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OPEN SURFACE ACTIVE AND PASSIVE MAGNETIC DIGITAL MICROFLUIDICS

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This thesis is dedicated to my family and friends who have supported me during this journey.

”As you start to walk on the way, the way appears” - Rumi

Declaration

I certify that the material presented in this thesis, which I submit for assessment of the Doctor of Philosophy award, is entirely my own work. I have exercised reasonable attention to ensure the originality of it and to the best of my knowledge it does not breach any law of copyright. It has not been taken from other's work unless referred works are cited and acknowledged with the manuscript.

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Summary

Liquids form the biggest portion of this world and our body. Life grows in liquids in tiny scales and the microfluidics field tries to offer methods to study liquids in a similar scale. We see water droplets on different surfaces everywhere, thus one of the general questions we face: is it possible to move or manipulate a water droplet on a surface in the direction we wish.

This work targets this question, and asks about how to move water droplets on a surface with another liquid, a synthesized magnetic liquid, in a robust and controllable way. This work shows how we can control the interaction between two liquids in order to move water droplets in a programmable manner, on a surface. Moreover, it presents a novel approach to use this magnetic liquid for micro-structuring surfaces, will be used for passive manipulation of water droplets by altering their interaction with the surface.

Resumen

Los líquidos forman la mayor parte de este mundo y de nuestro cuerpo. La vida ocurre en líquidos en escalas diminutas y el campo de la microfluídica intenta ofrecer métodos para estudiar líquidos en escalas similares. Nosotros vemos gotas de agua en alrededor de nosotros en diferentes superficies y una de las preguntas generales aquí es: si podemos mover o manipular una gota de agua en una superficie en la dirección que deseemos.

Este trabajo aborda esta cuestión y pregunta cómo mover las gotas de agua en una superficie con otra gota de líquido que es un líquido magnético sintetizado, de una manera robusta y controlable. Este trabajo muestra cómo podemos controlar la interacción entre dos líquidos para mover las gotas de agua de una manera programable sobre una superficie. Además, presenta un enfoque novedoso para utilizar el líquido magnético sintético para microestructurar una superficie que es una manipulación pasiva de gotas de agua al alterar la interacción de las mismas con la superficie.

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CHAPTER 1

OUTLINE OF THE THESIS

Including human body, the world around us is abundant in liquids, specially in water form. In order to study the life inside liquids such as water, it is necessary to manipulate it in smaller volumes. Smaller volumes are important due to the scale of reactions and the physics that happen in liquids, for instance to study cell-cell interactions, it could be of interest to do studies using small liquid vessels of an equivalent scale. Therefore, a multidisciplinary field, microfluidics, has been recently introduced in science. Microfluidics is a research area under rapid development which offers a great platform for fundamental studies or for the development of Lab-on-a-Chip Devices. Manipulation of a liquid is the most important task to be achieved in microfluidics. Liquid can be subjected for study inside micron sized closed channels or open surfaces. The later one is the most seen form of liquid in the nature and therefore it has gained great interest to be studied by researchers.

Controllable and programmable manipulation of liquid droplets on a surface is generally called, digital microfluidics. Digital refers to the form of manipulation as a droplet can move on a surface in a programmable way in 2D. In this regard, digital microfluidics involves techniques in which a droplet can be moved on a surface in a desired direction. However, since it happens on open surfaces it is also referred as open surface droplet microfluidics. The interaction of the droplet with the surface and type of the applied forces on it defines its dynamics on the surface and whether a controllable manipulation can be achieved. Magnetic force is one of the main forces in nature and when it is used to manipulate liquids in small volumes then we can talk about magnetic digital microfluidics.

This thesis is focused on using magnetism for digital microfluidics and it highlights the importance of soft matter droplet manipulation by oil-based ferrofluid. It suggests three experimental approaches that can be useful for magnetic digital microfluidics purposes. In this regard, it is structured with following chapters as the main body of the manuscript, Figure 1.1:

- **Introduction and Objectives:** This chapter aims to familiarize the reader with background of open surface droplet microfluidics and concludes with remarkably challenging objectives to be achieved throughout this work.
- **State of Art for Magnetic Digital Microfluidics:** It gives an overview of the relevant methodologies that have been developed so far, targetting magnetic digital microfluidics purposes. The chapter divides these methodologies in two categories as passive and active magnetic manipulation and concludes the gap and challenges that can be addressed.
- **Tunable Superparamagnetic Ring (tSPRing) for Droplet Manipulation:** It represents a novel methodology for manipulation of water droplets by spike shape instabilities of ferrofluid. It introduces a formation of tSPRing, a self-organization of ferrofluid spikes around water droplet that encloses it and enables its robust manipulation on the surface.
- **Microfluidics in Oil-based Open Surface Channel:** It demonstrates the formation of a ferrofluid liquid channel on a surface by polymer-bonded magnets and its application for droplet mixing and manipulation.
- **Dried Ferrofluid Spikes-Stable Micron-sized Cone Shape Pillars for Molding Applications:** It communicates a novel work for the microstructuring of polymeric surfaces by a ferrofluid spike pattern.

- **Conclusions and Future Prospective:** Conclusions of the main achievements generated by the experimental chapters highlighting the opportunities that this work offers in future investigations.

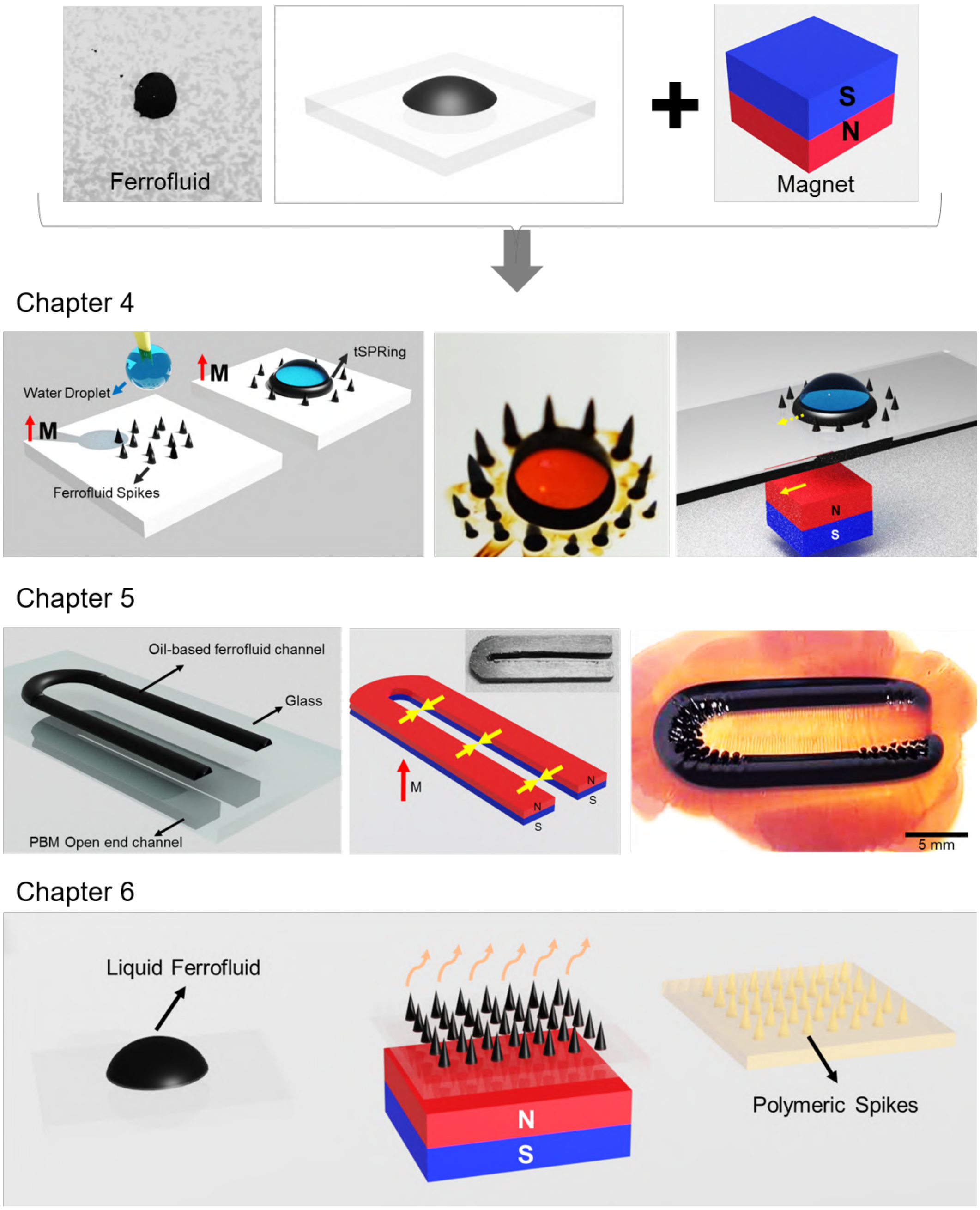


Figure 1.1: Graphical abstract of the three experimental works conducted in this thesis using oil-based ferrofluid for digital microfluidics.

CHAPTER 2

INTRODUCTION AND OBJECTIVES

Fluids are the phase in which life takes place and studying or engineering it requires well controlled manipulation. When it comes to the manipulation, Volume is the parameter that matters the most and thus to reach small values enables many applications, specially in the field of life sciences. Microfluidics is a toolbox which does this task using different approaches by studying new methodologies to produce efficient, non-expensive and multi-applicable devices. Often, liquids are treated on an open surface in droplet form (so called digital microfluidics), like a drop of blood introduced in a biosensor for sensing or for diagnosis purposes, or in a continuous form by flowing droplets inside of a channel. Manipulation of a droplet on an open surface requires either controlling its interaction with the surface or applying a force on it. Droplets can be stimulated with various external energy sources to be reshaped or transported. Magnetic field is a fascinating way of applying force at small scales, which has been applied in microfluidics. Magneto-responsive surface, magnetic liquid marbles, magnetically loaded droplets and ferrofluid liquid-liquid interaction are approaches that are successfully used and reported in literature. Here, we present a short yet comprehensive prospective review of magnetic digital microfluidics, focusing on the physics involved for manipulation. Moreover, we highlight the limits and complexity of developed solutions aiming that it would represent a practical view for multidisciplinary readers to get them familiarized and allow to use this technology for further apply them for further applications.

Among the phases of material, liquid offers a unique environment in which life has been formed. Better to say, forming life requires liquid phase to support and offer many possibilities in one phase. Blood is one of these examples, though it seems liquid at first sight, it has many constituents with a variety of shapes, size and morphology. To understand life inside a liquid such as blood, we would need to manipulate it to know its interaction with surfaces, its dynamics, rheology among other characteristic parameters[78]. Therefore, manipulation is the base of chemical or biochemical sensing, which nowadays is used for many medical applications in daily basis. However, specially in the case of biological samples, liquids are delicate and require gentle manipulation in order to do not damage their composition. For this reason, there should be soft manipulation approaches to manipulate liquids.

Microfluidics is referred to study and manipulation of liquids in smaller volumes, as the name implies[94]. Liquids are manipulated in microfluidics devices either in continuous or discontinuous phases[108]. Flowing a liquid inside a closed micro channel is considered continuous flow, while the formation of droplets and their manipulation is called droplet microfluidics. Proper force application is required to move a liquid in both cases[34]. For continuous flow operations, pumping (active or passive[111, 59]) is the most used approach, but in droplet-based systems the active pumping approach can satisfy the task of manipulation. Droplet microfluidics can be divided in two categories, in closed channel and in open surfaces. Often, droplet microfluidics refers to the manipulation of droplets inside a second liquid in a closed microfluidic channel, and it has been widely studied in the literature[88, 83]. In this case, the secondary liquid is manipulated to carry or address the droplets. Other strategies rely on open surface droplet manipulation, called ”digital microfluidics”[14, 81] which is the scope where this thesis is framed. In digital microfluidics, the interaction of the liquid with surface hinters the probable approach that can be used for manipulation[9]. Depending on the type of the liquid and substrate or surrounding atmosphere we can come up with manipulation methodologies.

A droplet sitting on a surface is called sessile droplet. The shape of a sessile droplet defines the scale of its interaction with the surface underneath the droplet (substrate)[99, 60]. From basic fluid mechanics we know that fluids do not tolerate shear stress and therefore applying mechanical stress will reshape them and cause them to move on the surface[61]. Any sessile droplet has two different interfaces, an air-droplet and a droplet-substrate interfaces[26]. Applying force on either interfaces can result in the deformation of the droplet, but due to the presence of gravity droplet-substrate interface is more crucial for the definition of its final shape[116]. The molecular interaction of the liquid with the surface of the substrate defines the contact angle of the droplet[30]. So, one should consider the shape of a droplet before defining an approach to move it, since lower affinity of the droplet with the surface would require less force to move the droplet. Therefore, the process of manipulation involves to know about material science and the physics of liquids and its combination.

As there are different sources of energy and consequently forces in nature, we find numerous studies that investigate the feasibility and applicability of different forces such as mechanical, light, wave and magnetic on liquids and sessile droplets. In particular, magnetic field offers remote force application and compatibility with biological samples since it is not an invasive force[28]. Magnetic digital microfluidics, liquid droplet manipulation with magnetic field, can be achieved either by changing the interaction of the liquid with the surface (here we call as passive manipulation) or adding the magnetic property to the liquid (active manipulation). The main challenge for active manipulation, in order to apply a magnetic field and consequently a force on a droplet, is making the liquid be responsive to the applied magnetic field. But in the passive method the magnetic property is introduced in the substrate in a way that it can be modified by an external field, therefore the droplet does not need to be modified. The next chapter gives a critical review of available research works that have reported novel approaches both in active and passive manipulation. However, the main questions in these approaches are the complexity of the systems and the challenges to apply them for in real applications. It is desirable to to have a well understood system based on a simple methodology that could be easily applied. Nevertheless, magnetism is not commonly used in many fields and may require a basic understanding of the magnetic field and the physics involved compare to other microfluidics approaches such as continuous flow microfluidics.

Considering the gap and improvements that can be addressed based on existing works in literature, the aim of this work is to develop methodologies, by using ferrofluids, for open surface microfluidics. This is considered as main objective because ferrofluid based digital microfluidics would benefit from soft matter property to move the droplet, that would bring a great advantage for manipulation of delicate liquids. Therefore, the oil-based ferrofluid was chosen to achieve three main objectives as:

1. To manipulate water droplets by a drop of a ferrofluid and a permanent magnet. Oil-based ferrofluid forms spike shape instabilities due to the saturation of magnetic field. Spikes move in a fast way on a surface compare to continuous phase of ferrofluid deposited on a surface. The objective is to answer if the

spike pattern can move a droplet on a surface in a robust manner. Moreover, to understand the interfacial interaction of ferrofluid spikes with water droplet on a flat surface. Once the interaction is understood, to characterize the dynamics of droplet manipulation by ferrofluid instabilities on upside and upside-down surfaces.

2. To study the possibility of forming channel like ferrofluid assembly on a surface. The idea would be to have a liquid channel that can offer bigger surface area to accommodate droplets or bigger volume of liquid. The channel would be applied to mix multiple water droplets or moving a water volume filled inside the channel.

3. To study the possibility of using ferrofluid for micro-structuring a surface in order to apply passive manipulation. This goal would be addressed by solidifying ferrofluid spikes preferably with a simple method such as drying and followed by fabrication of polymeric spike shape pillars by using solidified ferrofluid spike pattern.

CHAPTER 3

STATE OF ART

The chapter aims to give a comprehensive overview of the developed methodologies for magnetic digital microfluidics. The developed techniques are categorized as passive and active manipulation techniques in which the passive ones target the interaction of substrate with the droplet and active ones target applying direct forces on the droplet to move it on the surface (Figure 3.1). Likewise, this division is done with respect to the involved engineering techniques. In passive technologies, the focus is on the substrate while in active the focus is on the droplet. However, in the case of the ferrofluid, the combination of substrate and droplet are involved, but from the physical point of view the droplet is manipulated by the interfacial interaction of ferrofluid and therefore it is considered as an active approach.

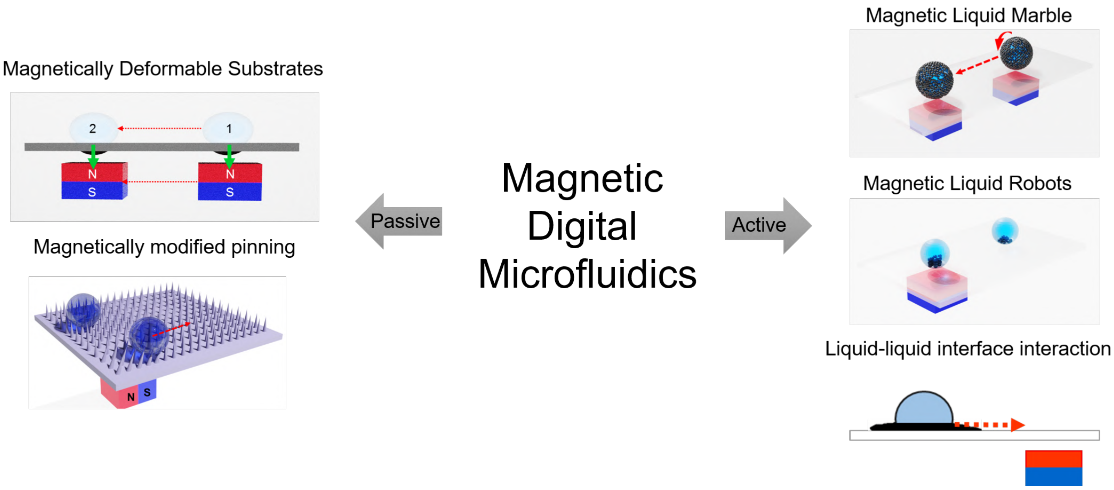


Figure 3.1: Graphical representation of different methodologies applied for magnetic digital microfluidics.

3.1 Passive Manipulation Approaches for Magnetic Digital Microfluidics

What is called here as ”Passive manipulation of liquid droplet” refers to techniques that modify the interaction of a liquid with substrate and resulting in the manipulation for the droplet. In other words, the magnetic force is primarily applied at the substrate rather than to the droplet. This implies that the substrate underneath the droplet is a magnetic material that can be deformed by an external magnetic field. The deformation can be achieved in microscopic or macroscopic scales. This approach in general is called magneto-responsive surfaces (MRS) and can be categorized as two main concepts:

- deformation of the substrate to trap the droplet in a bowl shape cavity and move it along the surface.
- modifying the pinning of the droplet by manipulation of magnetic pillars in contact with the droplet (underneath the droplet)

In the first approach, the substrate is formed of an elastic platform that can deform as a bowl like cavity where the magnetic field is applied to trap the droplet. The cavity is then moved along the surface by displacing the magnetic field. A certain volume of liquid can be fitted in the cavity and moved over the surface. However, having a super-hydrophobic surface would be crucial in this approach in order to avoid spreading and wetting of the liquid on the substrate and being immobilized at one spot on the surface.

In the second approach, the surface of MRS has pillar shaped features that are magnetic and elastic at the same time. It is known that micron size pillars apply pinning of the droplet and defines its shape[48]. Tilting the pillars underneath the droplet will unbalance it (breaks its symmetry) and consequently it will reshape itself reaching a new steady state. This gradual sliding of the droplet results in its displacement if the pillars can be manipulated in a controllable manner.

A summary of the approaches in which the composition of the droplet is not changed and its manipulation only affects the substrate is presented next.

3.1.1 Magnetically Deformable Substrates

Figure 3.2 shows the schematics of this approach and gives examples from the developed devices. The force applied by the magnet (Figure 3.2 A) make a inward curvature of the substrate that leaves behind a cavity at the surface of the substrate. Therefore, a droplet can be positioned inside the cavity (Figure 3.2 A,B). If the droplet does not wet the surface, it will form a soft ball trapped inside the cavity. Since the displacement of the magnet will move the cavity along the surface, the droplet also will be manipulated along the movement of the magnet.

In order to form the cavity, the surface should be flexible and magnetically actuatable. For instance, elastomers such as polydimethylsiloxane (PDMS) doped with magnetic particles were used as the magneto-responsive substrate [56, 104]. The material needs to have quick elastic response and relaxation to the applied field in order to provide a rapid displacement of the droplet. Moreover, the field needs to be applied continuously to keep the droplet at one specific spot on the substrate. As the shape of droplet depicts, the magneto-responsive surface needs to be super-hydrophobic too in order to avoid the droplet to be

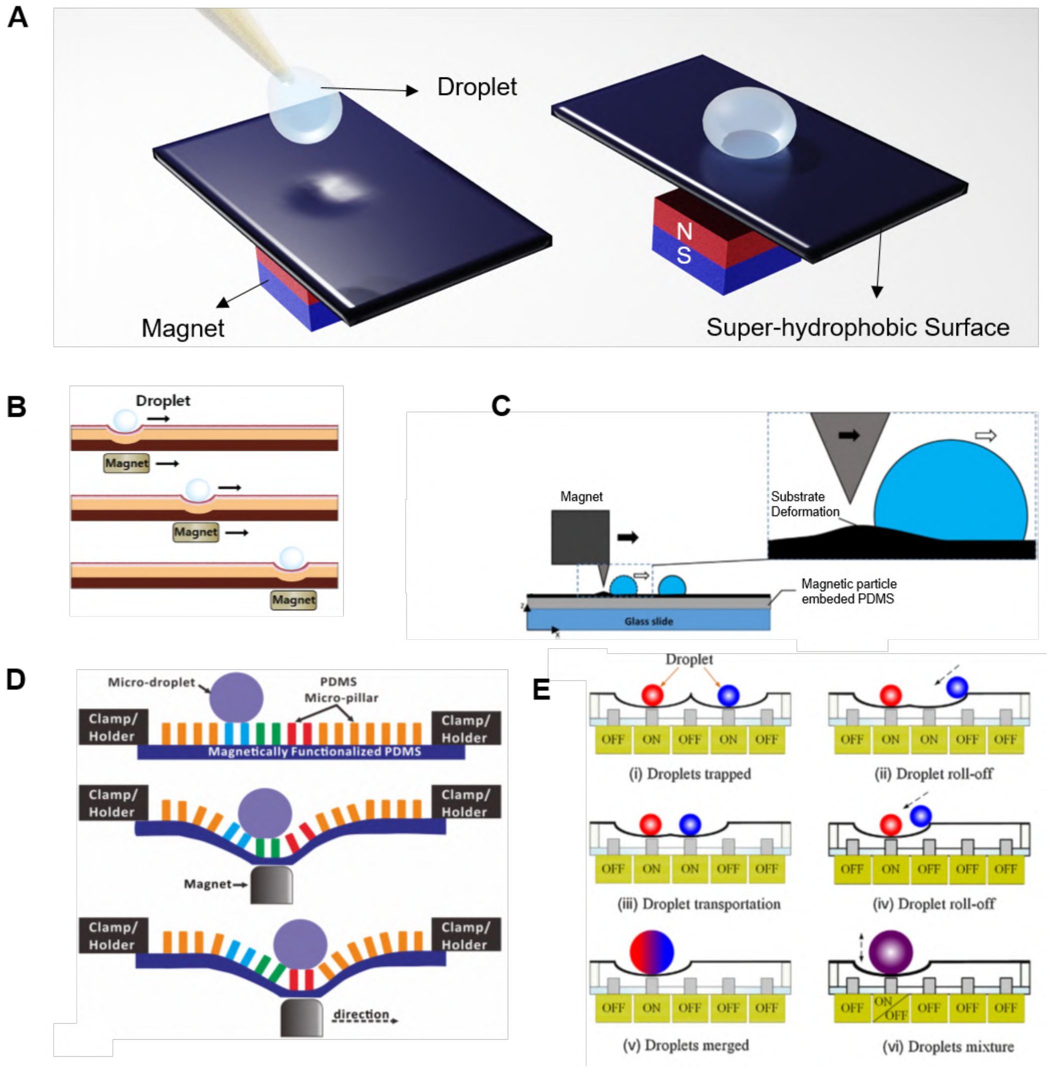


Figure 3.2: Magnetically deformable substrates for droplet manipulation on open surfaces. A) Schematics of droplet manipulation by a deformable substrate. B) Bowl shape deformation to move the droplet[115]. C) A magnetic tweezers is used to locally deform the substrate and to push the droplet over the surface[17]. D) Deformable magnetic substrate with micro pillars [12]. E) Digital ON-OFF magnetic platform for automated MRS surface manipulation[86].

attached to the surface and to allow rolling off easily over the surface. Therefore, beside the fact of having elastic magnetic substrate, the substrate should be functionalized to have super-hydrophobic characteristics. If the elastomer is a super-hydrophobic material, the extra fictionalizing step would not be necessary. In the case of hydrophobic materials such as PDMS the surface patterning with pillar shape features can increase the hydrophobicity of the substrate (Figure 3.2 D) [12].

Deformation of the substrate is not limited to the formation of bowl like cavities. Out of plane deformation was proved to initiate the rolling of droplets on a surface (Figure 3.2 B) [17]. This approach is analogous to tilting the surface, with the difference that the tilting locally happens in a micron scale. Even though by changing the topology of the surface the droplet moves this method has the drawback of poor accuracy in guiding the droplet. As a result, in the case of magnetically deformable substrates, the guiding of a liquid volume and the possibility of programmable manipulation needs to be taken into the consideration to have a control on droplet manipulation.

