potential is negative when $\theta_{ij} < 54.7^\circ$ as can be seen in figure 6. As the negative potential decays with

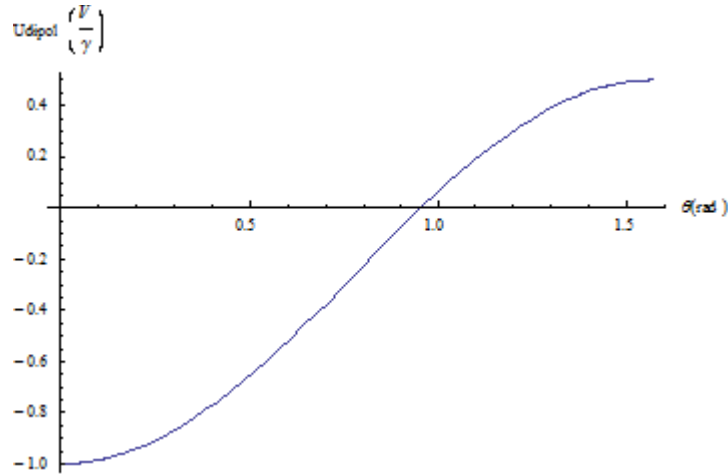


Figure 6: potential as a function of θ at r_{ij} is σ

$\frac{1}{r_{ij}^3}$, the potential increases with increasing r_{ij} and the interaction is attractive. When $\theta_{ij} > 54.7^\circ$ the potential is positive and interaction repulsive. as θ_{ij} decreases, the attractive force increases, and this causes the particles to align in strings as can be seen in fig 7

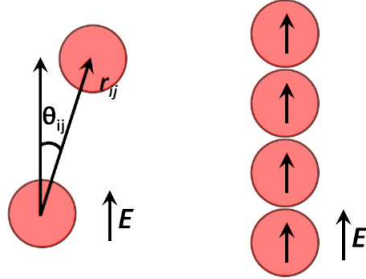


Figure 7: schematic image of electric field induced dipole-dipole interactions[3]

3 Results and discussion

3.1 Preparation of the fluorescent PMMA particles

Highly cross-linked fluorescent sterically stabilized PMMA particles were successfully synthesized using the following method. The reaction starts by heating a homogeneous solution consisting the monomer, the initiator, and the stabilizer. This heating will cause the initiator to decompose, releasing free radicals in the solution which will react with the monomer and cause them to form small oligomers, meanwhile the cross-linker and dye are slowly added to the solution with a constant rate. When these oligomers have grown till a certain critical size they will precipitate out of the solvent and form nuclei because they absorb stabilizer preventing them from coalescing with other oligomers. These initial particles will swell and absorb the remaining monomer, dye and cross-linker and initiator and after a short while the nucleation stops.[1] (see figure 8).

3.2 Measurements and creation of strings with the electrical field

For most measurements in this project we used a Leica sp2 confocal microscope with a (63x) oil objective and a Leica immersion fluid type

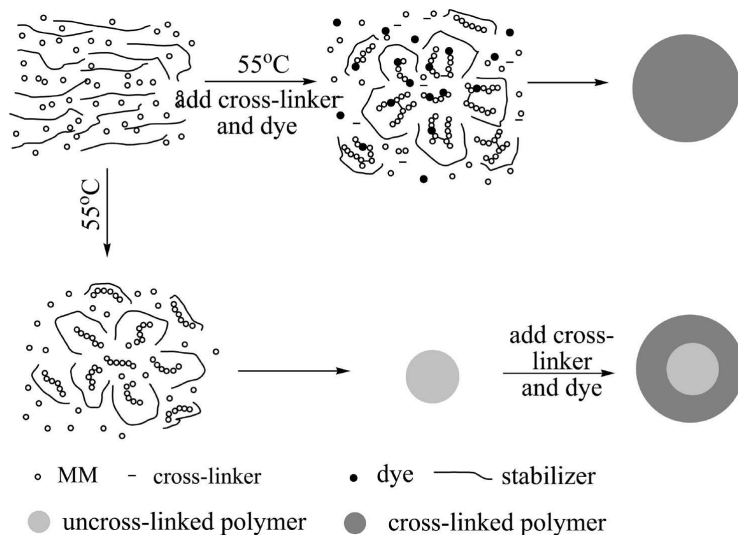


Figure 8: picture of the dispersion polymerization as described in[1]