For the actuation, permanent or electro-magnets were used. The size of the magnet is related to the mechanical properties of the substrate material and the volume of the liquid that wanted to be manipulated. To have a degree of control over these parameters, electro-magnets would serve better functionality since the applied magnetic force can be regulated by the applied electrical current and offering flexibility on the droplet volume. However, miniaturized electromagnets showed programmable manipulation, which was used for multiple droplet manipulation and mixing of droplets on a platform (Figure 3.2 E) [115].

3.1.2 Magnetically modified pinning

In the case of magnetically modified pinning, instead of deforming all the surface to roll off the droplet, the interface of droplet with the substrate is subjected to manipulation. The shape of a sessile droplet on a surface is defined by its microscopic interaction with the surface where the droplet is placed. If the surface is microscopically modified, the droplet can change shape and consequently move on the surface. The manipulation being done in this way is called droplet pinning [95]. Due to the soft matter nature of liquids, the pinning unbalances the droplet (breaking its symmetry in the sense of contact angle, Figure 3.3 A) and therefore the droplet reshapes to reach to a new equilibrium, resulting in the movement of the droplet on the surface. Figure 3.3 B shows sequences of the manipulation of a droplet by magnetic pillars placed underneath the droplet. Tilting the pillars to the right side modifies the contact angle on that side of the droplet, therefore the droplet moves along the direction with lower contact angle. Sequential tilting of the pillars provides continuous movement of the droplet [103].

In modified pinning approach, the pinning is done by microscopic pillars that can apply force on the droplet. Pillars are fabricated with conventional lithography techniques[13] or self-organizing magnetic pillars[97], wide range of magnetic particles such as iron, iron oxide, rare earth magnetic particles are used. The loading of particles in the polymeric material, their magnetic properties and mechanical properties of the elastomer, the size, and the aspect ratio of the pillars define their response to the external magnetic field. However, the patterning density of the pillars defines the volume of the trapped air and as a result, the contact angle. In order to apply this methodology, all the mentioned parameters need to be optimized to apply sufficient force on the droplet.

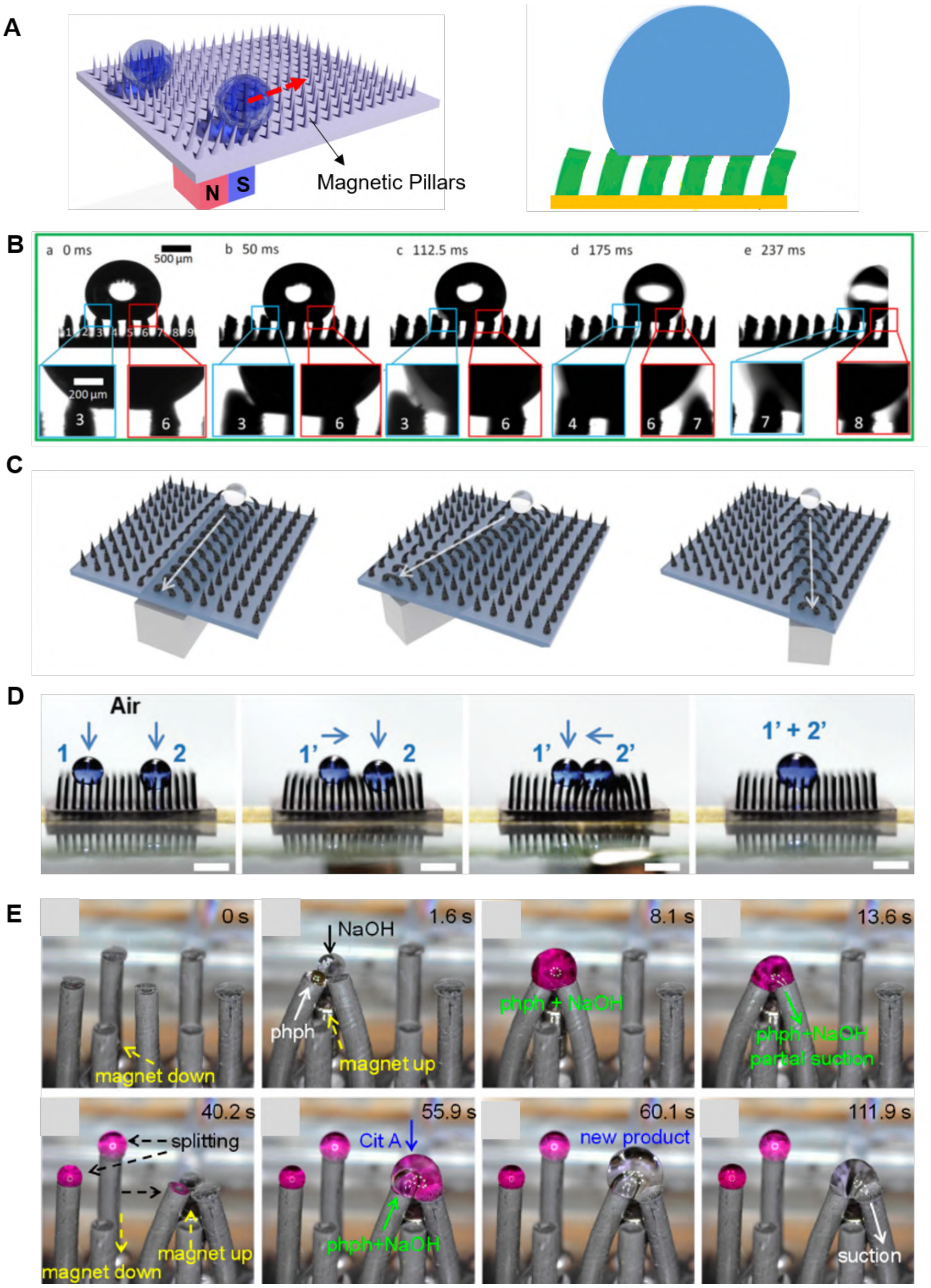


Figure 3.3: Magnetically controlled pinning for droplet manipulation. A) Schematics droplet manipulation of controlled pinning. The pillars are aligned by on-the-plane magnetic field. B) Shows the mechanism behind the pinning and how the droplet can slide on the pillars in the same direction that the pillars are pinned[103]. C) Remote manipulation of droplets on a flexible magnetically responsive film [39]. D) Multiple droplet mixing by manipulation of micron size magnetic pillars [5]. E) Magnetic-Responsive bendable nozzles for open surface droplet manipulation [76].

However, controlling the pinning of droplet is not only used for total displacement, it is used for microscopic manipulations such as mixing inside the droplet in delicate manner. Pinning and de-pinning can apply local flows inside the droplet to increase the reaction rate or mixing in it [120, 25, 13]. Moreover, pinning offers advantage on tilted surface, since the pillars can maintain the droplet on a tilted surface against gravity, or increase the rolling off speed and therefore resulting in self-cleaning surfaces.

3.2 Active Manipulation Approaches for Magnetic Digital Microfluidics

In active manipulation, instead of controlling the interaction of droplet with the substrate, the droplet itself is subjected to manipulation. Where a force is actively applied on the droplet. In contrast to the magneto-responsive surfaces or pinning by pillars, the droplet needs to be responsive to the magnetic field. To achieve this goal, magnetic materials are added into or around the droplet (at the interface). The external magnetic force is applied on the magnetic material and due to the interaction between them and the droplet, it moves along the applied force. Adding magnetic property to the droplet has been done so far by three main approaches:

- Magnetic liquid marbles.
- Magnetic liquid robots.
- liquid-liquid interface interaction of droplet with magnetic liquid (Ferrofluid).

The first two cases are achieved by adding a solid or a gel type magnetic particles to the droplet, but third one uses a magnetic liquid to manipulate the droplet. These approaches are new and under development. Here, the concepts and improvements that have been developed so far in each method will be reviewed below.

3.2.1 Magnetic Liquid Marbles

Magnetic liquid marble is the way to introduce magnetic particles around a droplet adding magnetic properties [124]. Liquid marble is an observation reported in literature, occurring when bringing in contact super-hydrophobic particles with a polar liquid such a water [2] (Figure 3.4 A). In order to have the particle only at the interface of the droplet, it is necessary to have repulsive interactions between the particles and the droplet, as if the droplet is hydrophilic particles should be super-hydrophobic, or vice versa. Since the particles can not be integrated inside the droplet, they wrap around it to minimize the stress (to reach thermodynamic equilibrium) [107, 52]. Therefore, the marble is a stable configuration, forming the base of droplet manipulation. The coating creates a membrane like shield around the droplet, allowing it to be stable even on a liquid surface[66, 65]. As a result, liquid marbles can be manipulated either on solid or liquid substrates.

In order to form magnetic polar liquid marbles, there is the need for a super-hydrophobic surface with certain amount of free particles on it [52] (the particles are made of magnetic materials with a coating on them to having hydrophobic properties). If there is affinity between the liquid droplet and the surface, the liquid will spread on the surface and therefore the marble will not be formed

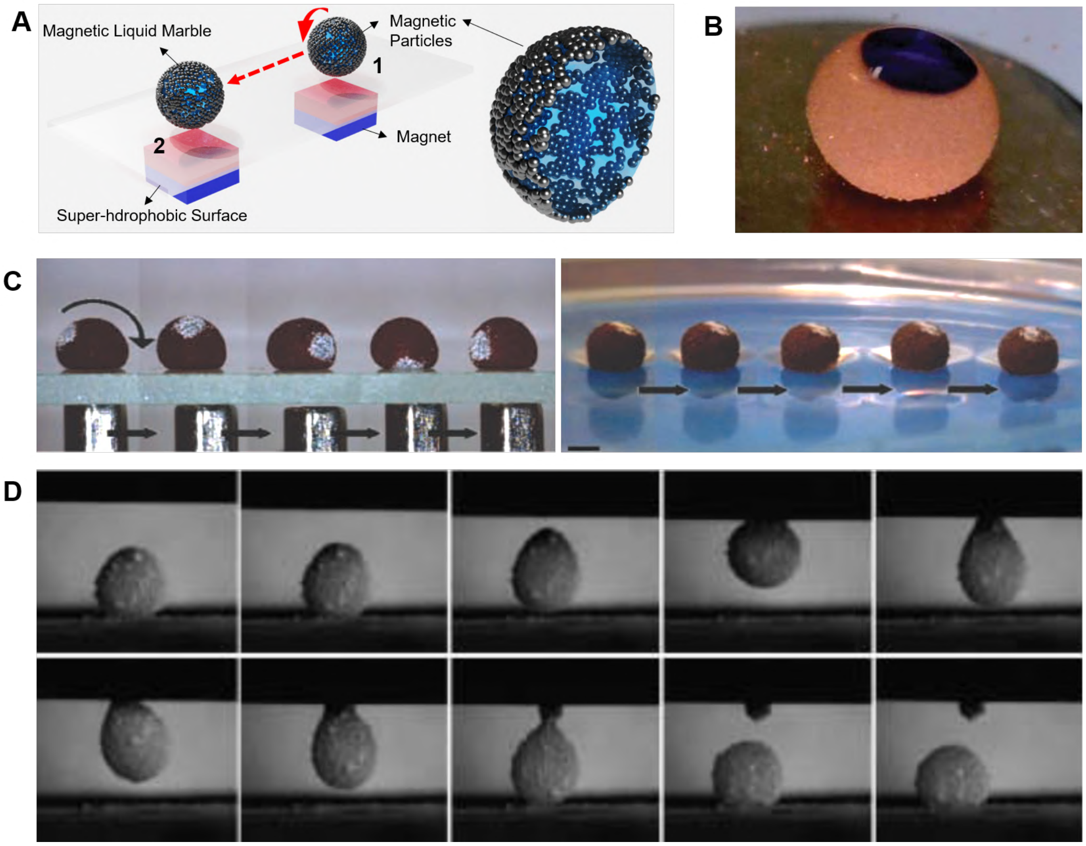


Figure 3.4: Magnetic liquid marble concept for manipulation of droplets on super-hydrophobic surfaces. A) Schematics of the magnetic liquid marble and its manipulation on an open surface (super-hydrophobic), displacement of the magnetic underneath results in rolling of the marble along the direction of magnet. B) Show a picture of magnetic liquid marble partially opened on the top of it by the influence of a magnet [124]. C) Manipulation of magnetic liquid marble with a permanent magnet on a solid surface (left) and on water layer (right) [112]. D) Manipulation of magnetic liquid marble as pendant droplet [3].

[7]. Often, magnetic particles such as Fe_3O_4, $NiFe_2O_4$, $MnFe_2O_4$ and $CoFe_2O_4$ need to be coated or functionalized to provide hydrophobic surface properties [36]. Moreover, to achieve an effective manipulation, the size of particles is an important factor, bigger particles tend to cluster at the bottom of the marble due to gravity and therefore the manipulation gets limited [46]. Therefore, smaller size particles wrap around the droplet in a homogeneous form, showing during the manipulation more stability [52]. Nevertheless, the particle size defines the scale of the response that the liquid marbles has with respect to an external magnetic field. The particle to droplet volume ratio should be well optimized to conduct manipulation [124].

Figure 3.4 shows the concept and examples of magnet liquid marble droplet manipulation. The schematics of the marble in Figure 3.4 A shows particles around the whole droplet, covering it. Placing a magnet underneath, and translocation of it permits rolling off the marble like soft liquid ball on the surface (functionalized surface, to not let the particles attach on it). The experiments in Figure 3.4 C shows how the marble rolls off like a ball. Moving the magnet, it applies a gradient force and therefore makes the marble moves along the direction of the magnet.

Manipulation of liquid marble requires some adjustments and proper engineering methodologies. This is due to the fact that applying a magnetic field under the substrate can tend to cluster the particles at the bottom of the marble and open up top part of it (Figure 3.4 B). Therefore, translocation of the magnet may not result in a robust manipulation of the droplet. For having a steady manipulation, the magnetic field needs to be applied in a certain strength and the displacement should be in steady state [112]. Permanent magnets offer higher field curvature and therefore the gradient field manipulates the marble in faster way [38].

Figure 3.4 B shows that by applying an static field the particles can get open up at the top part of the marble. Opening up the top part of the marble is beneficial for applications such as micro-reactors where the marble acts as a dynamic membrane to introduce substances inside the marble or to be used for bio-sensing applications. This is not a spatial displacement of the droplet but yet exposes the droplet to certain environment [63].

To facilitate the manipulation of liquid marbles, having a stick like magnet to lift up the marble and take it to the position where it should be released would be practical [3] (Figure 3.4 C). In this context, there is the need for electromagnetic manipulation by which the field can be turned on and off in a programmable manner. The magnetic field strength needs to overcome the gravity of the droplet in order to have it as a stable pendant droplet. To conclude, the magnetic liquid marble offers a simple physics to roll a droplet on a surface, nevertheless it requires some calculations and engineering to form proper shape of a marble in order to acquire programmable manipulation.

3.2.2 Magnetic Liquid Robots

In a magnetic liquid robot, the magnetic particles are introduced inside the droplet and have the affinity to stay in it (particles stay inside the droplet due to the capillary forces). The droplet needs to have a minimum affinity to the substrate in order to preserve the integration of the particles in the droplet. The manipulation is done in a gentle and steady manner to avoid that particles leave the droplet [47, 91] (the force applied by the magnetic field should not be higher than the surface tension force that liquid applies on the particle). The magnetic

properties of the introduced particles and their volume defines the dynamics of the droplet manipulation. However, the particles occupy volume in the droplet and the interaction between particles and the droplet needs to be taken into consideration if the approach is used for biological liquids such as manipulation blood.
Figure 3.5 shows the schematic drawing for this approach and gives a glance of the developed techniques found in literature. The droplet can be assumed as a soft ball with particles in it, an applied magnetic field induces the dipole interactions between the particles aligning them along the direction of the applied field (Figure 3.5 A). Moving the magnet, pulls the particles to one side of the droplet and therefore modifies the contact angles at the same side [24]. If the movement of the magnet and consequently the gradient forces applied on the particles does not exceed the interaction between the particles and droplet, the particles will stay inside the droplet. The contact angle, change on one side will roll the droplet until it relaxes the contact angle changes and equalize it. In this manner, droplet moves along the surface with the particles in it. Figure 3.5 B shows that the speed of the magnet needs to be optimized to avoid breaking of the droplet or leaving of the particle cluster from the droplet [47]. It was shown that a droplet can be moved to mix with fixed droplet and use for further manipulation [122] (Figure 3.5 C). The interaction of the particles with the droplet was calculated to be bigger that the gravity applied to hold it. As a result, the droplet was lifted by an electro-magnet and displaced spatially to mix with another droplet (Figure 3.5 E)[114].

The idea of having particles inside the droplet simplifies the complexity presented in the liquid marbles, since manipulation can be done in a simpler way. From physical point of view, an unsteady manipulation of the solid material

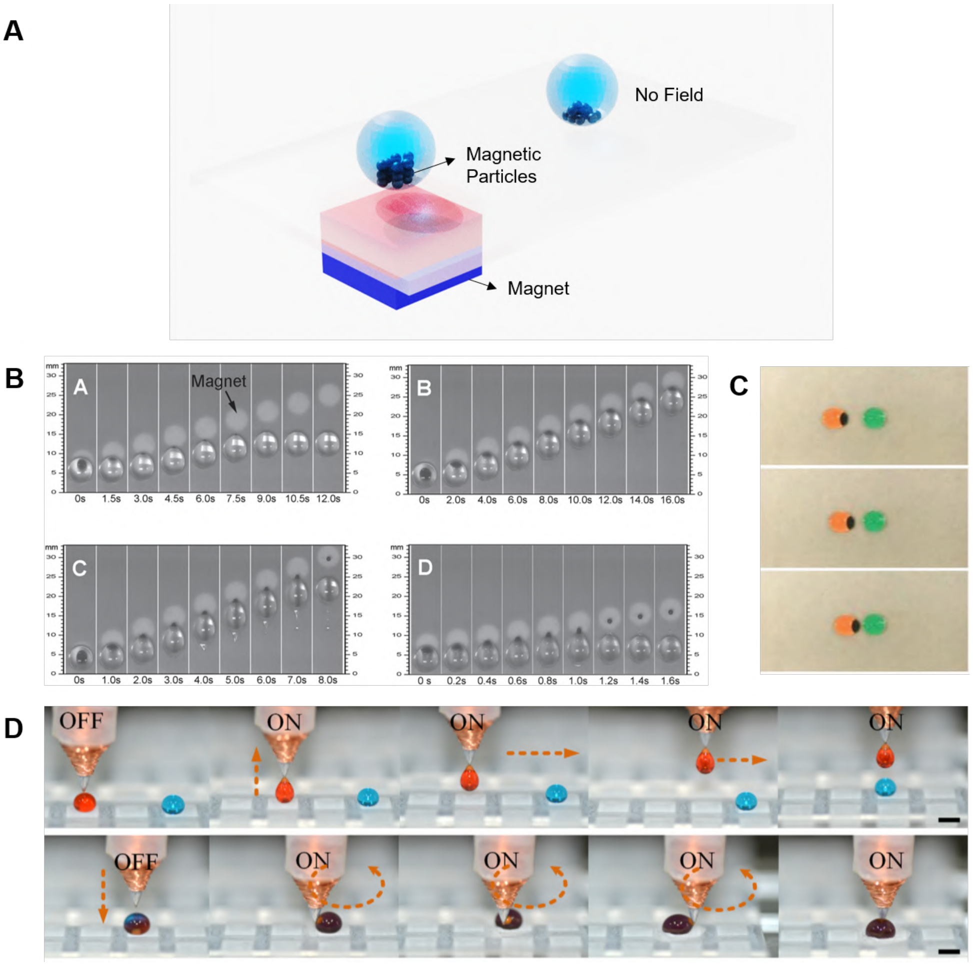


Figure 3.5: Magnetic liquid robot, droplet manipulation by particles inside the droplet. A) Schematics of droplet manipulation with the particles inside the droplet. B) Open surface manipulation of magnetic liquid robots [47]. C) Droplet mixing by magnetic robot concept [122]. D) Manipulation of the droplet in a digital manner by lifting up the droplet [114].

may leave the droplet behind, which is not the case when the particles are introduced all around the droplet. Beside the optimization of the magnet speed, the particle size and load should be calculated to achieve sufficient capillary forces. The size and density of the particles should be calculated in a way to apply adequate forces and interactions to move certain volume of a droplet. Moreover, the surface of the particles should have capillary interaction with the droplet in order to increase the interaction in between them. To conclude, this approach offers a simple solution, which by proper engineering, it can be used for programmable manipulation of liquids on a surface, [44] where the particles inside the droplet can be removed if needed.

3.2.3 Liquid-liquid interface interaction

In previous sections of active manipulation, the magnetic property was added to the droplet in the form of solid particles, that by introducing a magnetic field it caused their attraction to the magnet. Particles could leave the liquid phase and get extracted. But If the magnetic particles are added in a liquid medium in a stable manner (the particles behave as part of the liquid) all the liquid would respond to the magnetic field. The resulted engineered liquid is called magnetic liquid and if the particles are iron it is called ferrofluid [6]. On one hand, ferrofluid can be moved in a robust way by the external magnetic force. On the other hand, liquids have interfacial interaction that can bring two liquids together. Combining these two, it would result in the interface interaction of ferrofluid with a another liquid (a droplet) that can indirectly manipulate the droplets.

The idea that proposes to move a liquid by another liquid calls attention from two aspects. First, liquid is a soft mater and thus benefits the manipulation of another soft matter; second, the understanding that we can acquire from liquid-liquid interaction throughout the applied magnetic force. Ferrofluid can be either in oil or water-based forms in which the oil or water is the medium that accommodates the magnetic particles[27]. Oil-based ferrofluid is immiscible with the water droplet, therefore there will not occur any mixing of two liquids if

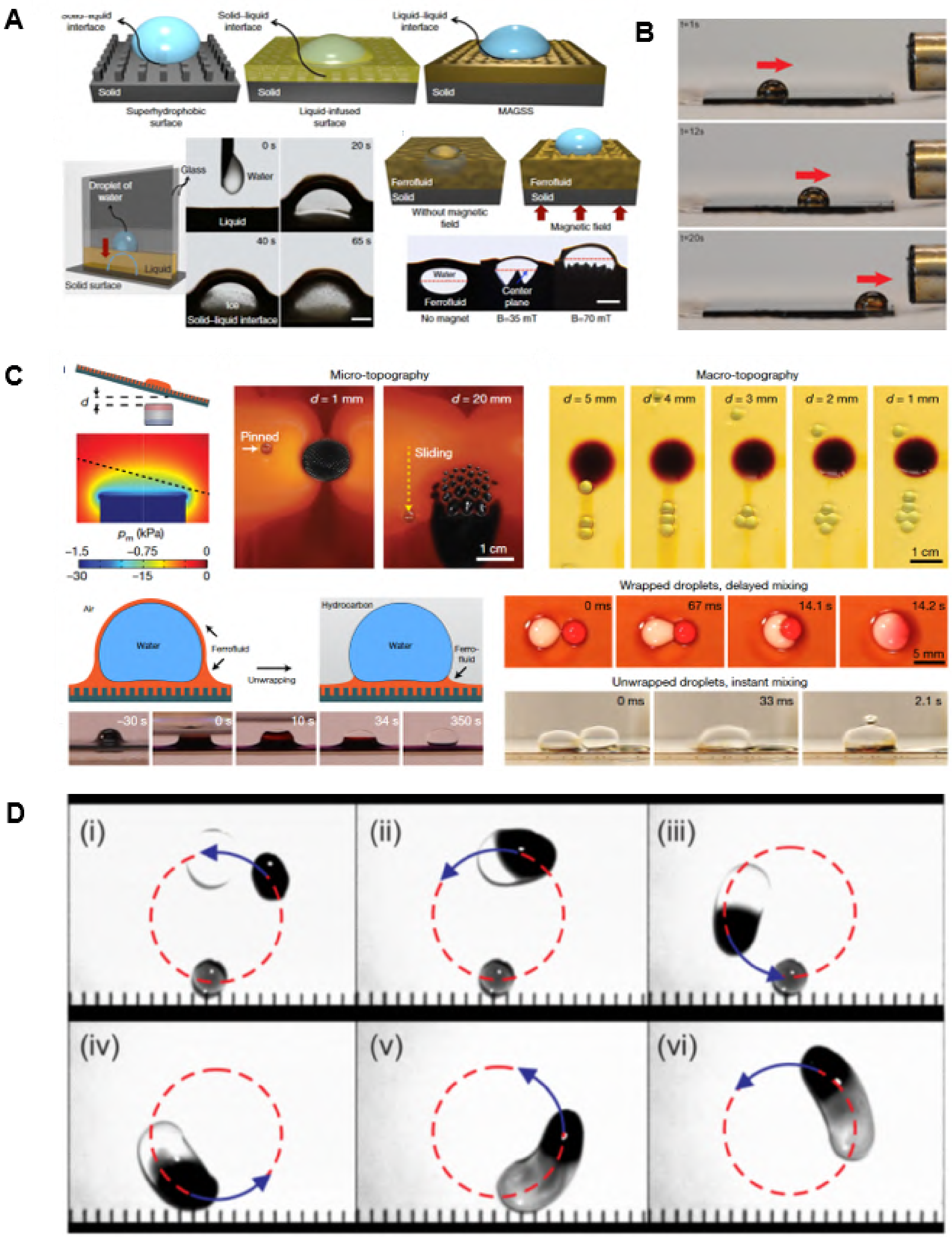


Figure 3.6: Manipulation of droplets with liquid-liquid interface interaction, using ferrofluid as magnetic liquid. A) Cloaking method on patterned surface filled with ferrofluid [33]. B) Time-lapse figures the movement of cloaked droplet towards the magnet positioned on the side of the substrate[37]. C) Ferrofluid-infused surfaces with re-configurable multi scale topography to manipulate droplets on tilted substrates (top left), and controllable mixing of two droplet (bottom right) [105]. D) Manipulation of non-magnetic droplet by a ferrofluid droplet on a surface[30].

they are brought in contact. From oil and water interaction on an open surface, putting a droplet on an oil layer makes a wrapping of the oil phase around the droplet, similarly to what it was observed in the marble case [18, 29, 87, 101]. If the interaction is sufficient to keep the ferrofluid around the water droplet, with an external field manipulation the ferrofluid can result in the manipulation of the droplet as well. In other words, the droplet can stay integrated in ferrofluid and consequently be manipulated with it.

In order to have cloaking or covering of the droplet by a magnetic liquid, the spreading coefficient (S_{DL}) between the droplet and the ferrofluid should be positive, given by:

$$S_{DL} = \gamma_D - \gamma_{DL} - \gamma_L \tag{3.1}$$

Where, γ_D is the surface tension of the drop saturated with lubricant, γ_L is the surface tension of the lubricant, and γ_{DL} is the interfacial tension between the droplet and the lubricant [82]. This coefficient defines if the surface tension of the droplet is bigger than the sum of the surface tension between the droplet and the lubricant (in the case the magnetic liquid is a ferrofluid) plus the surface tension of the lubricant.

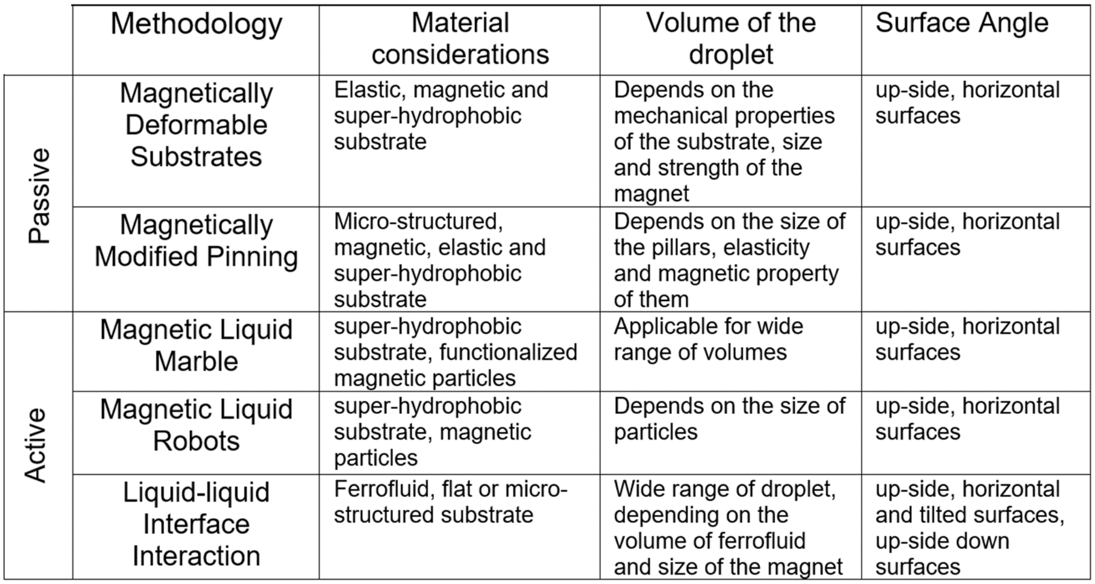
This idea was used in two different scenarios, First, using ferrofluid as an infused surface (called lubricant-infused surfaces, LISs). It is a surface with groves that gets filled with the ferrofluid, to make switchable surfaces modifications once the field is applied. To adjust the interaction of the droplet with the surface [105, 33, 37, 29]. Second, the direct interaction of the ferrofluid with droplets on a flat surface [113, 110].

A ferrofluid responses to the external magnetic field and can undergo normal field instabilities, appearing as an spike pattern [8, 98]. In infused surfaces, the deposition of the ferrofluid in the grooves resulted on a slip surface in the absence of the magnetic field, increasing the drag force between the droplet and surface once the field was applied. The shape of ferrofluid changes under applied magnetic field and the changes of the liquid-liquid interaction at the interface of the ferrofluid-droplet results the combination of two effects to manipulate the droplet. Nevertheless, since the manipulation mostly happens due to the direct interaction of the ferrofluid with the droplet is considered as an active approach.

Figure 3.6 shows examples of developed methods using liquid-liquid interface interactions for open surface droplet manipulation. The oil-based ferrofluid used in these studies are lubricant as well. In order to have control over the ferrofluid deposition and topology on a surface, the surface is used as an infused surface with micro structures on it. Applying the magnetic field changes the topology of the ferrofluid on the surface and consequently the interaction with the droplet. The droplet is clocked due to the surface tension interaction and a layer of ferrofluid covers the deposited droplet on the ferrofluid layer. This approach can be used on tilted surfaces as well as to trap the droplets or manipulate them (Figure 3.6 A-C) [97, 105]. Besides the micro patterned surfaces a flat surface with a drop of ferrofluid was successfully used to manipulate non-magnetic liquids as well [113, 110] (Figure 3.6 D). These examples prove that a soft matter magnetic liquid can successfully manipulate droplets on open surfaces (flat and tilted surfaces). However, the droplets are cloaked by the ferrofluid, which would bring some limitations such as optical observation of the cloaked droplet.

3.3 Conclusions

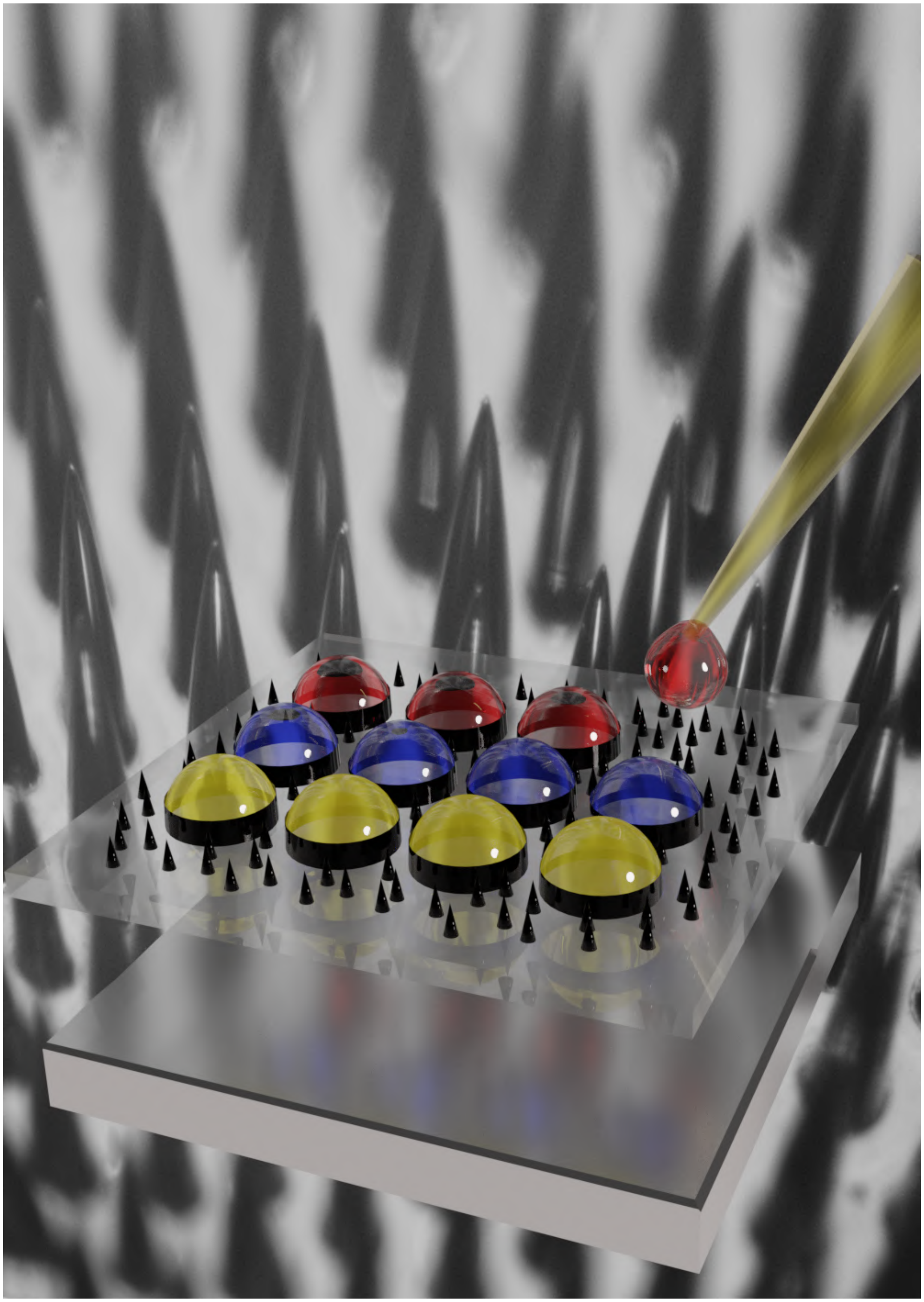
This chapter reviewed the methodologies that have been developed for magnetic digital microfluidics. For any application related to open surface droplet manipulation, there are certain parameters that need to be considered. Table 1 compares the reported methodologies from the aspect of the material (where material refers to the complexity of the method which affects indirectly the time and cost involved for building up the set-up), the droplet volume and the angle of the surface. As the comparison points out, ferrofluid offers simplicity for application and covers wide range of droplet volumes. Moreover, it can be used on tilted surfaces. Therefore, liquid-liquid interaction with ferrofluid would be important to address further studies and applications.



	Methodology	Material considerations	Volume of the droplet	Surface Angle
Passive	Magnetically Deformable Substrates	Elastic, magnetic and super-hydrophobic substrate	Depends on the mechanical properties of the substrate, size and strength of the magnet	up-side, horizontal surfaces
	Magnetically Modified Pinning	Micro-structured, magnetic, elastic and super-hydrophobic substrate	Depends on the size of the pillars, elasticity and magnetic property of them	up-side, horizontal surfaces
Active	Magnetic Liquid Marble	super-hydrophobic substrate, functionalized magnetic particles	Applicable for wide range of volumes	up-side, horizontal surfaces
	Magnetic Liquid Robots	super-hydrophobic substrate, magnetic particles	Depends on the size of particles	up-side, horizontal surfaces
	Liquid-liquid Interface Interaction	Ferrofluid, flat or micro-structured substrate	Wide range of droplet, depending on the volume of ferrofluid and size of the magnet	up-side, horizontal and tilted surfaces, up-side down surfaces

Table.1: Comparison of different methodologies of magnetic digital microfluidics from the aspect of complexity of material, volume of the droplet and surface angle.

Ferrofluid cloaks the droplet when it comes in contact with it. Cloaking affects the robustness of the manipulation as there is a delay between the movement of the magnet and the cloaked droplet, following the trajectory of the magnet. However, since the droplet is cloaked with the ferrofluid (black color) the possibility to observe inside the droplet is limited, specially if the droplet is used as a bio-reactor. Therefore, the interaction of the ferrolfuid with a water droplet and the application of an external magnetic field needs to be adjusted in order to achieve a robust manipulation of the droplet and to reduce the complete cloaking of the droplet. If so, ferrofluid can offer very robust and programmable manipulation of droplets on different surfaces.



CHAPTER 4

TUNABLE SUPERPARAMAGNETIC RING (TSPRING) FOR DROPLET MANIPULATION

The manipulation of droplets via a magnetic field forms the basis of a fascinating technology. Often, the movement of droplets with magnets involves adding magnetic particles in or around the droplet; alternatively, magneto responsive surfaces may also be used. This chapter, presents the formation and characterization of a tunable superparamagnetic ring (tSPRing), which precisely adjusts itself around a water droplet, due to liquid–liquid interaction, and enables the physical manipulation of droplets. The ring is made of an oil-based ferrofluid, a stable suspension of ferromagnetic particles in an oily phase. It appears spontaneously due to the oil–water interfacial interaction under the influence of a magnetic field. The ferrofluid–water interaction resembles a cupcake assembly, with the surrounding ring only at the base of the droplet. The ring is analogous to a soft matter ring magnet, showing dipole repulsive forces, which stabilizes the droplets on a surface. It enables robust, controllable, and programmable manipulation of enclosed water droplets. This work opens the door to new applications in open surface upside or upside-down microfluidics and lays the groundwork for new studies on tunable interfaces between two immiscible liquids.

4.1 Introduction

Droplet manipulation is gaining great interest in various fields, including technological applications and fundamental studies in dynamic systems [108, 128]. Special interest is adopted by the Lab-on-a-chip and microfluidics community, interested in the precise manipulation of small volumes of fluids, droplet microfluidics [88, 23, 64]. Non-invasive displacement of droplets on surfaces has been already achieved by different actuation mechanisms triggered by magnetic fields, (magneto manipulation [57, 121, 42, 47]), electrical signals (electrowetting [74, 75, 70, 106]), light [40, 4], chemical reactions [20, 55], sound [22, 43] and vibration [19]. The most successful method to control the movement of several droplets on a dielectric surface for microfluidics applications is electro-wetting. Some disadvantages of this approach are the need of specific type of substrate, complex fabrication process and limited compatibility with biological samples since it applies an electrical field into the droplet. Instead, the magnetic manipulation of droplets, driven by an invisible and remote magnetic field, is harmless in a big extend for biological samples [73]. Up to date, magnetic manipulation commonly relies on loading magnetic particles inside [44, 62] or outside of the droplet to move (magnetic liquid marbles and cloaked droplet [2, 124, 112, 125]), or on magneto responsive surfaces [127]. Ferrofluids have been already used as magnetic soft substrates [30, 105, 50, 113, 58] to induce a change in the interaction between droplets and substrates enabling droplet manipulation. Despite all the progress in droplet microfluidics, a number of challenges remain in this field, such as applicability for wide range of droplet volume and avoiding fabrication of complex substrates. Current systems can mainly handle large droplets and their manipulation is highly dependent on the interaction between the substrate and the droplet.

Ferrofluid is a magnetic liquid that is formed by a stable colloidal suspension of iron nano particles in a carrier medium such as an oil or water. Under the influence of a magnetic field, it experience experiences Rosensweig instabilities and creates regular self-organized patterns seen macroscopically as peaks and valleys [6, 15]. We have observed that the introduction of a water droplet in a Rosensweig instability pattern spontaneously forms a ferrofluid ring around the water droplet that remains integrated within the regular pattern of instabilities. This ring surrounds the base of the water droplet all along its perimeter and behaves like a magnetic instability, allowing the droplet to stabilize and separate from other droplets.

In this chapter, the formation and characterization of a new type of instability, the tunable superparamagnetic ring (tSPRing) is reported, as well as whether this phenomenon could be exploited for the programmable magnetic manipulation of non-magnetic droplets in an optically addressable manner. Our experimental observations indicated that the interaction of ferrofluid instabilities with other liquids can form the basis of a very versatile and robust methodology for handling droplets on open surfaces using magnetic fields. Likewise, the manipulation of droplets through soft materials such as ferrofluids gives insights for new fundamental studies on the interaction between immiscible liquids.

4.2 Results of Discussion

4.2.1 Formation of Ferrofluid Ring

A suspension of nano-sized iron particles in ferrofluid responses to a magnetic field (alignment of magnetic moments) and it disappears once the field is removed [80]. Up to a certain magnetic field strength (saturation magnetization, Ms), a ferrofluid stays as a continuous liquid phase. However, when the field strength overpass the saturation level, it undergoes Rosensweig instabilities[8] and self organizes as an ordered spike pattern (Figure 4.1 A). The size and interspace distance of the spikes in that pattern is related to the viscosity of the ferrofluid, field strength (H) and field curvature of the magnetic field[98]. By turning on and off the magnetic field it is possible to switch between the continuous liquid phase and the discontinuous spike pattern phase.

The interaction of oil-based ferrofluid with a polar liquid such as water, is like a conventional oil-water interface which is widely studied and described in literature[18, 1]. In the absence of magnetic field, when a water droplet comes in contact with a layer of ferrofluid (deposited on a surface), the ferrofluid tends to envelop the droplet, due to the capillary phenomena, to minimize the interfacial tension. But, would this effect be valid for a water droplet in contact with ferrofluid under a magnetic field, when it is already forming a spike pattern? In order to study that, we performed several experiments, first we placed a water droplet inside a ferrofluid static spike pattern. On a different experiment, the water droplet was placed on top of a continuous layer of ferrofluid, and after the magnetic field was applied. Finally, ferrofluid was slowly added dropwise between two droplets of water placed on a surface on top of a per-

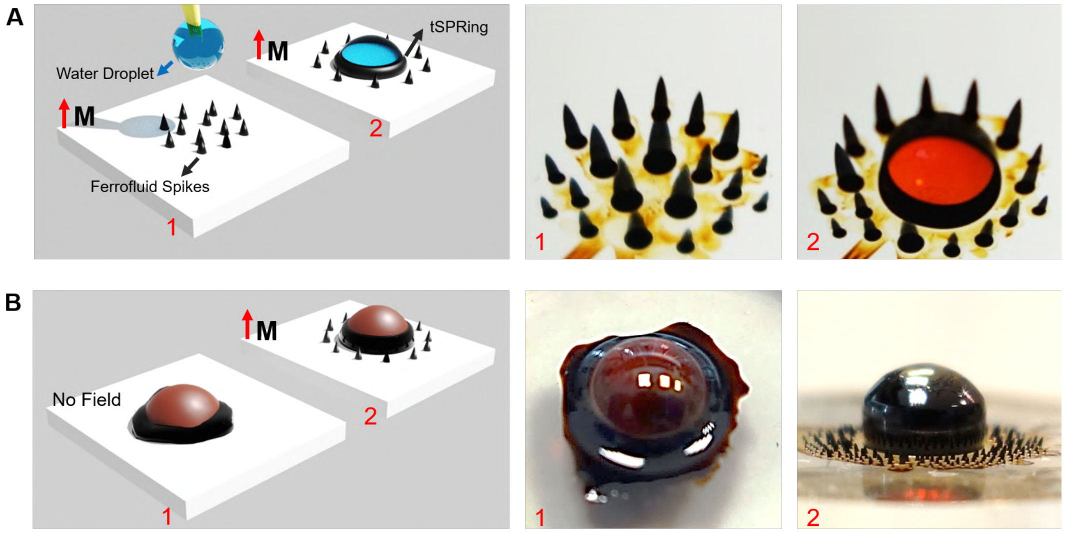


Figure 4.1: Shape Formation of tSPRing by two different methods. A) (left) A magnetic field over the Ms of the ferrofluid is applied to a layer of ferrofluid deposited over a surface, the instabilities form and the droplet of water is loaded between the instabilities. (middle) Photograph of spike pattern formed by out-of-plane magnetic field induced by a magnet positioned underneath, and (right) photograph of the tSPRing formed around a water droplet, which was pipetted in between the spikes (right). B) (left) A water droplet loaded on a continuous ferrofluid phase (deposited on top of a surface), and subsequently the magnetic field over Ms of the ferrofluid is applied. (middle) Photograph of the water droplet covered by a continuous layer of ferrofluid , and (right) photograph of the droplet after applying the magnetic field to form the instabilities (right). The tSPring forms in both cases around the water droplet as one more instability.

manent magnet. Figure 4.1 A shows the result of introducing a water droplet in between ferrofluid spikes. The spikes touching the water droplet turned into a continuous liquid medium around the droplet, forming a ring that could be observed macroscopically. In the second experiment, the ferrofluid covered the whole water droplet in the absence of magnetic field, once the field was applied, the ferrofluid shaped to form instabilities, including the ring around the water droplet (Figure 4.1 B). In the third experiment, the spike pattern dynamically formed and broaden by increasing the volume of ferrofluid that touched the surface. As soon as the spikes reached one of the water droplets, the ferrofluid surrounded the perimeter of the water droplet in less than a millisecond acquiring the form of a ring (Figure 4.2). The ferrofluid-water interaction was shaped like a cupcake, with the surrounded ring only at the base of the droplet, in contrast to the ferrofluid cloaking method in which the ferrofluid covers the whole of the droplet[37] . However, although the droplet remained translucent (it was possible to see inside), it was covered with a thin cloaking layer of oil (oil phase of the ferrofluid) (Figure 4.3).

We examined the geometry of the ring, which presented an asymmetric cross section. Its longitudinal profile was oblique to the surface at the ferrofluid-air interface but concave at the ferrofluid-water interface (Figure 4.4), following the lines of the magnetic field as a magnetic instability.

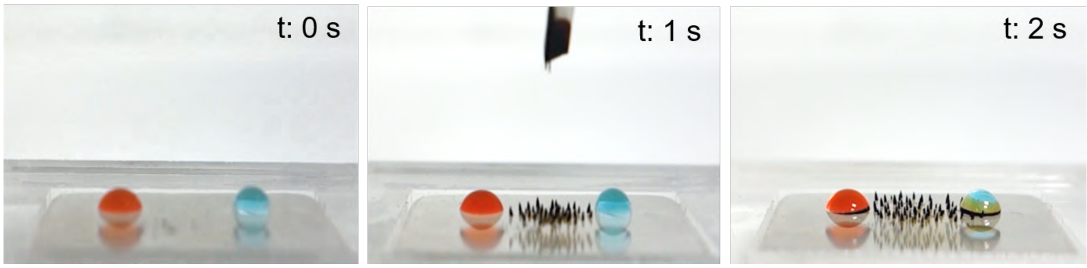


Figure 4.2: Time sequenced photographs of the formation of ferrolfuid ring around water droplets pipetted on a PMMA substrate (dyed as blue and red).

The formation of the ring happened due to the introduction of an immiscible liquid in contact with the ferrofluid spike pattern, which disturbed the thermodynamic equilibrium of the spikes. Moreover, the system was then forced to reshape itself to find a new state of minimum energy. Since the surface tension of ferrofluid is lower than the surface tension of water, the ferrofluid changed

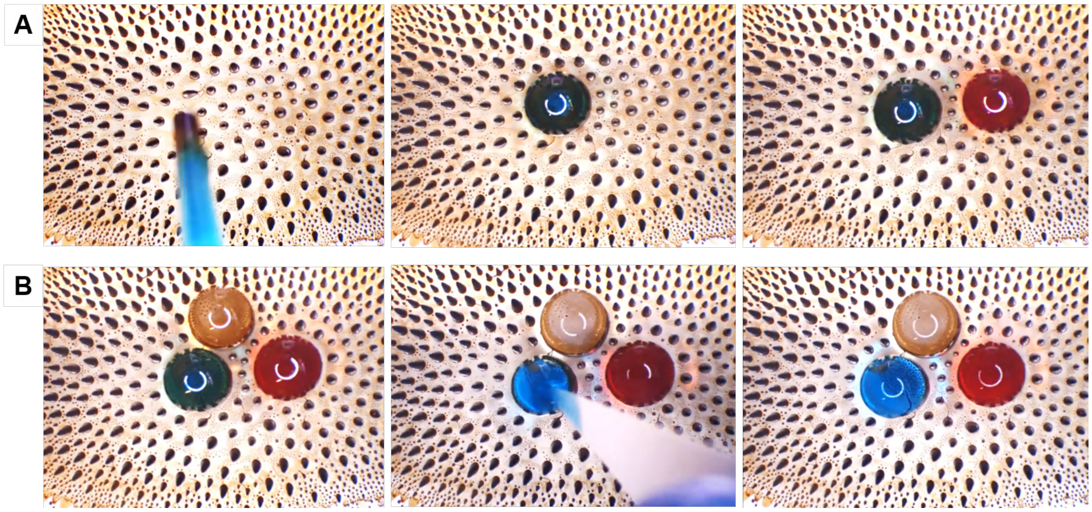


Figure 4.3: Experimental demonstration of the oil layer presence on top of the droplet (cloaking oil layer). A) Top view images of adding droplets (in different colors) in between ferrofluid spikes. B) Top view image demonstrating the removal of the covering oil layer from the blue droplet by a paper. The image of droplets before (left) and after removal (right) of oil layer.

its shape to tackle the higher tension dictated by water droplet. After the formation of the ring, the system reaches a new thermodynamic equilibrium. Regarding the asymmetric cross section, normally the spikes are in contact with two phases, the substrate and the air. When the water droplet was introduced in the pattern and touched some ferrofluid spikes, three phases were in contact with the ferrofluid, solid, liquid and air phase, producing three different interfaces. For this reason, the ring presents an asymmetric cross-section, which is expected considering that the surface tension of the water-ferrofluid interface is lower than the surface tension of the ferrofluid-air interface.

In view to its morphology and its superparamagnetic properties, we named the enclosing ferrofluid ring as tunable superparamagnetic ring, shortly tSPRing. Below, we describe a set of experiments to understand the characteristics and properties of tSPRings.