F. using confocal microscopy we measured particle sizes which we used to calculate the average diameter and polydispersity. This method led to a result of a particle diameter of $810nm$ and a polydispersity of 8.45% To create strings we turned on a AC-electrical field, set at a frequency of 1 MHz and an amplitude of 2 VPP . The electrical field was gradually increased to a root means square field strength(E_{rms}) of $20 - 30V/mm$, in a time scale of 3 minutes strings were formed, but because the particles are slightly positively charged and the walls are slightly negatively charged all the particles and strings moved to and stucked to the walls in a time scale of 20-30 minutes leaving few particles/strings in the suspension that were free to move. In order to prevent the particles from sticking to the wall we started coating the capillary walls with a $1wt\%$ PVP solution , filling the capillary with the solution and drying it with nitrogen before adding the sample. By using this method we formed strings of more than 10 particles formed (as can be seen at figures 9 and 10), the longest strings were usually found near the wires.

3.3 Fixating the strings

Next we tried to fixate the strings through heating by using the electric field, to accomplish this we increased the E_{rms} to $35V/mm$,

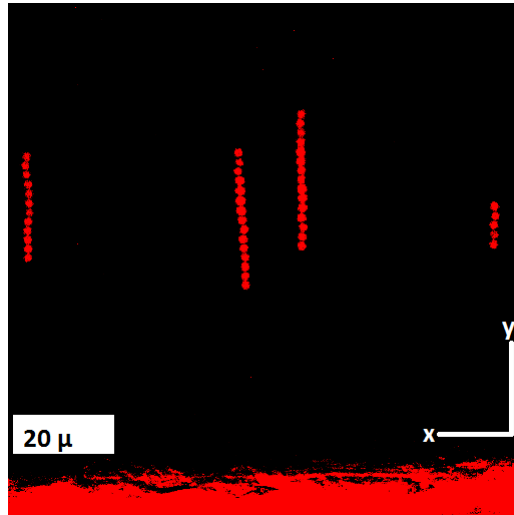


Figure 9: strings formed near an electric wire using a suspension with a 0.011 volume fraction PMMA, and an electric field strength of 35V/mm for about 25 minutes

and applied it for 30-60 minutes, but we encountered a few difficulties using this method.

1) Increasing the electric field strength caused the solvent to decompose, we used a polar solvent which is easily decomposed by the electric field.

2) When the electric field was increased the electrical wires were stretched. While the ends of the wire are well fixated, the middle of the wires have more room to manoeuvre causing the wires to touch and short circuit

3) At lower field strengths we were unable to fixate the strings

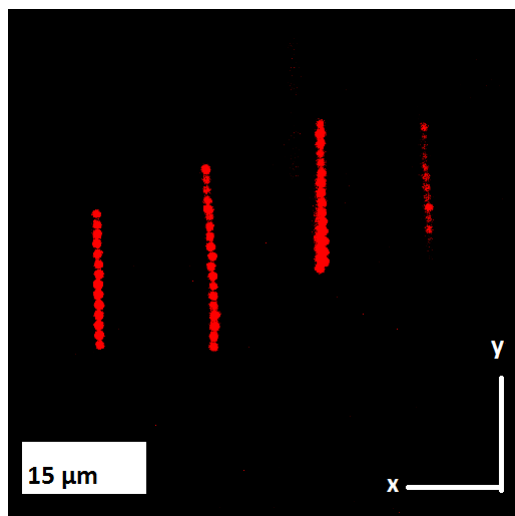


Figure 10: strings formed out of 1wt% PMMA suspension with the electric field turned on ($37\text{V}/\text{mm}$) for about 35 minutes shortly after this picture was taken the wires started to touch each other, after which there were no strings remaining in the suspension.

As a consequence we then started using ITO-coated cell as described in 2.5 which has the advantage that the electrodes are attached to the wall, which reduces the risk that the electrodes will touch each other as the walls are considerably stiffer than the wires. However using this method we encountered a few difficulties as well.

1) In the ITO-coated cells the electrical field is pointing in the z -direction and the z resolution of the confocal microscope is considerably lower than that in xy direction making it harder to analyse the data (see figure 11)

2) Making the ITO cells is considerably more time intensive, especially glass cutting and waiting for the UV glue to dry are time consuming.