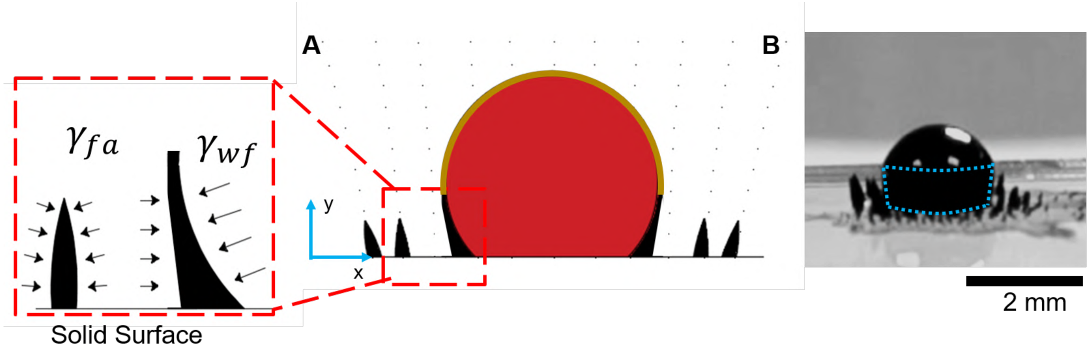


Figure 4.4: Cross sectional and side view of a tSPRing. A) Schematic drawing of the longitudinal profile of the tSPRing. The ring showed oblique wall at ferrofluid-air interface but curved line inward to the substrate-ferrofluid-water interface. The yellow layer on top of the droplet represents the oil later (carrier liquid of ferrofluid) coating the droplet. B) Side view of a tSPRing enclosed droplet, dash lines highlight the ferrofluid cupcake assembly section.

4.2.2 Magnetization of the tSPRing and Stability of Water Droplet

Each spike, in the classical Rosensweig pattern, behaves as an independent dipole, which is attracted to the center of the magnet (higher field gradient) and is repelled by the neighboring spikes. A similar behavior was expected from the tSPring. To confirm this hypothesis we pipetted several droplets of water on a PMMA surface containing ferrofluid spikes and observed the dynamic behavior of the system. A tSPRing formed immediately around each droplet, each tSPRing repelled nearby tSPRings and spikes, inducing the movement of droplets and spikes through the surface until the whole system reached an equilibrium (Figure 4.5). The obtained pattern comprised of spikes and ringed droplets followed the critical periodicity described by Rosensweig instability periodicity[98].

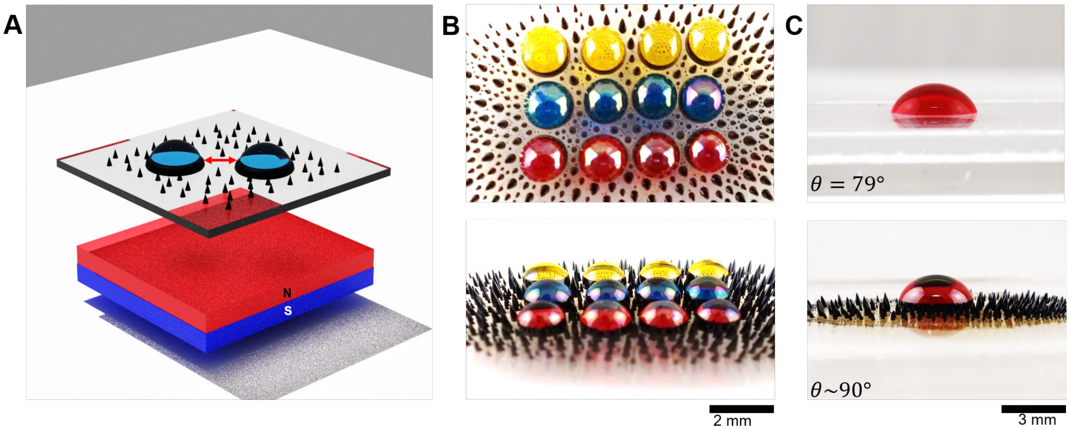


Figure 4.5: tSPRinged water droplets array under Rosensweig instability. A) Schematic drawing of two drops enclosed in tSPRingss that are part of the instability pattern of a ferrofluid created by the influence of a magnetic field on a PMMA surface. B) Photographs of a tSPRing enclosed water droplets array on top of a PMMA substrate, tSPRing and spikes showed dipole magnet behavior keeping a characteristic distance among themselves. C) Side-view of comparison of the shape and contact angle of a droplet being pipetted on clean PMMA surface and a droplet being pipetted in between ferrofluid instabilities.

The droplets that were stabilized by the rings did not spread or mix with neighboring droplets (Figure 4.5) which confirmed that the tSPRings repel each other like the ferrofluid spikes, maintaining a fixed distance between them. Likewise, it was observed that the contact angle of the tSPRinged droplet was greater than that of the droplet without tSPRing (Figure 4.5 C). This implies a smaller droplet radius, suggesting that tSPRinged droplets can support larger volumes while occupying a smaller substrate surface area. In a subsequent experiment, the distance between droplets was minimized to few microns by reducing the volume of ferrofluid (Figure 4.6).

In view of these results we postulate that the repulsion between tSPRings as

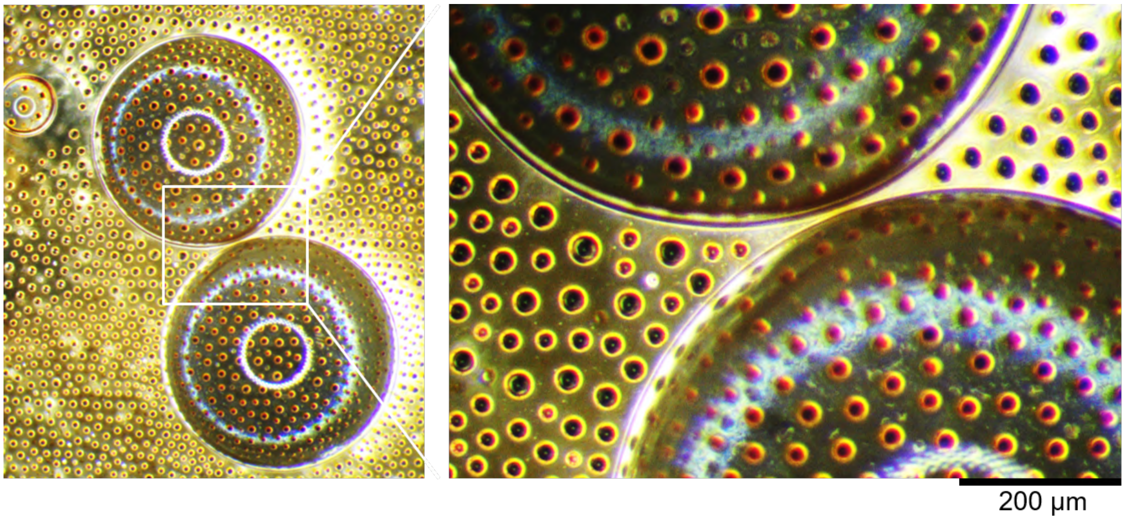


Figure 4.6: Repulsion between multiple tSPRinged droplet. The distance in between two rings can be minimized to few microns (10 microns in zoomed image).

the spikes was due to the magnetization of the ferrofluid in the direction of the applied magnetic field (out-of-plane), confirming that tSPRing and spikes are small soft magnets (surperparamagnets with aligned magnetic domains of internally self-assembled magnetic particles in the ferrofluid) following the same magnetization axis as the external magnet underneath (Figure 4.5 A). In other words, the ring is not only an oil surrounding a droplet; it is a soft matter ring magnet that provides stability to the water droplet as long as the external field is applied.

4.2.3 Tunability of tSPRing

Ferrofluid is a soft material, it undergoes physical changes in the presence of a magnetic field. The response of tSPRing to fluctuations of an applied magnetic field was investigated. A 10 μL water droplet was placed on a ferrofluid layer, of 3 μL, deposited on top of a PMMA substrate. The magnetic field strength (H) was gradually increased by approaching a magnet, located underneath the substrate. The formation and the changes in the aspect ratio of the ring and the enclosed droplet were monitored using a video camera. In the absence of magnetic field, the droplet and the ferrofluid were relaxed over the surface with a certain degree of spreading due to the influence of interfacial tension and gravity. By introducing a 39 mT magnetic field, the spreading of the ferrofluid on the surface was reduced as it accumulated at the interface with the water droplet. The combination of droplet and ferrofluid ring started resembling a "cupcake" configuration. Further increasing of H above the saturation magnetization produced the formation of the ring with a sharp end all around the water droplet perimeter and the expected pattern of spikes around the ring. The spikes were separated from the ring keeping a characteristic distance. Figure 4.7 A shows three snapshots at different H values as 0, 39 and 179 mT. The aspect ratio of the ring around the droplet changed with the magnetic field strength (H), reducing its diameter and increasing its height that forced a similar change in the morphology of the water droplet. We measured the height of the water droplet (h) *versus* the H, the data are plotted in Figure 4.7 B and showed that up to the saturation of the magnetization (around 90 mT) the height of the h increased notably, but remained unchanged once the instabilities were formed. The increase in the height of the water droplet is related to a narrowing of the diameter of the ring (Figure 4.8 and Figure 4.9). The cupcake configuration was maintained the entire time while the magnetic field was on. In a subsequent experiment, we increased volume ratio between ferrofluid and water; water droplets of 20 and 30 μL were pipetted over 3 μL of ferrofluid. The ferrofluid ring around the water droplets was formed in all cases. The height of the ferrofluid ring and the slope h/H was lower for a larger water-ferrofluid ratio. While the perimeter of the water droplet was larger for larger droplet volumes, the ferrofluid volume was constant and therefore it was a limiting factor to obtain a higher ring. If more ferrofluid would be added, the ferrofluid first would be consumed to increase the height of the ring and subsequently a spike pattern would be formed.

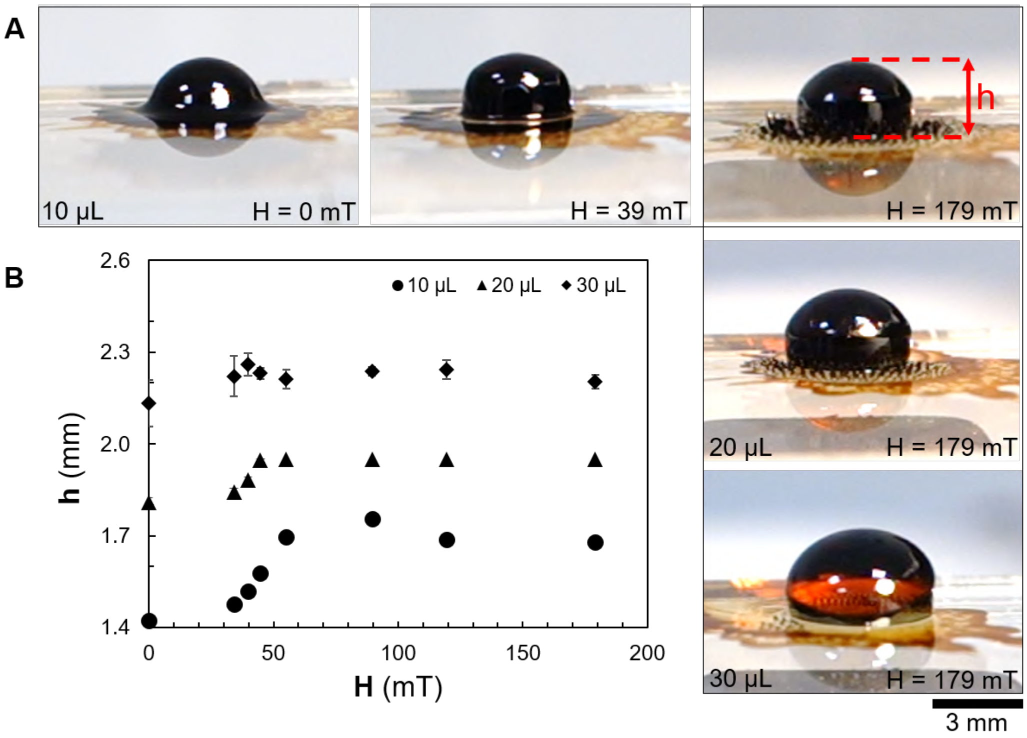


Figure 4.7: Aspect ratio tunability of tSPRing on up-side substrate. A) Photographs of a water droplet deposited on top of a ferrofluid film on a PMMA substrate, taken under different magnetic field strengths (horizontal series), or at constant field strength with different water-ferrofluid volume ratio (vertical series). B) Data plot of the h as a function of H for different water-ferrofluid volume ratio (ferrofluid volume of 3 μL, droplet volumes as 10, 20, 30 μL)

Similar experiments were carried out on the bottom face of a PPMA substrate in order to understand if the ferrofluid ring could also effectively encloses

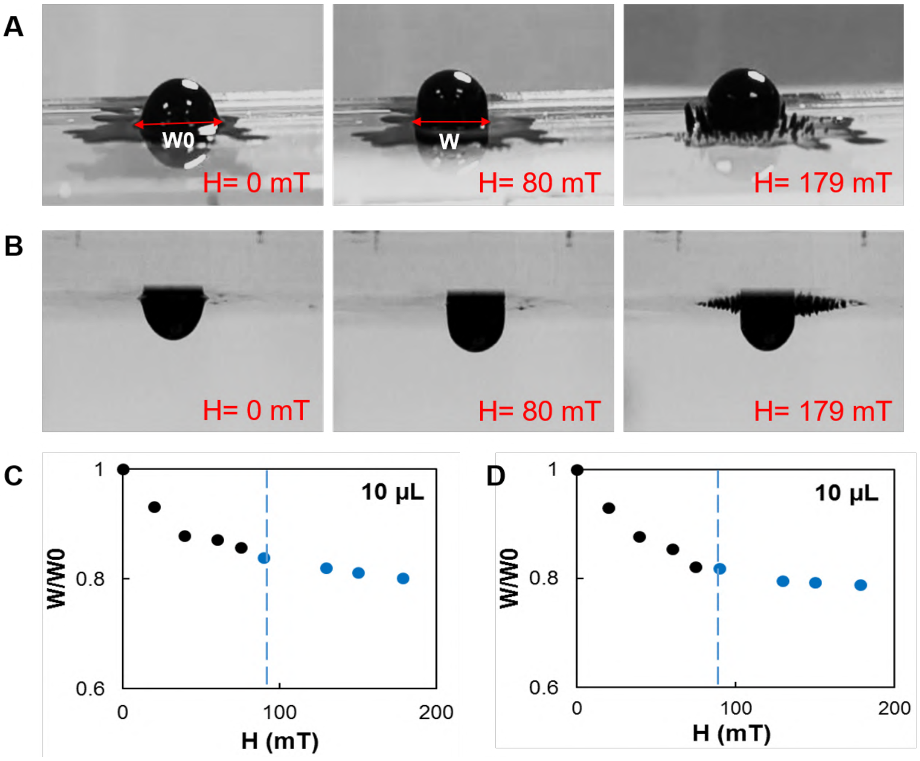


Figure 4.8: Ferrofluid-droplet cupcake assembly deformation by tSPRing modulation. A) Upside surface, cupcake assembly deformation by increasing the field from 0 mT up to 179 mT. B) Hanging droplet, cupcake assembly deformation by increasing the field from 0 mT up to 179 mT. C) The graph shows changes of the width normalized by the initial width (no applied magnetic field) on upside surface. The blue dash like represents the saturation magnetization (Ms). D) Similar to upside surface, the graph shows the data for hanging droplet.

hanging droplets. In order to obtain a hanging water droplet on the ferrofluid layer, we increased the volume of ferrofluid up to 3 μL to hold a 30 μL water droplet (Figure 4.10 A). At that point, the system reached a balance between the two competing forces: the capillary force at the interface of water-ferrofluid and the gravity.

The ferrofluid and water droplet interaction in absence and presence of ap-

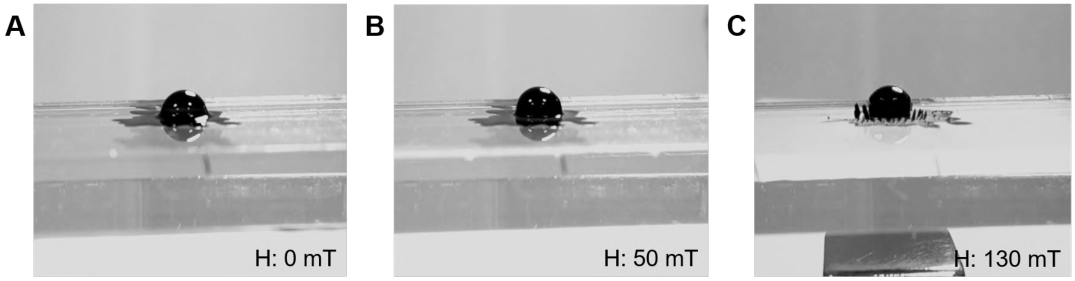


Figure 4.9: Formation of tSPRing (cupcake assembly). A) Side image of a water droplet pipetted on ferrofluid layer (in the absence of magnetic field). B) Side image of the same droplet under influence of magnetic field, 50 mT. C) Side image of the same droplet under influence of magnetic field, 130 mT.

plied external field was similar to prior experiments in Figure 4.7. When the magnetic field was applied we observed again the formation of the ring around the water droplet, which underwent an increase of its aspect ratio with the strength of the magnetic field (Figure 4.10 B), after the saturation of the magnetization we observed the formation of the spikes as in the upside surface experiment. The elongation of the droplet caused by applied external magnetic field was measured and plotted showing a similar behavior (Figure 4.10 C).

These observations demonstrated the tunability of tSPRing as a dynamic adaptation of its aspect ratio in response to the variation of an external magnetic field. tSPRing acted as a dynamic pinning ridge for water droplets enabling the tuning of their morphology and contact angle with a solid substrate (droplet-solid substrate point).

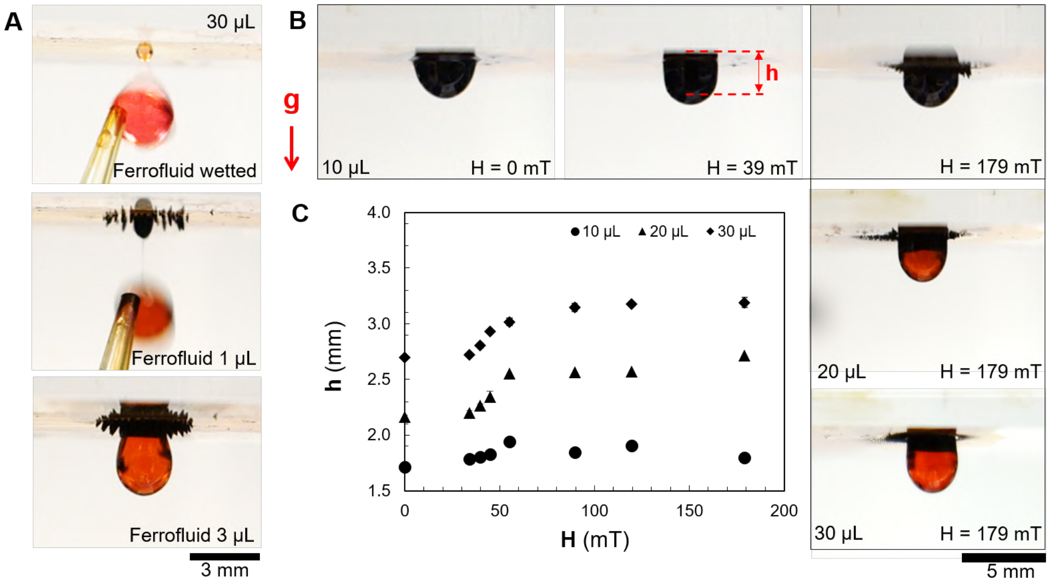


Figure 4.10: Aspect ratio tunability of tSPRing on up-side down substrate. A) Photographs of 30 μL water droplet being pipetted on a PMMA up-side down surface, wetted with ferrofluid(top), with a 1.5 μL of ferrofluid (middle) and with 3 μL of ferrofluid (bottom) under the influence of a 90 mT magnetic field. Increasing amount of ferrofluid at the upside-down surface resulted in holding the droplet against the gravity by ferrofluid-water interactions. B) Photographs of a water droplets of different volumes deposited on top of a ferrofluid film on an up-side down PMMA substrate, under different magnetic field strengths (horizontal series), or at constant field strength with different water-ferrofluid volume ratio (vertical series). C) Data plot of h as a function of H for different water-ferrofluid volume ratio (ferrofluid volume of 3 μL, droplet volumes as 10, 20, 30 μL).

4.2.4 Controllable and Programmable Manipulation of Droplet by tSPRing

The results in section 4.2.2 showed that tSPRing behaves like a soft material magnet, analogous to a solid dipole ring magnet. Once it has been formed, it should be possible to translocate it in a controlled manner by moving the magnet on the other side of the substrate, as indicated in Figure 4.11. Our observations confirmed that the ”water-ferrofluid cupcake” could be handled in a controlled manner by the movement of the magnet. Both cases, sessile and pendant droplets could be moved along the substrate through simple translocation of the ring induced by the movement of the permanent magnet located at the other side of the substrate (Figures 4.12, 4.13).

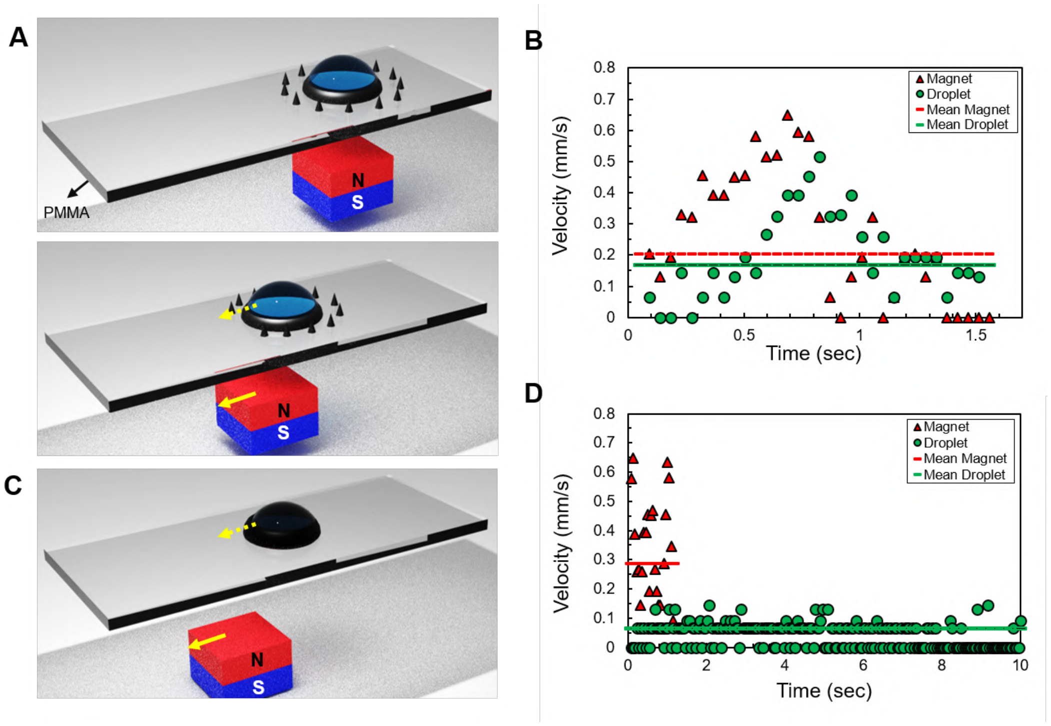


Figure 4.11: Translocation of water droplet by ferrofluid tSPRing. A) Schematic representation for translocation of tSPRinged droplet at H values over Ms. The movement of the magnet under the substrate forced the ferrofluid to move in the same direction. The magnetic instabilities, both the spike pattern and the ring that wrapped the water droplet moved according to the movement of the magnet. B) Plot showing the velocity of the magnet and the water droplet versus time for case B. C) Schematic representation of the translocation of droplets wrapped in cloaking manner at H values below Ms. D) Plot showing the velocity of the magnet and the water droplet versus time for case D.

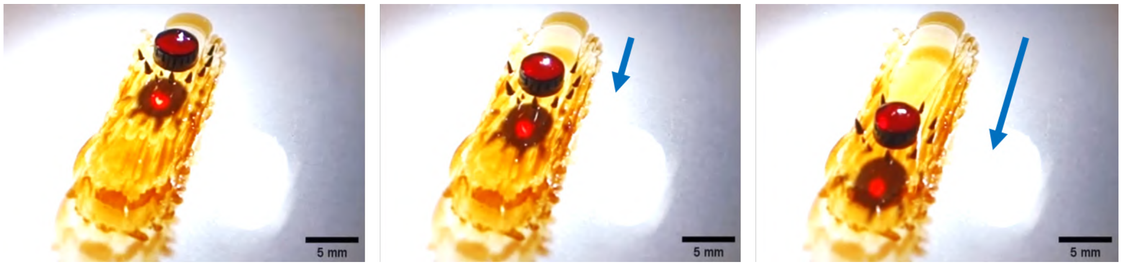


Figure 4.12: Manipulation of tSPRinged droplet on upside surface by translocation of the magnet underneath.

Figure 4.13: Manipulation of tSPRinged droplet on upside-down surface by translocation of the magnet. The cross sign shows the location of the droplet before manipulation.

To compare the movement of the magnet with the movement of the water-ferrofluid assembly, the magnet underneath the substrate was moved manually and the movements of the magnet and the droplets were optically tracked. Figure 4.11 B and D shows acceleration values of the droplet plotted in respect to the acceleration of the magnet underneath. The graph D shows that the acceleration of the cupcake was very similar to the acceleration of the magnet in H values over Ms, what resulted in similar mean velocities. But, in the case of H values below Ms there was a considerable delay between the acceleration of the magnet and the cloaked droplet. These results indicated that water-ferrofluid cupcakes can be robustly moved by moving the external magnetic field enabling a precise and programmable manipulation of the enclosed droplet. Moreover, relocation of the ringed droplet was as fast as the relocation of permanent magnet. It is especially remarkable the robust translocation of pendant droplets, a non-usual example.

4.2.5 On/Off Switchable tSPRing, Mixing of Droplets

In the previous sections of this chapter, the formation of a ferrofluid ring and the ferrofluid-water cupcake has been described. It would be of interest to study the possibility of mixing the contents of two cupcakes (droplets) in a controlled way. To do this, we formed water-ferrofluid cupcakes with two different droplets of water. Using a small mechanical force, we joined the two cupcakes, which interacted through their ferrofluid rings, but did not mix because the two droplets of water were physically separated by a ferrofluid barrier that was formed in between the two droplets (Figure 4.14 A). By removing the magnetic field, the tSPRing began to behave like a liquid oil phase; the ferrofluid barried between both droplets feel, gravity expanded it across the surface and finally allowed contact between the water droplets. In a few seconds the system was reconfigured to go from a figure of eight (resembles the shape of number 8) in which both droplets were independent, to a circular shape where the content of both droplets slowly mixed by diffusion (Figure 4.14 B). By removing the external magnetic field, both Brownian motion of the iron colloids inside the ferrofluid and the gravity force helped the expansion of the ferrofluid on the substrate in any direction. Consequently, this allowed the water droplets to join and forced the reconfiguration of the system into a state of minimum internal energy, the circle. By turning on the field again, the cupcake assembly could be mechanically approached and merged with another enclosed droplet and so on. The paramagnetic nature of the ferrofluid enabled that the ring structure could be

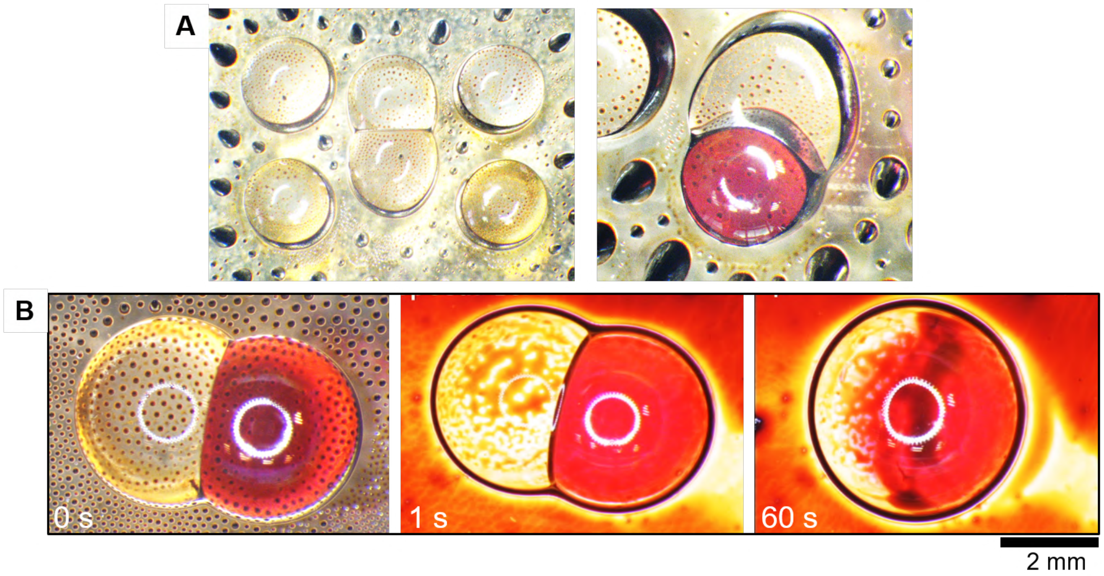


Figure 4.14: On/Off switchable ferrofluid ring, mixing of droplets. A) Photographs of two droplets merged but not mixed, under the influence of a magnetic field. C) Screenshots 1 and 60 seconds after removal of the magnetic field. In the absence of the magnetic field the tSPRing spreads on the surface, the physical barrier between both droplets disappear and the droplets mix spontaneously.

turned on and off accordingly by applying or removing the magnetic field. This enabled both, the precise movement of the droplets along the substrate and their merging, when needed.

4.3 Conclusion

A tunable superparamgnetic ring (tSPRing) is spontaneously formed around a water droplet when an oil-based ferrofluid is in contact with the droplet under the influence of a magnetic field. The interfacial interaction between both liquids and the soft magnetic characteristics of the ring allows a robust, controllable and programmable manipulation of the enclosed droplets. The water droplet can be precisely moved by moving the external magnetic field. The combination of the tSPRing and water droplet, resembles the cupcake assembly. This assembly could be formed on top of a substrate, or as a hanging cupcake on the underside of a substrate. In contrast to the ferrofluid cloaking method, the geometry of the ring means that most of the drop is exposed and thus can be manipulated from the outside. The dimension of the ring depends on the volume relationship between the water and the ferrofluid, while its aspect ratio (height to diameter) is related to the magnetic field strength and the field curvature. The ring is a paramagnetic magnet and behaves as an instability staying away from other instabilities at a certain distance. The ring encloses the water droplets stabilizing them and preventing their mixing. Even when two or more cupcakes are mechanically brought together the water droplets do not mix, because their ferrofluid rings fuse to form a physical isolating barrier. However, the tSPRing is an on-off switchable structure and those droplets can be mixed by turning off the magnetic field.

In comparison with other droplet manipulation systems, tSPRing is based on liquid-liquid interfacial interaction. It allows droplet manipulation over wide range of substrates and does not require complex fabrication processes. tSPRing enables a versatile and generic fluidic control platform for droplets of any size and volume. The fact that both the liquids, the ferrofluid and the water, are immiscible prevents the contamination of the water droplets and allows the easy recovery of its contents. To the best of our knowledge, the use of tSPRing for manipulation of a hanging droplet is the first example of magnetic manipulation of droplets on an upside-down surface, what opens the door to novel applications. Likewise, it provides a new scenario for fundamental studies on oil

– water interface since the external magnetic field modifies the natural capillarity wrapping of the water droplet. We conclude that tSPRing constitutes an advantageous new approach for open surface droplet microfluidics.

4.4 Experimental Section/Methods

4.4.1 Ferrofluid

The ferrofluid used for experiments was a commercial type from the oil-based series, coded EMG900 (Ferrotech USA). It had the highest saturation magnetization (99 mT) in oil-based ferrofluids with 17.7 % volume of magnetic particles concentration. Among the oil-based ones, EMG900 has relatively low viscosity (60 mPa s) which allows easier formation of Rosensweig instabilities and a strong paramagnetic effect due to less viscosity which goes in favor of losing magnetic property once the field is removed by the help of Brownian motions.

4.4.2 Magnets and Controlling of Magnetic Field

Permanent neodymium magnets with magnetization of 450 mT were used during the experiments (purchased from firstformagnets). The sizes were as 10 mm square cubic and 20 x 30 x 10 (width x length x height) rectangular cubic one in order to have bigger surface area. Both had magnetization axis on the 10 mm side. Controlling of magnetic field strength was done by reducing the distance in between the surface of magnet and the deposited ferrofluid on PMMA surface. A standard Laboratory Scissor Lift Riser was used to move the magnet upward and downward. 10 mm magnet was used for experiments of the tSPRing formation, tunability on upside and hanging droplets, as well as droplet manipulation. For the remaining experiments the rectangular cubic magnet was used. Both magnets and all experiments were done with out-of-plane magnetic field by positioning the magnet underneath of a 4 mm thick PMMA surface. For the field strength calculations a simplified formula:

$$H_x = 2Ma^3/4\pi r^3 \tag{4.1}$$

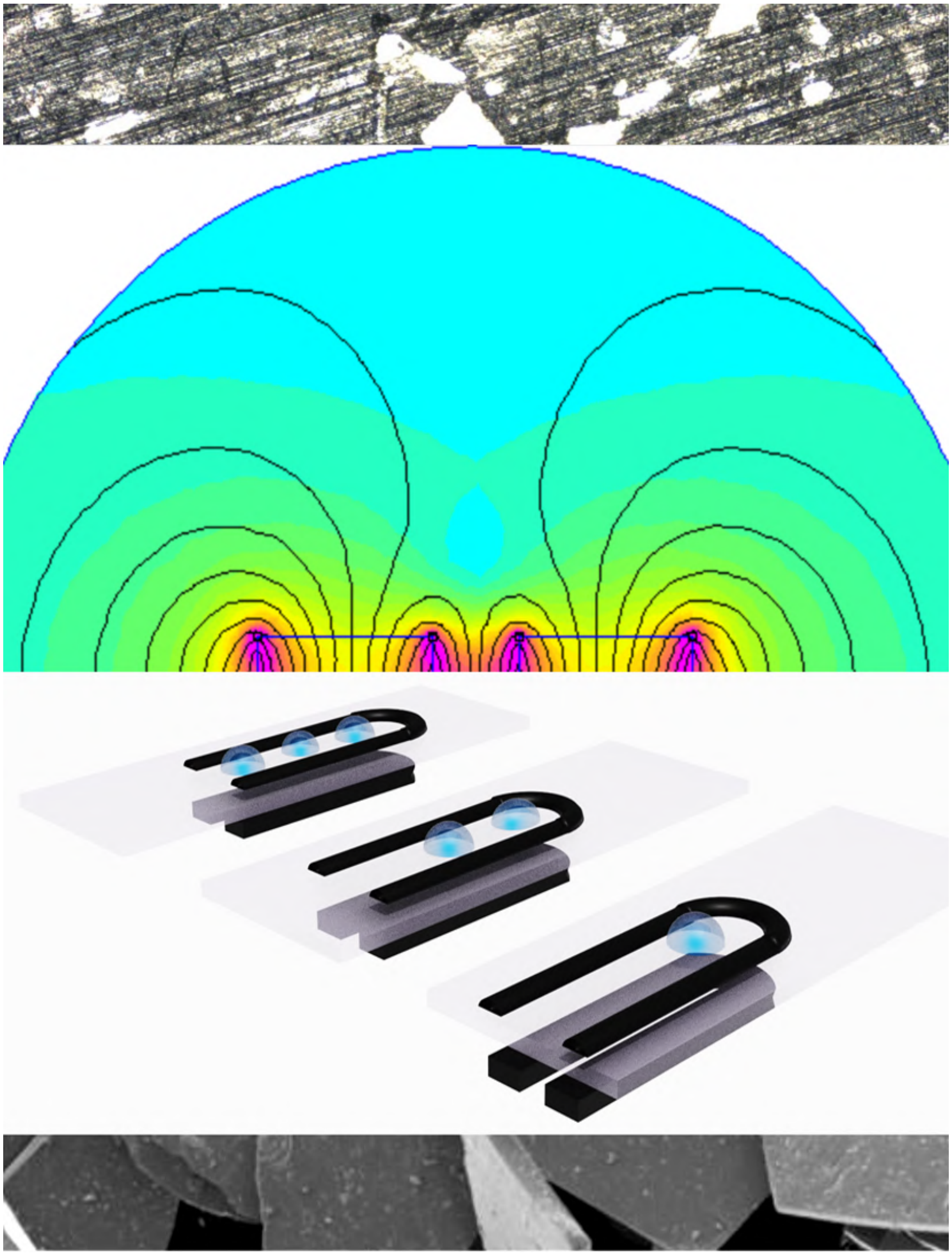
was used. Where, H is the field strength from a distance (x) far from the surface of magnet. M is magnetization of the magnet as 450 mT and a is the length of magnetization axis.

4.4.3 Image Acquiring and Analysis

Images and videos were acquired by both Nikon DI-Fi3 camera mounted on a stereomicroscope (BetaOptics- Plan1X objective) and a digital camera (Sony-Cyber-shot DSC-RX100 with max frame rate of 100 fps). Quantification of the images to measure the height and width of the droplet in Figures 4.7 and 4.10 were done by ImageJ software. The manual tracking plugin of the same software was used to track the droplet movement which gives velocity measurements in time frame.

4.4.4 Substrate

4 mm of thickness PMMA (purchased from PLEXIGLAS Evonik Industries AG) was used as substrate. It was cut by CO2 laser machine (Universal Laser Cutter System) for desired dimensions in different experiments. The surface of the PMMA was cleaned by DI water and dried prior to the experiments.



CHAPTER 5

MICROFLUIDICS IN OIL-BASED OPEN SURFACE CHANNEL

Open surface droplet manipulation is a great approach of microfluidics but requires proper methodology to adjust the interaction of the droplet with the surface and apply sufficient force to displace it. Enclosing of a single droplet by ferrofluid (tSPRing) was a successful for single droplet manipulation. Here, the oil-based ferrofluid was used to make a channel shape topology on the surface for multiple droplet manipulation. A polymer-bonded magnet (PBM) was machined in a channel shape, to self-organize the ferrolfuid as an oily channel on the surface. The channel made of ferrofluid allows confining droplets inside the channel accordingly to the shape of oil channel. Moving the PBM channel underneath the surface results in manipulation of the liquid channel which was used for mixing of the droplets or translocation of them on the glass surfaces. The shape of the channel provides accessibility for microscopy needs and suits effectively for controlled mixing applications. This is the first work reporting a switchable open surface liquid channel for multiple droplet manipulation that can be used for digital microfluidics. This new method can widen the applicability of magnetism for digital microfluidics by integration of PBM.

5.1 Introduction

Digital microfluidics targets controllable manipulation of droplets, but it is mostly achieved as a single droplet manipulation in controlled and programmable manner (see chapter 2). Many applications in real life demand manipulation of multiple droplets, specially for mixing applications in which multiple droplets need to be manipulated in order. tSPRing (chapter 3) demonstrated successful manipulation of water droplets by ferrofluid, but in order to expand the application of ferrofluid for further necessities in the field, this chapter questions the possibility to use ferrofluid for multiple droplet manipulation with targeting multiple droplet mixing.
The spike instabilities that ferrofluid shows takes the surface area of the magnet used underneath a surface. Therefore, it is possible to shape a certain volume of ferrofluid on surface accordingly to the shape of the magnet. In other words, the shape of magnet would define the outlines of the self-assembly of ferrofluid. This fact arises the question as if it is possible to make a rectangular outline of ferrofluid with avoiding the spike pattern formation. To achieve this goal, it is necessary to apply changes on the applied magnetic field and preferably to machine the magnet in certain way to achieve a rectangular channel shape self-assembly of ferrofluid on a surface. Figure 5.1 shows the schematics of this idea with using polymer-bonded magnets (PBM) give the possibility to machine them to a channel shape.

PBM are mixture of polymers with rare-earth magnetic particles such an neodymium or ferrites[49, 67]. It is a magnet resulted from a polymeric base and embedded magnetic particles in it. I was initially engineered to fabricate irregular shapes of magnets that are mostly used in industrial applications such a car

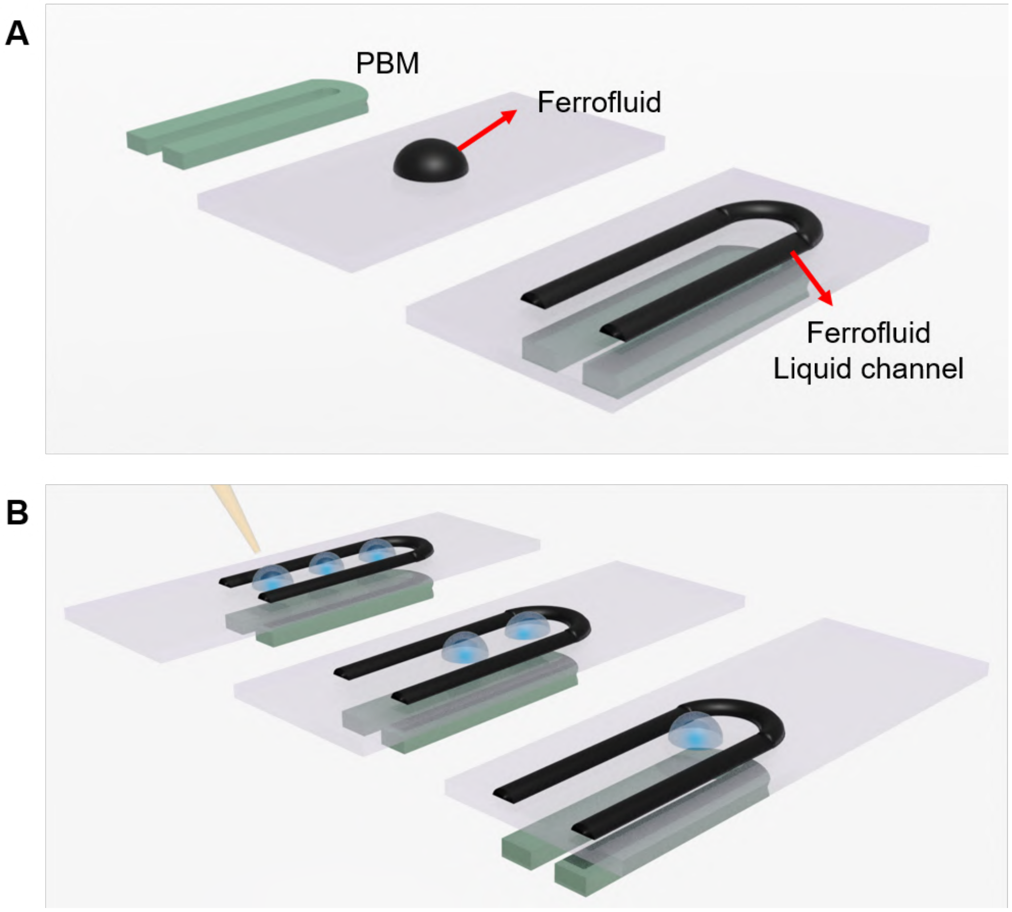


Figure 5.1: The idea of formation of ferrofluid liquid channel on a surface for and methodology for droplet mixing. A) Schematics showing the main components for formation of liquid channel as PBM, ferrofluid and a glass surface. B) Schematics of mixing multiple droplets inside liquid channel by manipulation of PBM underneath.

industry[102]. However, in these magnets additives are used to provide proper binding of particles to polymeric material, which affects the mechanical properties of them. Mostly, thermoplastic polymers are used which allow injection molding of the mixture in order to produce magnets in desired shapes. Due to the presence of thermoplastics, mechanical and thermal characteristics of these magnets allow machining them for further changes in shape and geometry[71]. This a great advantage that allows fabrication of irregular shapes of magnets that offers applications in industry. Moreover, the inject molded magnets can be magnetized in any axis with a magnetizer. Polymer bonded magnets offer the possibility to print them directly by 3D devices[32, 16, 90], but the magnetic properties of 3D printed magnets is lower than inject molded ones. Inject molding is processed in higher temperature and pressures compare to 3D printing, therefore it makes compact structures providing stronger magnetic properties, with the difference that molded magnets may need further machining to achieve the desired shape.

In this study, an oil channel was formed on a surface that is a dynamic feature and could be manipulated by moving the underneath PBM channel. Formation of the liquid channel on an open surface happens only due to the flexibility in shape and geometry that PBM offer. Rectangular channel shape magnet was used to form the liquid channel in which the magnetic field has repelling configuration inside the channel and therefore ferrofluid shapes itself as a clear channel on the surface. As the result, proper engineering with the knowledge regarding physics of ferrofluid under magnetic field resulted in formation and manipulation of oil-based liquid channel. The liquid channel was effectively applied for droplet mixing and manipulation of confined liquid volumes. The possibility of having a switchable liquid channel offers flexibility to address the droplet manipulation on a surface in which the channel can be moved along the surface to address the droplets positioned on it.

5.2 Results and Discussion

This work can be divided in two main sections: (1) study of the formation of oil- based liquid channel and (2) its application for mixing of droplets through digital microfluidics.

First part studies how the shape and magnetization of the PBM channel could define the form and topology of a liquid channel made of ferrofluid. The physical characteristics of the liquid channel are studied in respect to its in- teraction with water droplets. In the second part, the dynamics of the liquid channel under the influence of PBM located underneath the substrate was investigated. Moreover, the possibility of mixing droplets with this novel configuration of open surface microfluidics was examined.

5.2.1 PBM magnetic channels

In order to form a magnetic channel, smaller sizes of magnets with relatively high magnetization was necessary in this study. On the other hand, mechanical properties of the material needed to be sufficient to allow machining of it to acquire the channel shape. In this regard, polyphenylene sulfide (PPS) was used a thermoplastic polymeric material and rare-earth magnetic particle (neodymium-iron-boron alloy, Nd-Fe-B) with plate type particles (Figure 5.2 A) were used to fabricate rectangular magnets. PPS is semi-crystalline thermoplastic with a symmetrical rigid backbone chain composed of recurring para-substituted aromatic rings and Sulphur atoms that exhibit an excellent balance of physical and chemical properties[21]. As the result, PPS was selected as polymeric material since it allows machining and having sharp cuts of the PBM and offers resistance to corrosive environments and therefore longer stability (Figure 5.2 C). However, other commonly used thermoplastic materials such as Nylon was tested that did not satisfy fine cuts and integrity of magnetic powders in them throughout machining process. This is because machining heats up the

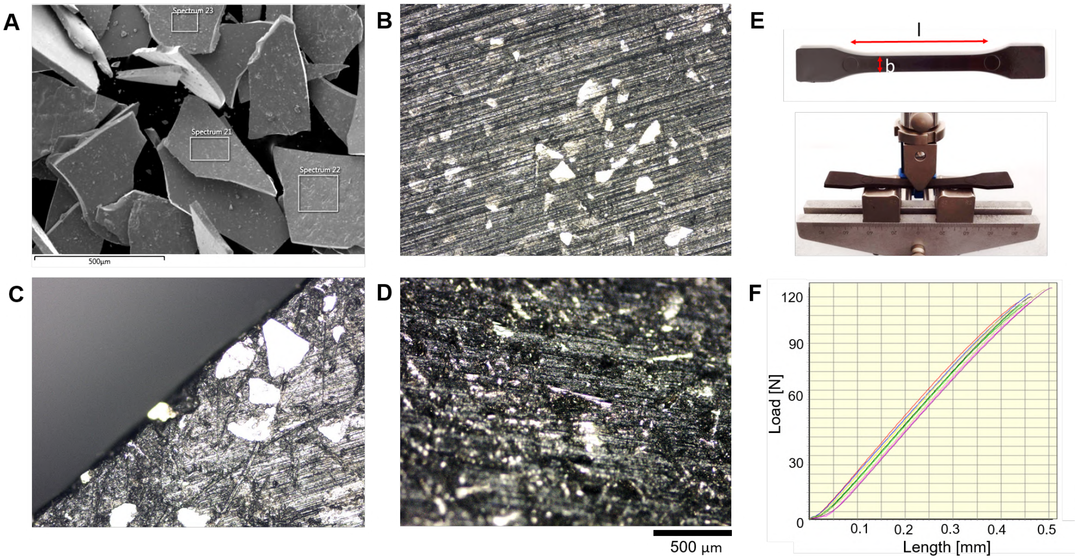


Figure 5.2: Characterization of polymer bonded magnets (PBM) which were fabricated to form the liquid channel. A) SEM image of plate shape Nd-Fe-B particles that were used for magnet production, the particles have a wide range of size from few microns up to hundred microns. B) Optical microscopy image from the surface of a bonded magnet with Polyphenylene sulfide (PPS) as the polymeric material. C) The optical microscope image of machined PBM magnet. D) Optical microscope image for the machined surface of PBM. E) The bending set-up for measuring the mechanical strength of the fabricated PBM. F) The graph showing results of mechanical test for PBM, the graph shows an average value around 118.7 N (test bar dimensions are: l = 80mm and b = 10mm) with a thickness of h = 3mm.

polymeric material and therefore results in deformation of it.