3) We had trouble creating strings that were longer than 4 particles while using the first method we managed to create chains of more than 20 particles before heating

4) We were still unable to fixate strings with the electric field

The problem with the resolution could be partially resolved by tuning the experimentation variables in the Leica software (laser intensity, changing offset and adjusting the size of the pinhole), especially greatly reducing the size of the pinhole improved the results. Since we were

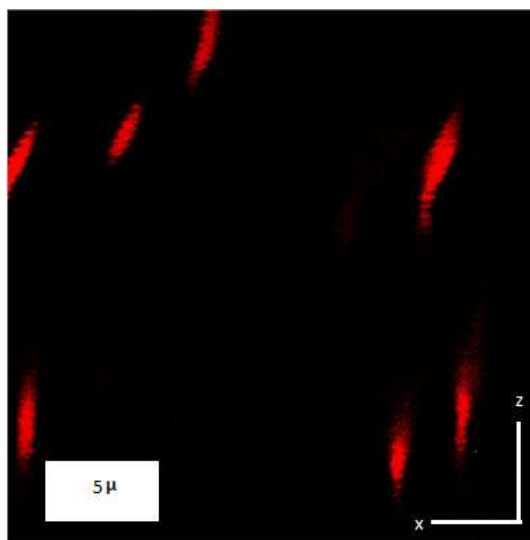


Figure 11: an ITO-coated cell before turning on the electrical field

having trouble in fixating the strings with the field we changed the heating method from heating by the electrical field itself to heating with a hair-dryer(3-5 minutes 60-70 degrees).

When this method of heating was used on the ITO-coated cells, strings with up to 4 particles were fixated(as can be seen in figure 12).

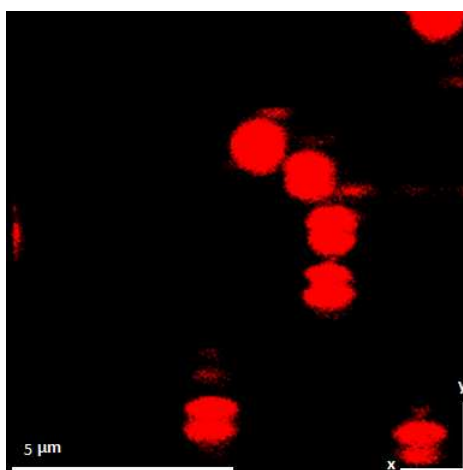


Figure 12: fixated strings in an ITO-cell after sedimentation

Since we were still not observing longer strings(even before trying to fixate them), we then chose to use the capillary cells again this time using the hair-dryer to fixate the strings(which would solve most of the difficulties we had experienced with the capillary cells earlier).

First we applied a field strength of 20V/mm for 10 minutes to make sure the long strings formed, since there was still a separation between the particles and later trying to fixate the strings had failed. Therefore we increased the field strength to 30V/mm for 10 minutes, using this method we managed to fixate longer strings(up to 8-9 particles) as can be seen in figure 13. Many of the longer strings(see a) in figure