Since the material will undergo cutting and machining processes, mechanical characterization of inject molded PBM was done to understand the scale of forces that can be applied directly on it for post processing. By using the standard test specimens of PBM (Figure 5.2 E), three-point bending test results showed breaking point at 118.7 N and flexural strength of 62.5 MPa for PPS-NdFeB molded material (Figure 5.2 F). These measurements define the scale of

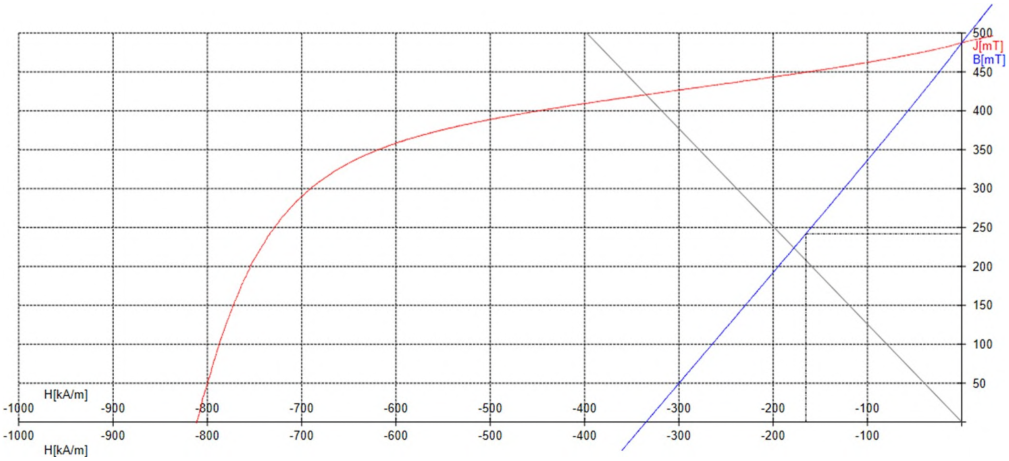


Figure 5.3: The result of permagraph measurements for fabricated PBM. Test cylinders with 10 x 10 mm dimensions were used for magnetic measurements. The results in the graph depict the Br = 487mT and (BH)max = 40.01kj/m3.

forces that it can be tolerated by the material and implies that the produced magnets could show sufficient mechanical stability for machining procedures. Bars of magnets with 3 mm of thickness was cut and used for post processing to create rectangular PBM channels. Finalized PBMs were magnetized in 3 mm thickness axis and were used to form liquid channel. Magnetized PBM with pulse magnetized were characterized by permagraph to determine the magnetic strength of the material (Figure 5.3). The maximum magnetization of 487 mT was achieved. To mention, these magnets can be demagnetized and magnetized again in desired strengths or be processed for further shape changes. The magnetization achieved PBM is sufficient to see spikes instabilities of ferrofluid and therefore the produced channel magnets could apply sufficient magnetic forces to shape ferrolfuid on a surface.

5.2.2 Formation and characterization of oil-based ferrofluid liquid channel

After fabrication of PBM with proper mechanical and magnetic properties, formation of oil-based ferrofluid liquid channel was examined on a glass surface. Ferrofluid was deposited on top of a glass substrate and the substrate was positioned on the fabricated PBM channel (with out-of-plane magnetization, Figure 5.4 A,D). Formation of ferrofluid liquid channel occurred spontaneously once the ferrofluid went under the influence of magnetic field (Figure 5.4 B). The liquid channel had the shape of PBM channel with the difference in dimensions. The liquid channel had wider width and length compare to PBM channel. However, there was no spike pattern formation between two liquid walls and only a layer of oil covered the surface (the area inside the liquid channel). This observation confirmed that the ferrofluid liquid channel could form on the surface with a channel shape PBM magnet.

The response of ferrofluid to the magnetic field applied by PBM was investigated to understand the shape of liquid channel in respect to geometry of PBM channel and the reason behind the absence of ferrofluid spikes in between the liquid walls. The numerical simulation explains the reason behind absence of ferrofluid spikes (Figure 5.4 D). The PBM channel is analogous to two parallel magnets with the same magnetization axis. Therefore, there was a repelling area in the inner part of the channel. Repelling forces pushed the ferrofluid toward the edge of PBM. Nevertheless, ferrofluid does not always maintain as continuous medium and may form instabilities (spike pattern), but it occurs in a certain field strength (above the magnetic saturation of ferrofluid MS) and magnetic field curvature plays an important role as well (a homogeneous field

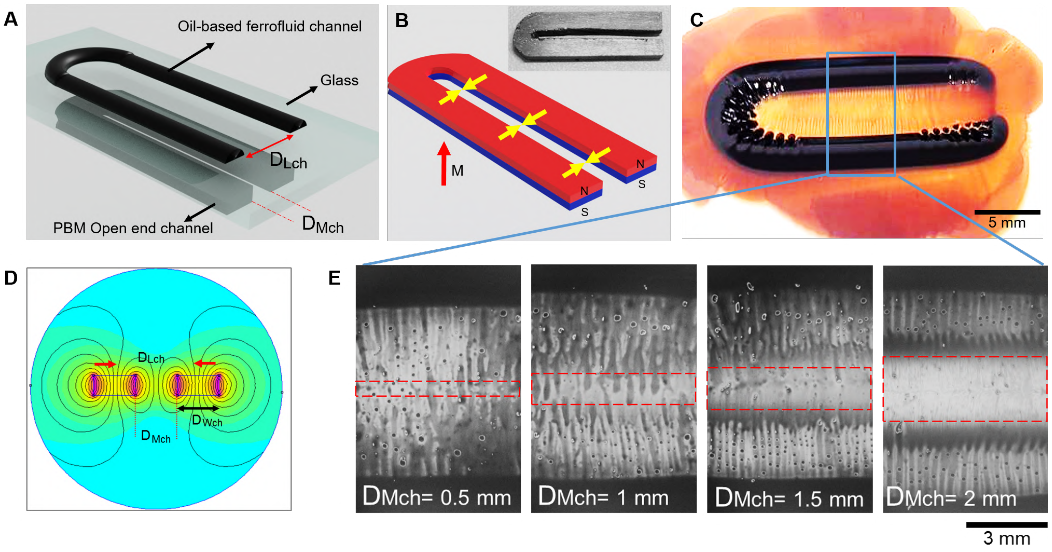


Figure 5.4: Formation and characterization of oil-based liquid channel by using a rectangular open-end PBM channel. A) Shows the schematics of the set-up for formation of liquid channel, the bottom part is the polymer-bonded magnet (PBM) with an open channel shape and having a width of D_{Mch} for the gap. Liquid channel was has a width of (D_{Lch}). B) Shows a schematics of PBM channel which has out-of-plane magnetization axis, the area in between the walls of PBM has repulsive forces indicated by yellow arrows. C) Photograph of the liquid channel formed by the magnet demonstrated in B. Numerical simulation of magnetic field in the cross section of PBM channel. D) Numerical simulation of the PBM from cross-section of it for a magnet with $D_{Mch} = 1.5\ mm$. E) Gives images of a closer view for the inner surface area of liquid channel by increasing the gap of PBM channel, D_{Mch}.

will not apply gradient to break the fluid to spikes)[8, 51, 54, 53]. In the case of liquid channel the strength of applied field is sufficient to form the instabilities but having a repulsive configuration of magnetic channel walls results in continuous formation of clear liquid wall. We have examined the same magnetic filed strength (H) without a channel and spike pattern form on the surface of the magnet (Figure 5.5). However, the U shape of channel (close end of the channel) shows spikes shape instabilities that could be expected since there is not a

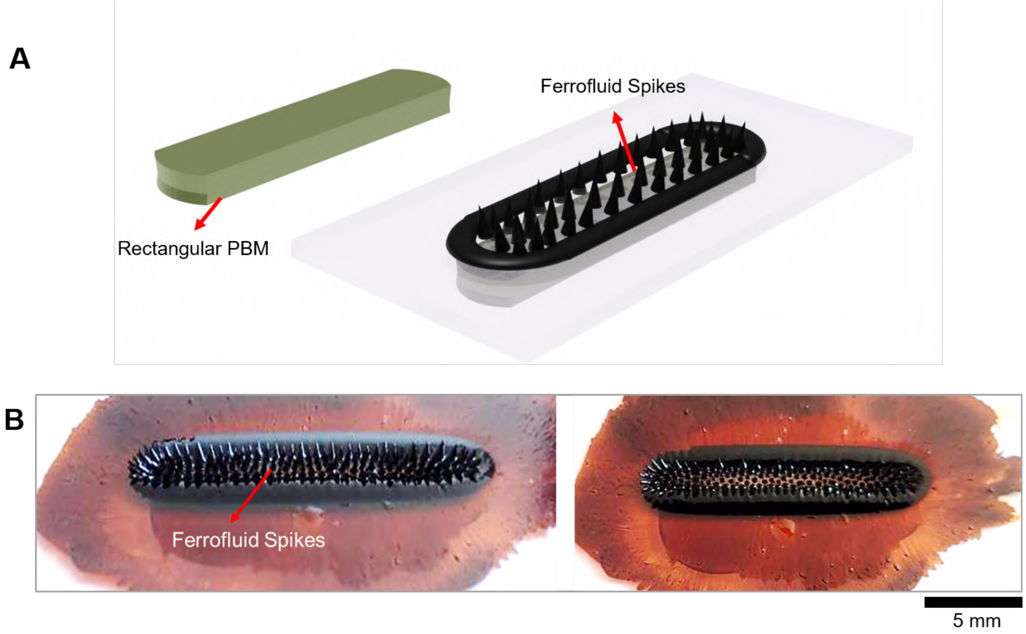


Figure 5.5: The formation of ferrofluid spikes in the middle area of the magnet in the absence of channel in PBM and consequently the repulsive forces in the middle of it.

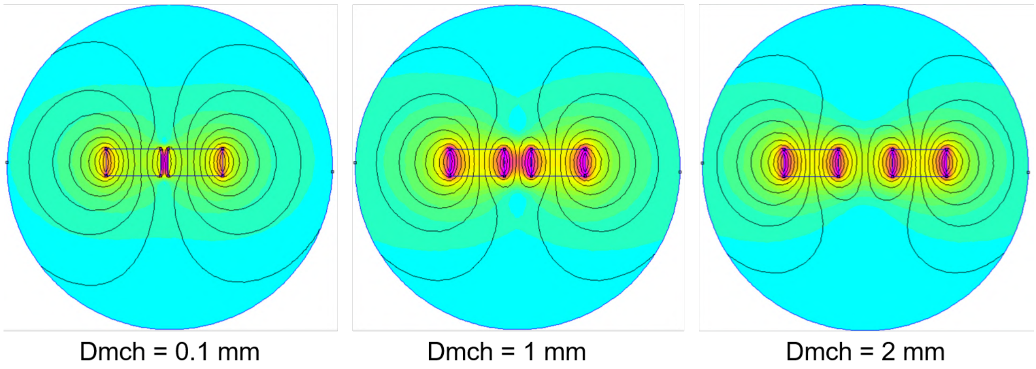


Figure 5.6: 2D Numerical simulations of magnetic field produced by PMB channel for different D_{Mch} values (The inner width of PBM channel). D_{Mch} values are increased gradually as 0.1, 1 and 2 mm in order to map repulsive forces .

repulsive field at the end of PBM channel.

Based on the experimental observations, increasing the inner width of magnetic channel (D_{Mch}) for the same dimensions of PBM resulted in increasing the inner diameter of liquid channel (D_{Lch}) (Figure 5.4 E and Figure 5.6). However, it can be seen that increasing D_{Mch} over 1 mm showed a clear rectangular area in the middle of liquid channel. This could be due to the sufficient gap to have stronger repulsion. The D_{Lch} could be either controlled by changing the D_{Mch} or the thickness of PBM (D_{Wch}). Ferrofluid ran to the higher gradient area that is the edges of the magnets therefore higher D_{Mch} values would result bigger width of liquid channel. This implies that the width of liquid channel was primarily influenced by overall width of PBM. Increasing D_{Mch} partially affected the D_{Lch} but is limited to the overall width of PBM.

To conclude, the novelty of this work or the mechanism to form a liquid channel on an open surface originate from the fact that the ferrofluid undergoing discontinuous instabilities is pushed with repulsive forces to form a continuous liquid line. Therefore, the absence of ferrofluid spikes in the middle section (between two walls) was due to the repulsive forces and it makes possible to form liquid channel on a surface.

5.2.3 Topology of the liquid channel

A closer view of the liquid channel is needed to understand the topology of liquid channel. Optical imaging from a formed liquid channel was acquired. The liquid channel showed a non-flat surface that can be understood by the liquid nature of ferrofluid (Figure 5.7). It has higher height in the middle of it (in the middle of liquid wall) since the surface tension at the top surface of the channel is different than the contact lines of it with the glass substrate (Figure 5.8 A). As the result, middle part of the channel is higher (similar to the contact angle of a sessile droplet on a surface, at the contact line of the liquid with the substrate the contact angle forms that is relevant to the affinity of the droplet to the surface). As it was mentioned earlier, the end of liquid channel shows spike shape instabilities (Figure 5.8 B). As a conclusion, the topology of liquid channel may apply sufficient patterning of ferrofluid as liquid barrier for droplet manipulation that would need to be investigated.

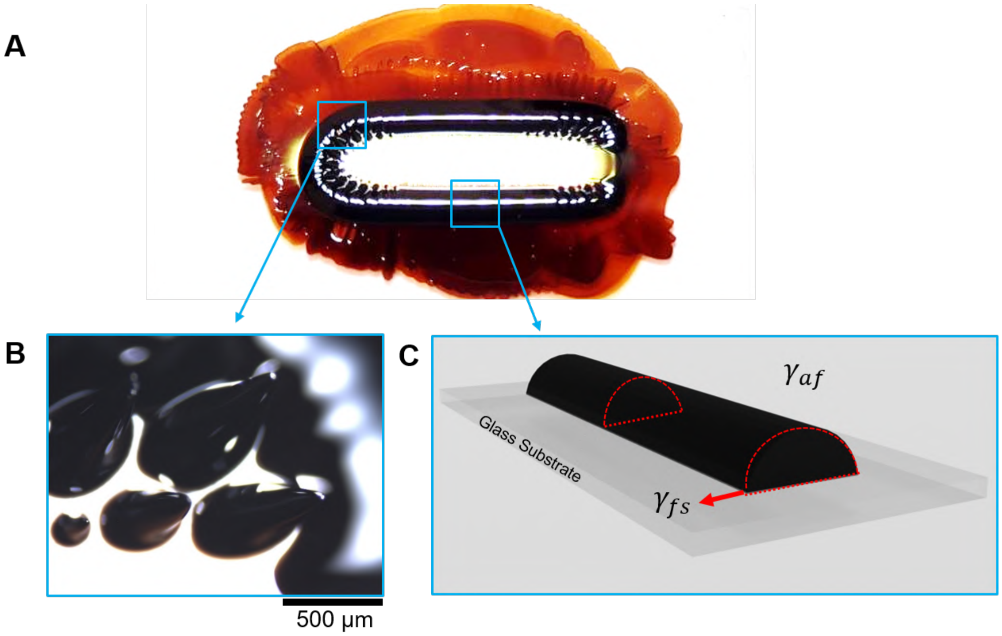


Figure 5.7: Topology of oil-based ferrofluid liquid channel formed by a U-shape PBM. A) Shows top view images of the liquid channel with spot light illumination to observe the topology of it. B) Shows formation of ferrofluid instabilities at the end of liquid channel wherein the repulsive forces are not present. C) Schematics of the liquid channel wall, it has higher volume in the middle of it which makes a wall shape, the surface tension at the surface (γ_{fs}) is different than the air-ferrofluid interface (γ_{fs}).

5.2.4 Interaction of water droplets with magnetic liquid channel

To understand the applicability of the magnetic liquid channel for droplet microfluidics, the interaction of it with water droplets was investigated. After formation of the magnetic liquid channel a droplet was pipetted inside the liquid channel and the interaction of it with the magnetic liquid at the interface of two immiscible liquids was studied. The liquid channel was formed and a water droplet was pipetted inside the channel. The volume of the droplet was increased gradually to have the droplet fitting in between two walls of the liquid channel (Figure 5.8 B). Moreover, the volume of the droplet was increased to overpass the distance between two walls.

The experiment showed that the droplet does not mix or wets the magnetic liquid wall in both cases. A thin ring of ferrofluid was formed around the droplet that it is a tSPRing (previously reported in chapter 4. It forms due to the field characteristics proper for normal field instabilities) but the ring formed here had very small volume. In the case of second experiment, the volume of the droplet and as the result the size of it overpasses the width of liquid channel (5.8 C). It shows that increasing volume of the droplet applied force on the magnetic liquid channel and therefore deforming the interface. Yet, the droplet did not break the liquid wall and there is a thin gap at the interface was observed. However, it was observed that in excessive volume of the droplet (adding water more than the volume that can fit inside the channel) the water over ran the magnetic liquid wall and falls out of it. This is understandable since any channel would have a limit of volume that can accommodate. On the other hand, overrunning the liquid from the wall shows the stability of the liquid wall since

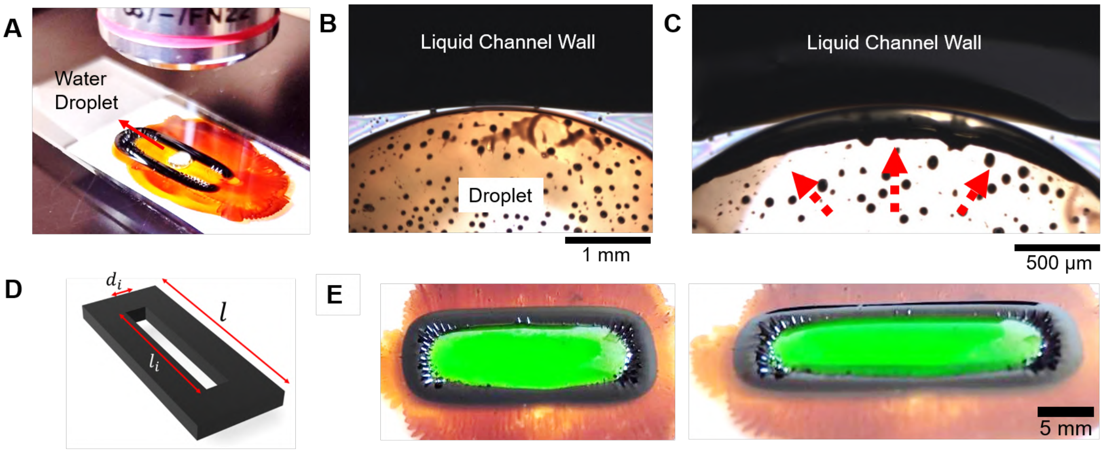


Figure 5.8: The interaction of water droplet with oil-based liquid channel. A) Shows the picture demonstrating the set-up to study the interaction of a droplet inside the channel. B) Shows microscope image of the interface of droplet with liquid wall for a droplet that fills the channel only up to the liquid wall line. C) Shows optical microscope image of the interface of droplet and liquid wall for a droplet bigger than the inner width of liquid channel. D) show the photograph of the liquid channel filled with water (dyed as green color). E) Shows the 3D schematics of the magnet used for formation of closed-end channel ($l = 30mm$, $l_i = 23mm$ and $d_i = 1.5mm$)

the interaction in between water and ferrofluid is immiscible and non wetting interaction.

As the water droplets showed non-mixing interaction with the ferrolfuid liquid channel, it was questioned if a closed-end liquid channel can be fully filled with water. For this purpose a closed end PBM channel was used, to have an closed liquid channel (Figure 5.8 D). Closed-end liquid channel was gradually filled with water to form a complete water channel on the surface (Figure 5.8 E). The repulsive interaction of two immiscible liquids allowed the water droplet to be elongated and take the shape of the liquid channel. As the result, the unique interaction in between the liquid channel and water droplet, non wetting interface, suggests that it can manipulate the droplet once the liquid channel is manipulated.

5.2.5 Droplet manipulation and mixing inside oil-based liquid channel

The previous experiments with the liquid channel showed that the liquid channel is a dynamic feature that can move on the surface by displacing the PBM. This means the channel could be moved on the surface in any direction. Therefore, we studied the possibility to manipulate the droplets inside liquid channel in order to mix multiple droplets in a controlled manner. The PBM channel (two different types as open-end and closed end channel) were used for these experiments. PBM channels were positioned under the glass surface and the ferrofluid was added directly on the surface that had taken the shape of the magnet.

In the case of fully filled liquid channel (Figure 5.9 A), it was translocated on the surface by rotation of the magnet underneath. Alongside the movement of the liquid channel the whole liquid inside it moved on the surface. Therefore, this experiment show that a relatively big volumes of liquids can be manipulated on the surface by liquid channel (tens of μL). Then, three water droplets of 19 μL were pipetted in the middle of the channel with an inter droplet distance to prevent their mixing. The PBM was displaced manually (a linear trajectory) and we observed the movement of the ferrofluid channel(Figure 5.9 A,B). In both channels, three droplets were pipetted to be mixed. As it can be seen from the images sequences, moving the PBM underneath pushed the first droplet and mix it with the second one and so forth. In the case of closed-end liquid channel,

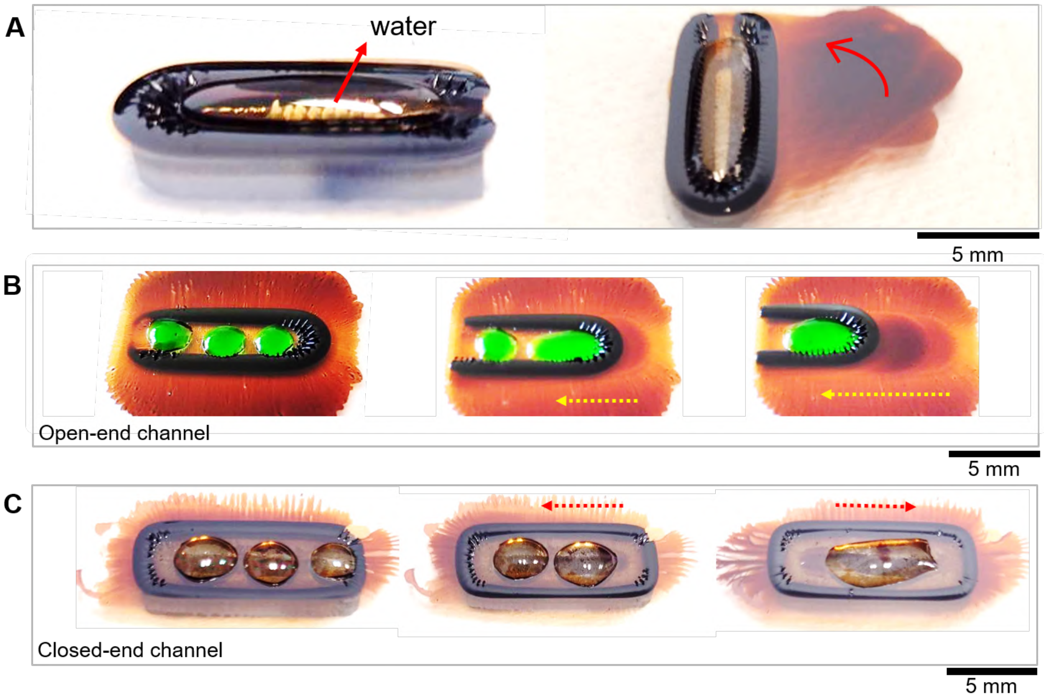


Figure 5.9: Application of open surface oil-based liquid channel for droplet manipulation and mixing. A) A filled channel with water that is rotated to show the applicability of the liquid channel to displace large volumes of water on a surface. B) Shows the experiment for mixing of three water droplets inside the open end channel, right to left linear displacement of the PBM moves the droplets along the direction of liquid channel and brings them in contact to mix. C) Shows similar experiment in closed liquid channel, due to the shape of it, the channel was manipulated from both ends (shown with red arrows).

it allows manipulation of the droplets from either ends of it (Figure 5.9 B) since it is closed from two sides. Once two droplets come in contact and mix, it forms a single droplet that can be manipulated further inside the liquid channel. Since the liquid channel does not mix with the droplets, movement of the liquid channel pushed the droplets at the closed end of the channel to move on the surface along the direction of the PBM's movement (red dashed arrow).

To conclude, oil-based liquid channel offers manipulation of water or mixing of droplets. This manipulation can happen in a controllable and programmable manner by translocation of PBM underneath the substrate.

5.3 Conclusion

This work reports a new concept in droplet microfluidics as open surface liquid channel and introduces a novel methodology for using magnetism in the field of fluidics. By taking advantageous of polymer-bonded magnets that can be shaped and processed in different ways, a magnetic liquid channel was formed on open surface. Oil-based ferrofluid was used as the magnetic liquid that it reshapes itself as the shape of the magnet and consequently forming a liquid channel on a surface. The base of this observation is the repulsive magnetic forces inside the PBM channel that pushes the ferrofluid to adjust as walls. The topology and interaction of the liquid channel suggests that it could be applied successfully for digital microfluidics. There is the place for further fundamental studies to fully understand the physics of the liquid channel under static and dynamics states, but here we communicate it to highlight the main characteristics of it that makes it suitable for digital microfluidics.

The immiscibility of the liquid channel with polar liquids such as water offers fascinating concept for open surface digital microfluidics that was shown and conceptualized by droplet mixing. The channels of PBM either with open and closed end offered robust and controllable mixing for droplets pipetted inside the liquid channel. However, we have shown that the dynamic nature of the liquid channel allows displacement of the liquid on a surface as well. We suggest using of open-end channel in which the droplets can be positioned on any location on the surface and the channel can move on the surface to trap the droplets and manipulate them. In summary, by using polymer bonded magnets and magnetic liquid a dynamic liquid channel can form on a surface, which can be applied for manipulation of sessile droplets. We foresee this novel combination and idea can introduce the possibility of open surface liquid channels, to be engineered further to use the channel chemically beside its physical properties. For further studies we propose using a modified ferrofluid can be used to convert the liquid wall to a medium to promote a chemical reaction of sensing application.

5.4 Experimental Section/Methods

5.4.1 Fabrication of Neodymium-PPS PBM

For fabrication Nd-Fe-B with PPS bonded magnets, we have used industrial extrusion line Leistritz ZSE 27. Extruder Leistritz ZSE 27 is a co-rotating twin extruder used for continuous compounding of thermoplastics bonded materials. As standard procedure for PBM, the mixture of PPS (Purchased from Ryton), isotropic Nd-Fe-B (Purchased from Magnequench) and additive (Pentaerythritol esters) were extruded as filaments and machined to small pieces to be used in the inject molding tool. The mixture was based of Nd-Fe-B with 87.96 wt% and PPS with 11.70 wt% and remaining as additive. The material was injected molded under high pressure and temperature optimized for material. Inject molding machine produces test bars that are normally used for mechanical characterization of the PBM and the same test bars were used to fabricate PBM channels. Test bars are fabricated in a non magnetized setting.

One of the protocols in the production of bonded magnet material is to establish T/t/p (temperature/time/pressure) characteristics of both magnetic powder and polymer to obtain the desired characteristics. To achieve better flowability of bonded material it is required to use different additives (adhesion promoters, cross linkers, anti-sticking additives, dispersing additives, coupling additives, surface modifier, etc.). These additives are used at relatively low dosage levels. Various modifiers and process additives are available to improve the mechanical properties of filled, thermoplastic com- pounds. Using process additives improves a compound's processing properties. Three different additives were used such as: Organic modified siloxane based wax Spherical, sub-micron particles of amorphous silicon dioxide (SiO2) and Pentaerythritol esters. Pentaerythritol esters was selected for final production due to advantages such as: preventing material from sticking to the hot machine parts (in inject molding process), easier mold release at higher tool temperatures, improved feed behavior, preventing the granules from melting in the feed zone (bridge formation), higher tool filling speed and better surface properties.

For fabrication Nd-Fe-B with PPS bonded magnets, we use extrusion line Leistritz ZSE 27. Extruder Leistritz ZSE 27 is a co-rotating twin extruder used for continuous compounding of thermoplastics bonded materials. A picture of the machine and schematics of the inner process of the extruder is shown in Figure 5.10.

5.4.2 Magnetic measurements

Magnetic hysteresis of permanent bonded magnet materials were measured with Permagraph EP3 from Magnet Physikon. Two cylindrical parts with max-

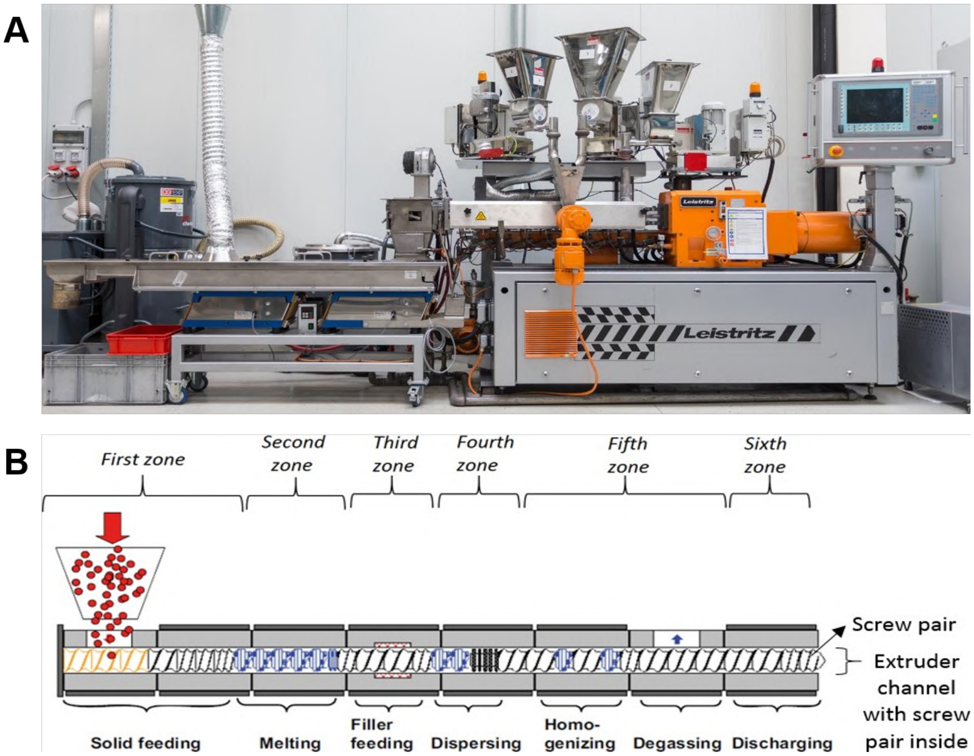


Figure 5.10: The extrusion of mixture of Nd-Fe-B, PPS and additives in a industrial scale machine to fabricate the material for inject molding. A) Shows the picture of Leistritz ZSE 27 extruder. B) The schematics of the steps taking place inside the machine in order to provide homogeneous mixture of the output material.

imum and minimum determined density is used in the system. For this measurement non-magnetic cylinder (1 mm diameter with 1 mm height) was magnetized with 2000 V in a magnetizing coil connected to the Impulse magnetizer (U-series). A hysteresis graph is used to measure the hysteresis loop of a magnetic material, generating as its output a hysteresis curve. To generate this loop, the specimen is placed in a magnetic field.

5.4.3 Mechanical tests

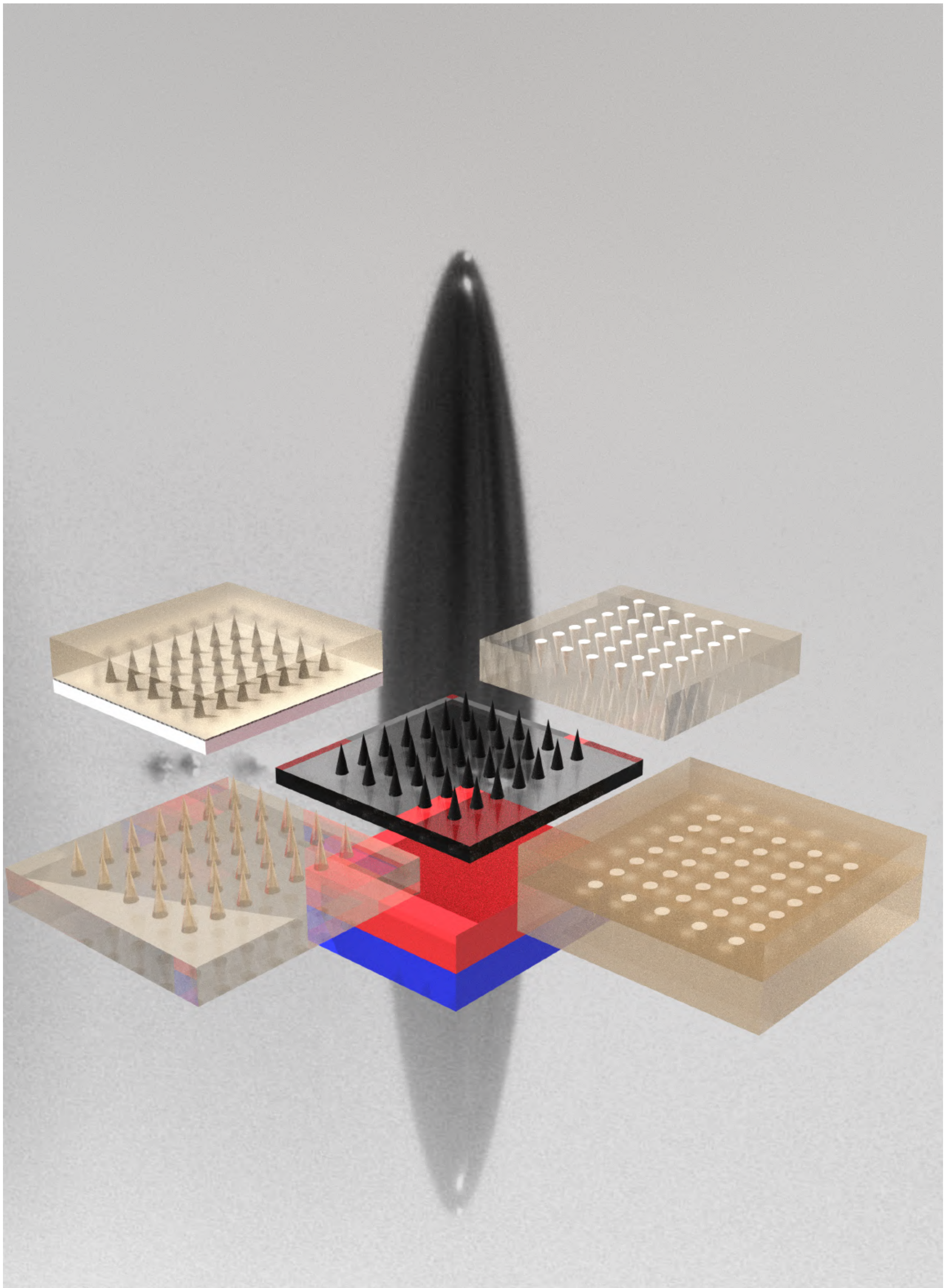
Mechanical test was done with Zwick Z010 tool to conduct 3 point bending of specimen and calculated the flexural strength of it. Dimensions of the test specimen are in accordance with the standard ISO 3167 and punch support unit for 3 point bending was used based on with ISO 178 (flexural test standard). Maximum force of breaking point was measured directly and the flexural strength was calculated with following formula:

$$\sigma_f = 3FL/2bh^2 \tag{5.1}$$

In which σ_f, F represent flexural strength and applied force. L, b and h are the dimensions of the specimen. σ_f was calculated as 62.5 MPa.

5.4.4 Numerical Simulations

The simulations was done with the software FEMM 4.2 (Finite Element Method Magnetics)[53].



CHAPTER 6

DRIED FERROFLUID SPIKES: STABLE MICRON-SIZED CONE SHAPE PILLARS FOR MOLDING APPLICATIONS

Ferrofluid undergoes normal field instabilities, which self-organizes it to cone shape spikes with regular pattern, according to the field curvature gradient. When the shape and pattern of these spikes are replicated with other materials, unique advantages can be obtained for surface engineering such as hydrophobic and self-cleaning surfaces. To replicate the ferrofluid spike patterns accurately negative molds could be made with polymeric materials, but ferrofluid spikes significantly deform when they get in contact with a viscous solution such as the monomer solutions, due to a change in the surface tension at the interface surrounding the ferrofluid structure. To enable the accurate replication of ferrofluid spike patterns, we introduce a novel approach based on the drying the oil-based ferrofluid spikes. Dried ferrofluid spikes showed sufficient mechanical and thermal stability for molding by heat or light curable polymers. Ferrofluid spikes patterns were successfully replicated on PDMS. This manuscript reports for the first time, the production of dried ferrofluid spikes and shows their applicability for molding. Therefore, we foresee it promotes the application of spike pattern wherein the shape and pattern benefit certain functionality that cannot be fabricated by conventional lithography techniques.

6.1 Introduction

Molding is an old technique to replicate an available pattern or shape on other materials either as positive or negative replica that is aimed mostly for mass production. Negative replica can be used as a secondary mold to get the initial pattern by second step of molding. In other words, to replicate an available pattern to another material, the pattern can be molded to fabricate a negative replica, and used once more to acquire the initial pattern. However, this implies that the presence of a pattern is required which may be useful for a certain application. Many patterns can be found around us in nature or in self-organizing systems[117] that show quite fascinating patterns which can be useful for surface engineering applications. These self-organized patterns are most of the time hard to achieve artificially, therefore, molding them would be the only option to replicate the same pattern.

Micro or nano structuring a surface is a requirement for controlled wetting or self-cleaning surface demands[35, 85, 109]. The topology of a surface directly affects the interaction of it with other material in any material phase and is much visible in the case of liquids. Hence, to control the level of this interaction by adjusting the surface energy, many surfaces can be modified chemically[77] or physically by introducing topographical changes such as micro or nano patterns[123]. A regular pattern of pillar created on a surface, modifies the surface energy due to air trapped between the pillars[72, 92]. By using proper engineering approaches such as lithography[96], electron beam patterning[93], chemical deposition[126] and chemical etching[84] tunable size and shapes of pillars with different cross-section shapes can be produced.

On the other hand, to take advantage of what the nature offers, innovative ideas like replication of plant's leave surface pattern to acquire hydrophobic surfaces by lotus effect[100] was introduced. Nevertheless, self-organized patterns found in nature like the surface of plant leaves, does not offer flexibility and control, therefore applying them in engineering applications has limitations. A self-organizing system which can be formed and controlled would be beneficial. Solid particles or liquid phases energized by an external source of energy can form different patterns to minimize the introduced stress[79]. Interestingly, combining solid particles in a liquid phase, as stable colloidal solutions, creates complex liquids which respond to external energy sources in the shape of instabilities, since stabilized particles inside the liquid can not abandon the liquid phase[69]. Nevertheless, due to the liquid phase of self-assembled features it would be challenging to use them as a template for molding purposes. This is the case of ferrofluids, ferrofluids form regular patterns of pillars in spike shape. The formation of spikes happens by introducing an external magnetic field (out of plane) and is notably subjected to the properties of ferrofluid such as viscosity and magnetization. Hence, there is a degree of geometrical control by either modifying the ferrofluid or the applied external magnetic field to adjust the shape and size of formed spikes[8].

A ferrofluid is composed of magnetic nano particles suspensions which are stabilized by a surfactant in an oil or water medium (carrier liquid). It is a soft material, a colloidal suspension, a liquid which can be magnetized and consequently reshaped by an external magnetic field[6]. Its magnetization induces dipole moments in each magnetic nanoparticle, which causes a reorganization of the particle distribution overcoming the thermal fluctuations and gravity which are governing forces for fluidity of liquids[45]. Macroscopic cone shaped pillars are the dominant form driven from internal self-assembly of iron oxide colloidal as the result of applied magnetic field higher than saturation magnetization (MS) of the ferrofluid. These features take the orientation of magnetic field lines running from the North Pole to South Pole with pointing sharp tips. Since the spikes are stable in the presence of magnetic field, they have been considered as a soft matter features to be replicated[118, 119, 10, 41, 31, 89]. In the reported works water-based ferrofluids were used with hydrophobic polymeric materials curable by UV light, the replicated patterns were proved to produce sufficient modification for controlled wetting and self cleaning applications[31]. However, the shape of the spikes and the pattern could not be replicated with high accuracy due to the deformation of the ferrofluid microstructures in contact with other liquid.

Regarding replication of ferrofluid spikes the ideal case would be to solidify the ferrofluid spike pattern before its replication. Replicating a solid structure is easier than replicating a liquid or soft material, and allows to preserve the aspect ratio of the mold in the replica. In this way, the advantages of the fine tuning of the microstructures that can be obtained with ferrofluids and the advantages of the molding technique could be combined. In this work, the drying process of ferrrofluid spikes and the possibility of replicating these microstructures by means of PDMS molding has been investigated (Figure 6.1).

6.2 Results and Discussion

Initially, we evaluated the interaction of a second liquid phase on top of ferrofluid spikes (in liquid phase as well). Ferrofluid spike were formed on a PMMA substrate by the influence of an out-of-plane magnetic field (perma-

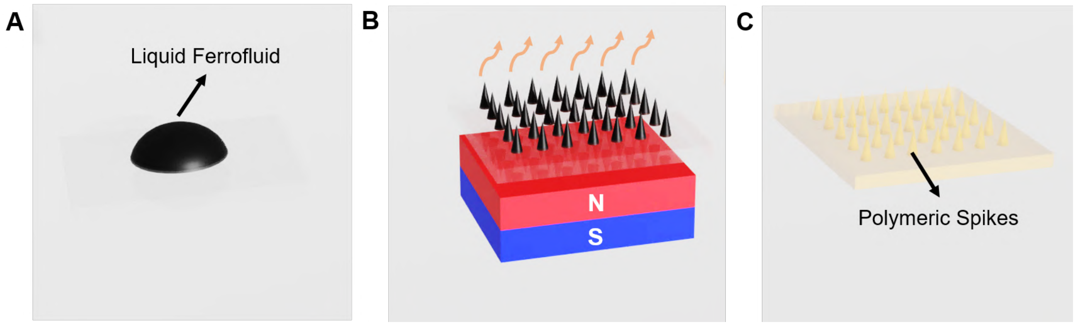


Figure 6.1: Fabrication of polymeric spikes by oil-based ferrofluid. A) A drop of ferrofluid on the surface (PMMA). B) Formation of ferrofluid spikes on the surface by introducing a permanent magnet. C) Demonstration of spike pattern on polymeric material.

nent magnet). Afterwards, two sets of experiments were conducted. First a thermally curable polymeric material widely used for replication of microstructures ,PDMS, was poured on top of a single oil-based ferrofluid spike. The spike greatly deformed in contact with PDMS compared with its original shape in air (Figure 6.2 A). Since PDMS is hydrophobic, in second experiment the interaction of oil-based ferrofluid with water medium was questioned. Adding water on ferrofluid spike totally removed the spike from the surface and the oil floated on the water-air interface. This could happen due to the surface tension difference between water and air, since the spikes were formed and stabilized in air medium, changing the medium disrupted its stability and removed it. Therefore, sodium dodecyl sulfate (SDS) was used as surfactant in water to reduce the surface tension and form spikes inside water. The spikes were formed on the vertical wall of a channel filled with lower surface tension water. The water was slowly depleted from the channel using a paper strand (see experimental set up in Figure 6.2 B). When the water level was lowered, the spikes got in contact with the air and were deformed from its original shape. Complete depletion of water resulted collapsing of ferrofluid on the bottom of the channel. As it was foreseen, the experiments demonstrated that the surface tension of the medium in which ferrofluid spikes are treated defines their shape and stability. Replacing air with PDMS or water, as well changing from water to air deformed the spikes completely. Therefore, this concludes that adding a second liquid phase on ferrofluid spikes is not practical for replication of their pattern and solidifying them would give the possibility to use the spike pattern for replication.

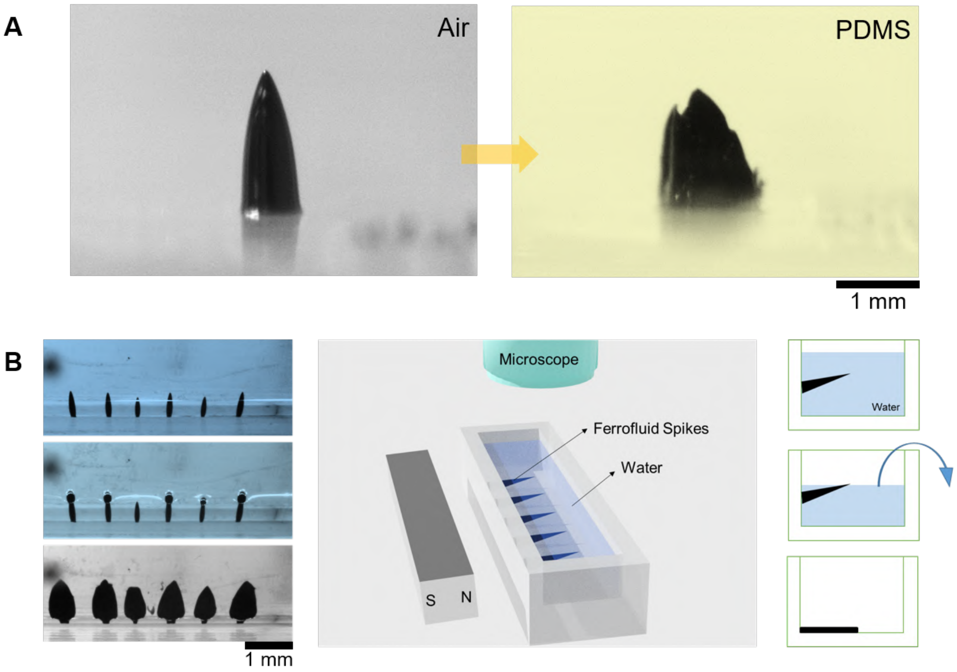


Figure 6.2: Effect of the ambient surface tension on formation and stability of ferrofluid spikes. A) Shows side view images of a spike formed in air medium and the same spike with PDMS liquid poured on it. B) Shows the top view images and schematics of the experiments to replace the water medium with air, wherein the spikes were formed in water and the water inside the channel was gradually depleted.

6.2.1 Drying of Oil-based Ferrofluid

To evaluate the possibility to dry ferrofluid microstructures, oil-based ferrofluid spike pattern was formed on top of a PMMA surface by applying 170 mT magnetic field with a permanent magnet to 0.1 μL of ferrofluid. Spikes with a classical cone shape with an average of 1 mm height were obtained. The spike pattern was left to dry at room temperature and the process was recorded over time from the side view of it to evaluate the changes in volume, shape, angle and position of the spikes (Figure 6.3).

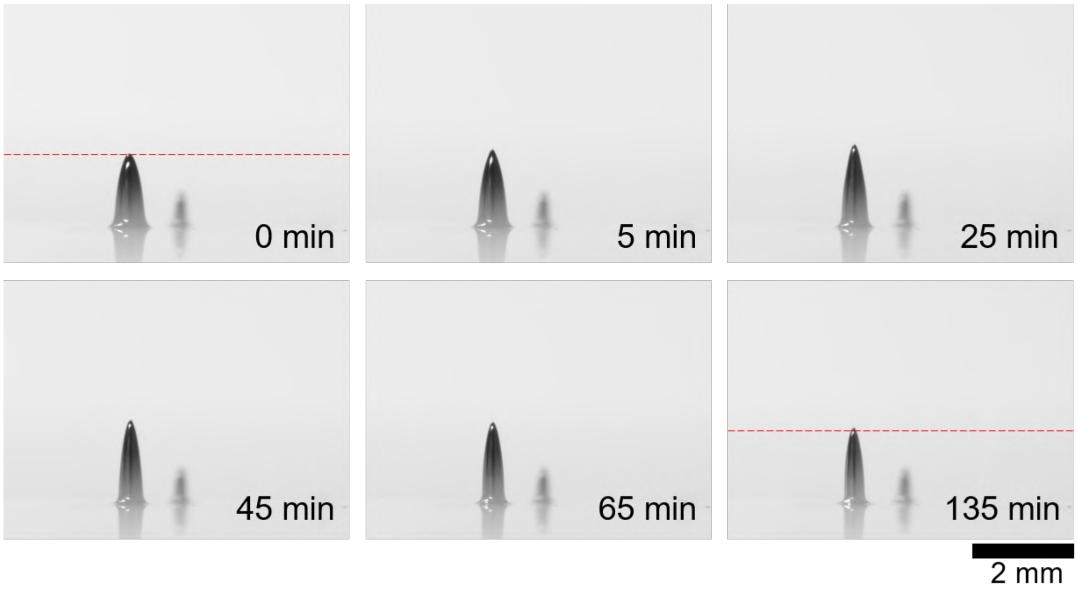


Figure 6.3: Gradual drying of a ferrofluid spike in room atmosphere. The profile images are taken throughout the drying process and red dash line shows the initial height of the spike in liquid phase.

By tracking the changes in height and width of the spikes, we observed two different regimes of drying. First, the spike height increases (the spike rises up). Decreasing the volume of the spike resulted in increasing the height since this resulted in increment of particles loading ratio in ferrofluid. Evaporation reduces the volume but the amount of magnetic particles are constant over time that results in stronger interaction with magnetic field. Therefore, the spike changes its shape to reach a thermodynamically stable state. Based on this observation it was concluded that the spike started to dry from the tip downwards to the bottom of it. This hypothesis was confirmed by removing the magnetic field in the middle of first drying regime and it resulted only solidification of the top part of spike (Figure 6.4).This drying pattern could be due to the fact that the spike is sharper at the tip, consequently the surface to volume ratio of it is higher and this results in evaporation of the solvent in higher ratio and consequently results in top to bottom drying. However, as seen in any classical sessile droplet evaporation would be dominant on the top part of the droplet as well[1]. Another explanation can be the self-assembly of iron oxide colloidal inside the spike that are more concentrated in the inner volume of it due to the dipole interaction between them.

In second regime, the overall volume of the spike from all directions started to reduce over time. The height of spike started to decrease in second regime. We assume that since the outer layer of the spike was mostly solidified in first regime, the inner volume of it dried in second regime.