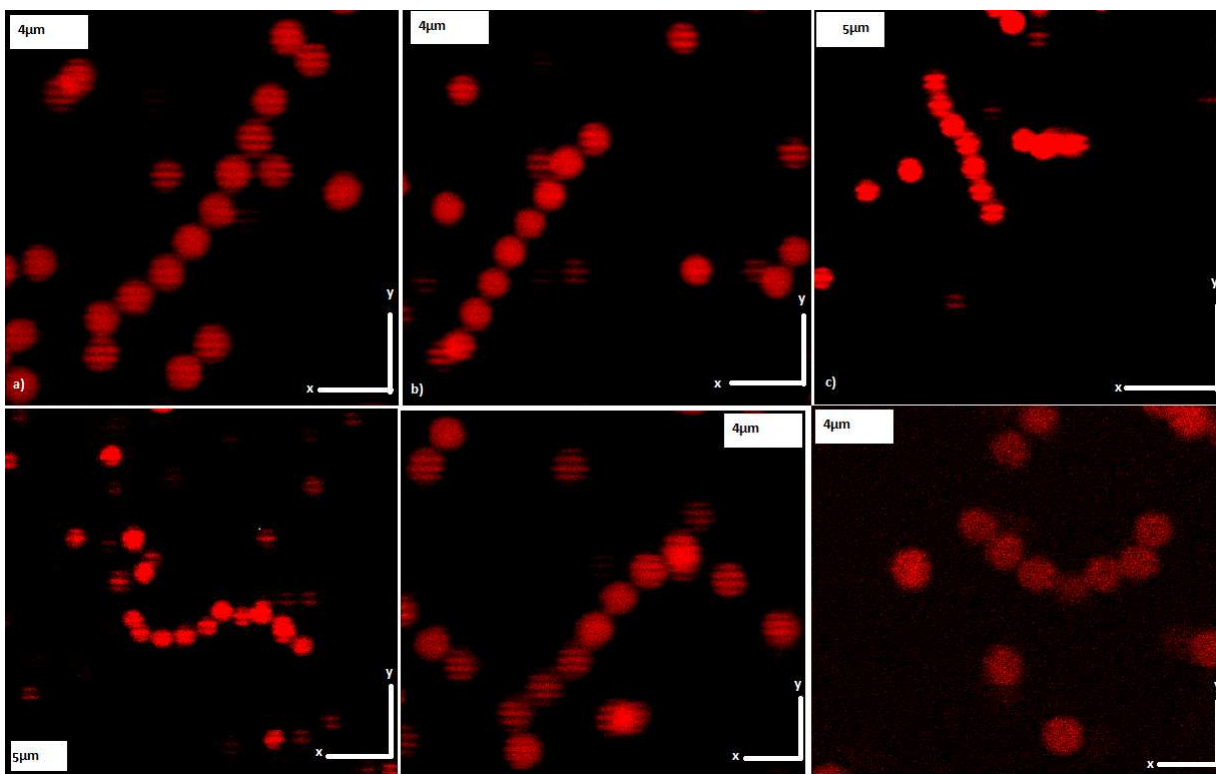


Figure 13: fixated flexible strings with the electrical field turned off

13), had particles sticking to the sides or even branched out(as can be seen in picture 14). Apparently the sideways repulsive force is not strong enough to prevent particles from getting near the strings during fixation.

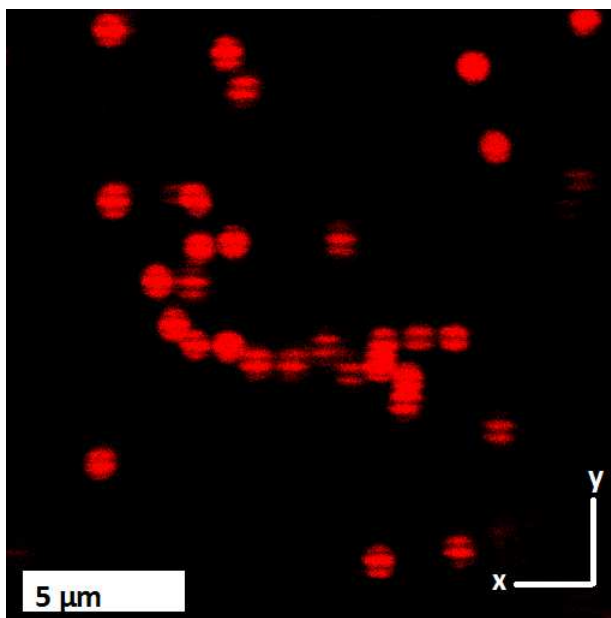


Figure 14: picture of a branched out string

4 Outlook

We managed to create flexible strings of fluorescent PMMA particles but were unable to do quantitative analysis of the created strings in the time period of this thesis, In the future research both 2D and 3D computer tracking can be used to track the position parameters of the strings and further calculate the persistence length, a property qualifying the stiffness/flexibility of the strings can be measured as well as the root mean displacement.

In addition would be interesting to change the experimental parameters, by increasing the root mean potential and heating time Rigid strings can be created, and by increasing the volume fraction as well as increasing heating time and root mean percentage rigid Rods or even 2D sheets can be created.

5 Acknowledgements

First I would like to thank Bo for guiding me through this research, I would not have been able to do this research without his help during experiments and his advice. Next I would like to thank Dustin for being able to discuss the project with. I also acknowledge Arnout for making this project possible and lastly I would like to thank the Soft Condensed Matter group for helping me out when I needed it and creating a nice work environment.

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