To characterize the shape changes of a single spike, the height (L) and width of spike from two planes (the middle of it, W1, and the base of it, W2) were measured (Figure 6.5 A). Moreover, the effect of initial volume of spike on final shape changes of it was questioned by having three different size of spikes (0.3, 0.6 and 3 mm in height) that were dried under same conditions such as magnetic field strength and ambient air. Normalized height of the spikes (L(t)/L(0)) show that the spikes increase in height depending on its size, the increment of it for smaller spikes is higher compare to bigger ones (Figure 6.5 B). The peak of L was achieved at the end of first drying regime, but started to decrease in second

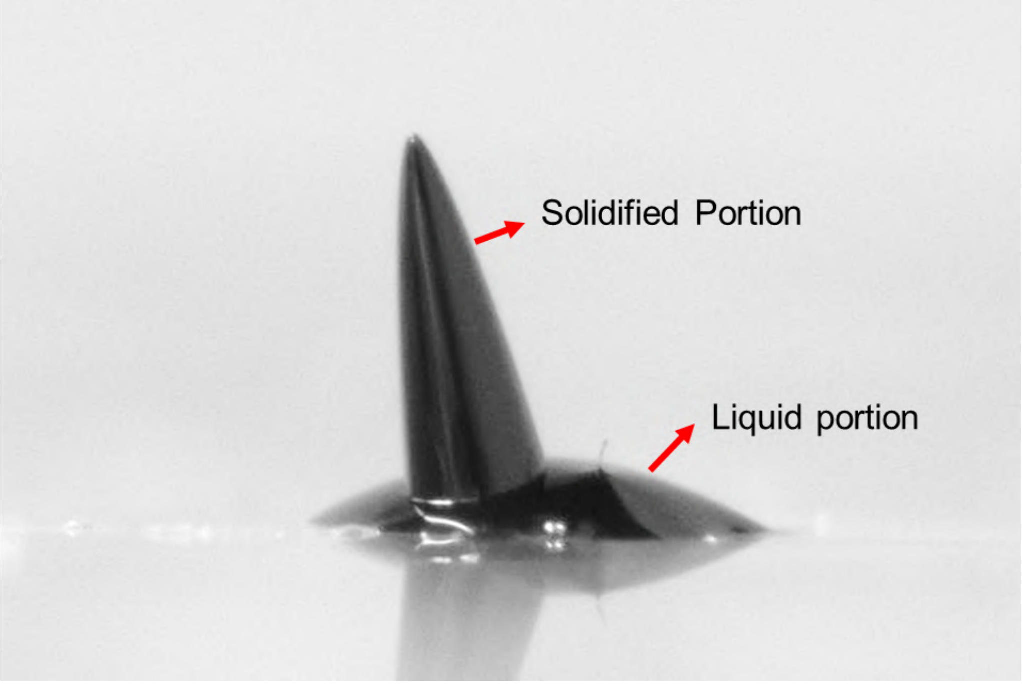


Figure 6.4: Semi-dried oil-based ferrofluid spike in room atmosphere. Magnetic field (the permanent magnet underneath of the substrate) was removed in the middle of first drying regime and the collapsed spike was imaged from side view.

drying regime nearly to its initial value (L(0)). The data also shows that drying time increases for bigger spikes that is due to higher volume to surface ratio in the case of bigger spikes. On the other hand, width values decreased with a logarithmic trend (Figure 6.5 C). The width values reduced nearly 35% of its initial values. By these measurements, we conclude that although the spikes diminish in volume and become slimmer, but they preserve their spike shape. Nevertheless, the height of spikes does not change considerably that is an important characteristic aspect of them.

Self-organization of spikes makes a regular pattern of them with defined space in between two single spikes. It is known that, spikes are analogous to dipole magnets which repel each other and get stabilized in certain distance

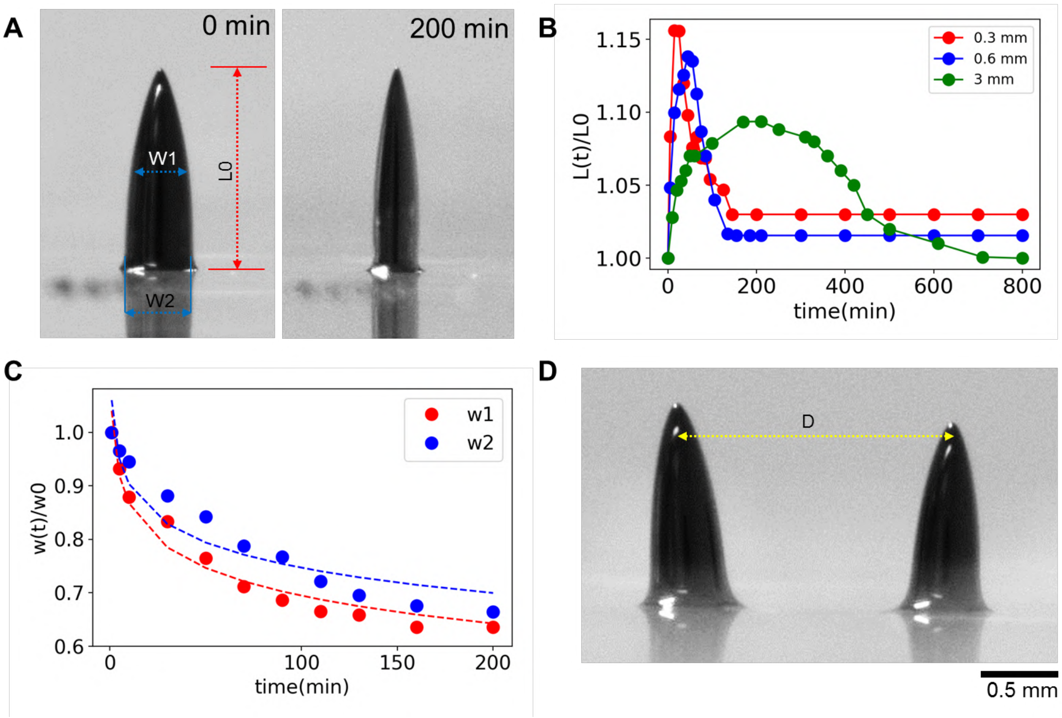


Figure 6.5: Shape characterization of the oil-based ferrofluid spike before and after being dried in room temperature. A) Shows side view pictures of a spike before and after complete drying of it, L0 refers to its initial height, W1 and W2 refer to body and basal width of the spike respectively. B) Plot of length measurements over time (L(t)) normalized by the initial length of the spike (L(0)) for three different spike lengths as L(0)=0.3, 0.6 and 3 mm. C) Plot of W1 and W2 throughout drying process for a spike with a length of 0.6 mm. D) Shows a side view of two spikes with a distance of D from center to center of spikes.

based on the profile of applied external magnetic field[11]. We also asked if the changes in spikes volume throughout drying process could affect the scale of interactions between the spikes and consequently the distance in between of them. Two spikes were formed with a certain distance as D from centre to centre of them (Figure 6.5 D). Dried form of these spikes showed that D does not change at all. This is important factor in order to preserve the initial pattern of liquid spikes in solidified form of it.

6.2.2 Alignment of the spikes

Ferrofluid spikes follow the field curvature lines resulting the alignment of them accordingly to the angle of magnetic field lines[8, 98]. The question arises weather the angle at which the spike is formed (in liquid phase) would be preserved throughout drying process or would undergo changes. To answer the question a magnet with a large surface area (20 x 30 mm^2) was used underneath a PMMA substrate and two spikes on top of the surface were formed. One of the spikes formed at the center of the magnet orthogonally to the surface and the other one formed closer to the edge of the magnet with a certain angle, θ , from the horizontal plane (Figure 6.6 A). Magnetic field lines were simulated at the plane wherein the spikes were formed (12 mm above the magnet) and it showed how the angle of spikes fit the filed lines. The spikes were left to dry at room temperature. The results showed that over time the angle stayed unchanged for both spikes (Figure 6.6 B, C) through the drying process. The angle of the spikes is an important parameter if the replicated spikes surface would be used as self-cleaning surfaces, in which the angle defines the pinning and self-guiding of liquid on a surface[31].

If the angle of magnetic field lines are changed by any mean, for example introducing a second magnet close enough to the first one, the angle of formed spikes can be controlled and adjusted. The alignment of spikes was studied in between two magnets attracting each other(Figure 6.7 A). Field lines of two magnets add to each other and makes new alignments depending on distance and position of two magnets (Figure 6.7 B). A zoomed area in between two attracting magnets demonstrated a high degree of alignment (Figure 6.7 C). As it was mentioned earlier since the angle of spikes stays unchanged throughout drying, similar to two magnet set-up, further engineering can be applied to acquire preferred

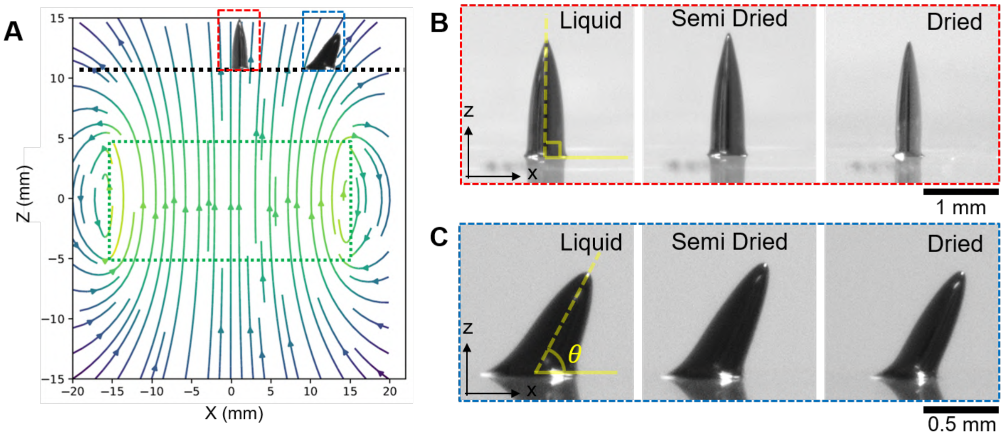


Figure 6.6: Tilted spikes. A) Magnetic field simulation of a rectangular cubic magnet (20 x 30 x 10 mm^3, xyz and with magnetization in z axis) to show the magnetic field lines at a plane 12 mm distance the surface of the magnet. B) Photographs of an orthogonal spike in sequence from left to right as liquid, semi-dried and fully dried C) Photographs of an tilted spike (θ = 65°) in sequence from left to right as liquid, semi-dried and fully dried

angles of dried spikes with a considerable degree of tunability.

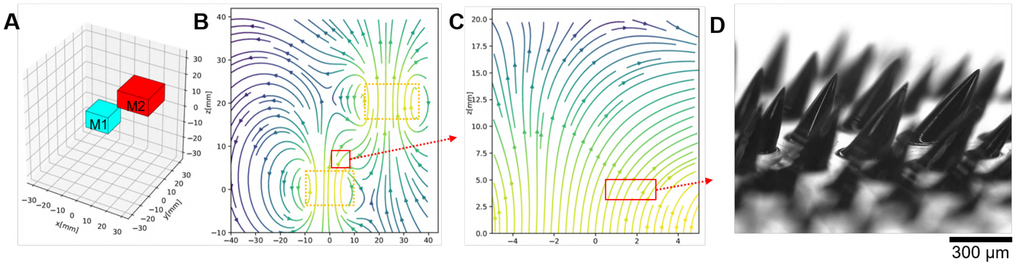


Figure 6.7: Adjusting the magnetic field curvature with the aid of a secondary magnet (attractive configuration). A) 3D demonstration of two magnets with opposite poles, blue one as primary and red one as secondary magnet. B) Visualizing the magnetic field lines in between two magnets attracting each other. C) A zoomed view above the surface of magnet, M1. D) Side-view picture of the formed tilted ferroflid spikes.

6.2.3 Molding of dried spikes on PDMS

In order to replicate dried spike pattern on PDMS, the spikes needs to show sufficient stability and attachment to the surface of PMMA substrate in order to keep them unchanged while curing of PDMS. However, curing PDMS at temperatures around 70 $^\circ C$ and this is parameter that needs to be considered about stability of dried ferrolfuid spikes. Although the sufficiency of mechanical stability of the spikes was proved by pouring PDMS solution on them, yet compression tests were done to understand the scale of the force necessary to break the dried spike in compression. Figure 6.8 A shows the snapshots of compression test before and after breaking. Part of the broken spike is attached to upper plate after breaking point. Three different spikes were tested and the results are shown in the graph. The maximum force was measured in the range of 1 to 1.5N that is applied at the tip of spike. These measurements conclude that the mechanical stability of the spikes is considerably high and the viscous polymeric solution would not affect their shape. Moreover, the compression tests show that the spikes undergo around 0.75 mm of compression before breaking point. This data implies that the structure of dried spikes allows certain degree of compressing deformation.
Moreover, to confirm the thermal stability dried spikes were heated up in an oven (70 °C) and no deformation was observed. As the result, pouring PDMS on spikes and processing it in an oven (in the limit of temperatures for curing PDMS) does not affect the physical characteristics of the spikes.

Before using ferrofluid for fabrication of a surface with spike shape pattern, the size of the spikes may be considered as well. Besides the shape and size of magnet, which directly influences the field gradient and curvature, deposition

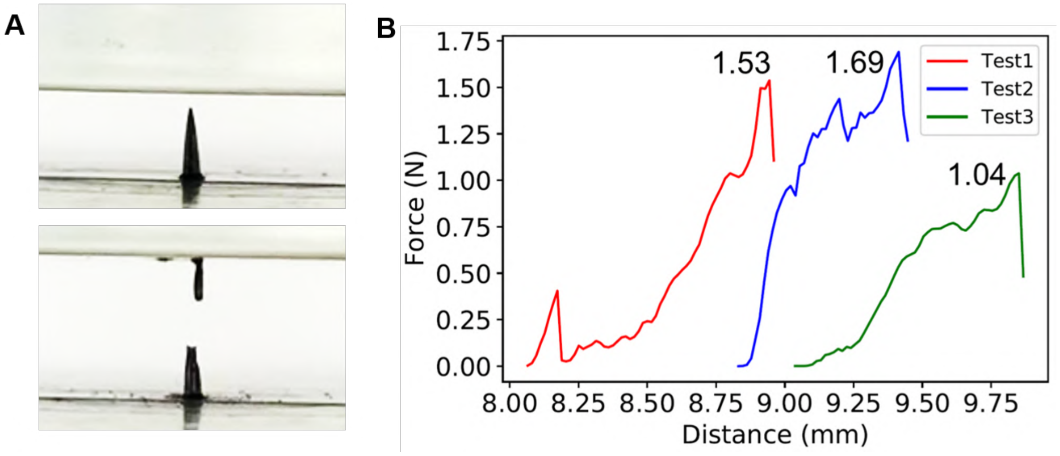


Figure 6.8: Compression tests on dried oil-besed ferrofluid spikes. A) The snapshots of compression test before and after breaking point of dried spike. B) Plots of measured force values in N in relation to vertical distance of the compression plate. The peak point is the breaking force.

of ferrofluid on the surface defines as well the size of formed spikes. Figure 6.9 compares two cases in which the volume of ferrofluid is kept same but in A it is spread widely on the surface and in B is less spread. Introducing the same magnetic field resulted in different size and pattern of spikes. Friction of the surface (the substrate on which the spikes are formed) plays an important role for dividing a continuous liquid phase to spikes pattern. In other words, friction on the surface of the substrate will favor formation of bigger spikes than smaller one[2,3]. In order to have smaller spikes, it is practical to spread the ferrolfuid in thinner layer. As the result, the spreading of ferrofluid and resulted size of the spikes can be adjusted beforehand drying of them to acquire desired pattern and size.

After characterization of the drying process, we evaluated the possibility of replicating the dried spike pattern by molding them with polymeric materials in order to create micro-structures on the polymer surface. A drop of ferrofluid

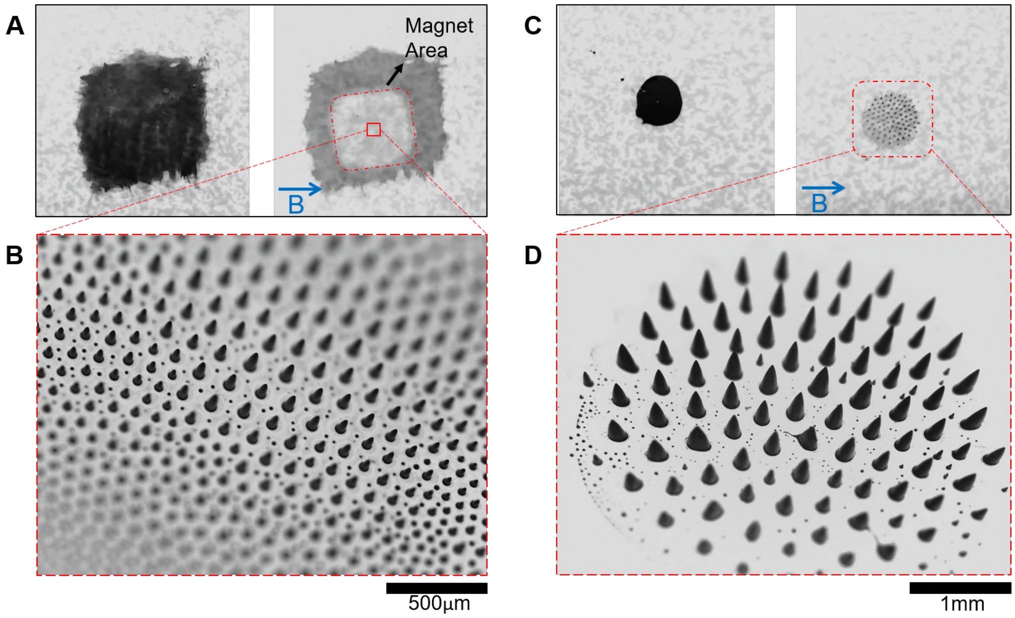


Figure 6.9: Effect of surface friction and spreading pattern of ferrofluid on size of formed spikes. A,B) shows a thin layer of ferrofluid spread manually on the glass surface before and after applied magnetic field and zoomed view shows the pattern and size of the spikes. B) Depicts formation of spikes from a ferrofluid droplet (pipetted) on glass surface.

was placed on a PMMA substrate and a permanent magnet was brought closer from bottom side of the substrate to form the spike pattern. Once the spikes formed and stabilized on PMMA surface, they were left to dry at room atmosphere. After complete drying of the spikes, the magnet was removed and ferrofluid spikes were used as a mold for replication. To replicate the pattern on PDMS, a mixture of PDMS with 10% of cross-linker was poured on ferrofluid mold and then was heated up to 70 $^{\circ}C$ for an hour to be cured. Afterwards, the PDMS replicate was peeled off from the mold (Figure 6.10 B, E) and it was characterized by optical imaging. As the result, a negative replica with spike shape cavities was obtained. Subsequently the PDMS slab containing the negative replica of the spike pattern was used to re-write the spikes pattern on PDMS. A second PDMS solution (with 10% cross-linker) was poured on negative replica and the spike pattern was made on PDMS (Figure 6.10 F).

The molding experiments with heat curable PDMS showed that the dried spikes pattern could be replicated either as positive or negative pattern on PDMS. However, as it was reported in literature for similar works, UV curable polymer could also be used [41, 31]. Using PDMS that is widely available and used polymer in research laboratories makes this work a bench-top technique with minimum equipment required to create a large variety of spike patterns on PDMS.

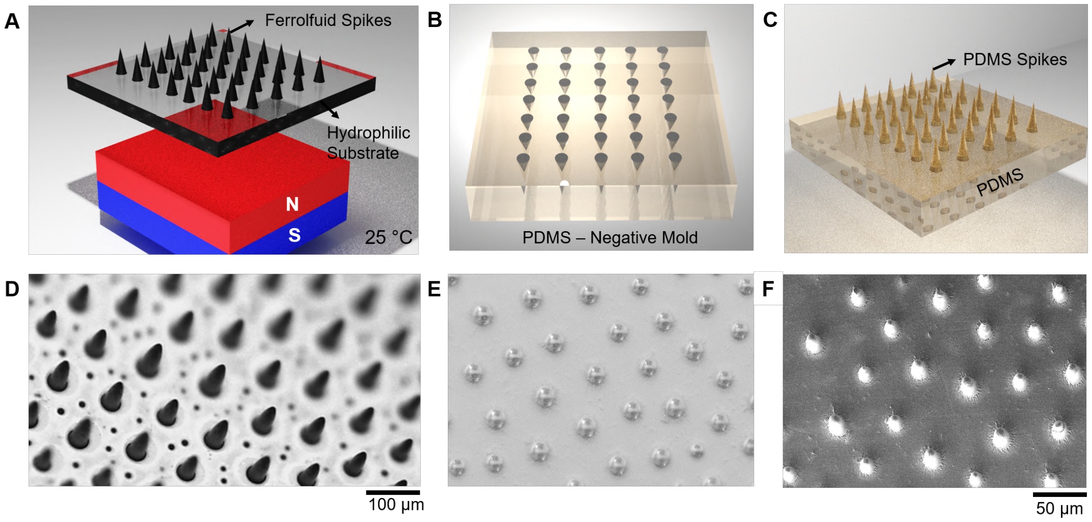


Figure 6.10: Schematics and experimental results of molding ferrofluid spikes pattern on polymeric material (PDMS). A) Shows the schematics of the setup for formation of spike pattern on PMMA substrate. B) Depicts schematics of negative replica. C) Shows schematics of PDMS spikes as positive pattern on the surface. D) Optical image of formed ferrofluid spikes. E) Top view image of spike shape cavities fabricated in PDMS. F) The SEM image of micron sized spikes replicated on PDMS.

6.3 Conclusion

In the presence of a magnetic field, ferrofluids form instabilities that are distributed over a surface creating a pattern. The geometric parameters of these patterns, such as the shape and size or inclination of the spikes, as well as the distance between them, are easily controllable because they depend on the magnitude and direction of the magnetic field to which they are exposed. Therefore, the number of possible spike patterns is infinite and covers a wide range, from a small number of millimeter-sized spike to a large number of micrometer-sized spikes. We observed that ferrofluid spikes dry at room temperature in the matter of few minutes. When ferrofluid dries, the spike turn from liquid to solid, preserving their size, shape, distance, and angle.

Controlling the topography of a polymeric material allows you to adjust its surface energy and control the interaction with other materials, which has myriad applications, such as wetting control. In this work we propose the use of dried ferrofluid peak patterns to modify the topography of PDMS. And we demonstrated that these patterns can be replicated in PDMS and in principle it would be possible to replicate it in other polymeric materials thanks to the fact that ferrofluid turned into a solid phase. In short, we present a very versatile, benchtop and easy-to-implement method for the manufacture of microstructures in polymeric materials. Moreover, the field lines caused by one magnet can be varied by placing a second magnet nearby. The field lines of both magnets are added together and new field lines are generated. Since ferrofluid peaks form in alignment with the magnetic field lines to which they are subjected, it would be possible to generate peaks with a wide variety of orientations.

6.4 Experimental Section/Methods

6.4.1 Material

EMG900 ferrofluid was purchased from Ferrotec USA Co. PDMS SYLGARD 170 kit was purchased from Farnell. 4 mm of thickness PMMA (purchased from PLEXIGLAS® Evonik Industries AG) was used as substrate. It was cut by CO2 laser machine (Universal® Laser Cutter System VLS 2.30, 30 watts) for desired dimensions in different experiments. The surface of the PMMA was cleaned by deionized (DI) water and dried prior to the experiments. Magnets and controlling of magnetic field: two permanent neodymium magnets with magnetization of 450 mT at the surface were used during the experiments (Purchased from firstformagnets Company). The sizes were as 10 mm square cubic and 20 mm width 30 mm length 10 mm height) rectangular cubic one in order to have wider surface area. Both have magnetization axis on the 10 mm side. Controlling of magnetic field strength was done by reducing the distance in between the surface of magnet and the deposited ferrofluid on PMMA surface. A standard Laboratory Scissor Lift Riser was used to move the magnet up and downwards.

6.4.2 Fabrication of dried spike patterns

Ferrofluid spikes were formed by introducing north or south pole of a magnet under the substrate. To mention, in general drying time depends on the size , density of spikes per unit surface area and the strength and dimensions of the magnet. In the case of smaller spikes, high surface area eases the drying and reduce the drying time. However, the initial distribution of ferrofluid before introducing the magnetic field defines the size of them and consequently the drying time (See Figure S5 Supporting Information).

6.4.3 Molding of ferrofluid spike pattern with PDMS

The ferrofluid spikes after getting dried on a PMMA substrate were positioned inside a frame (in order to confine the monomeric solution in a certain volume on dried spikes) made from PMMA. PDMS with 10% cross-linker solution was poured gently on the dried spikes. The setup was replaced in a vacuum chamber to degas the PDMS solution. It was observed that putting high negative pressure in order to degas the PDMS could lift the spikes from the substrate and to avoid it degassing was done smoothly. Afterwards degassing, the set-up was replaced inside the oven for one hour set to 70 °C. The cross-linked PDMS was removed by peeling off from the PMMA substrate and it was placed in DI water solution with commercial dish washer detergent was sonicated for one hour in order to wash out the ferrofluid residual from the mold. The negative replica was washed with DI water at the end and dried by air stream.

6.4.4 Fabrication of PDMS spikes pattern by using the negative replica

The negative replica was used as a mold to fabricate PDMS spikes. To prevent attaching of PDMS to the negative replica, a liquid lubricant (commercial Vaseline) was used on the negative replica (to coat the cavities made by spike pattern). It was replaced in a frame and then PDMS with 10% cross-linker was poured on it and it was cured for an hour in the oven (70 °C). After curing step the PDMS was gently peeled off from negative replica.

6.4.5 Confinement of ferrofluid spikes in between two permanent magnets

Two small set-ups were fabricated. The first one was printed by Forumlab 3D printer model Form 1+. It was designed to hold two magnets and make a distance in between of them. The set-up has adjusting mechanism in order to arrange the distance in between to magnets to control the tilting angle of the spikes. The idea behind the set-up is to prevent the two magnets crashing and any set-up that can does this function can be used.

6.4.6 Simulations of the magnetic field

The simulations were done by the open source Magpylib Python library[68].

CHAPTER 7

CONCLUSIONS AND FUTURE PROSPECTIVE

This thesis aimed to develop new methodologies using oil-based ferrofluid for digital microfluidics (programmable droplet manipulation on open surfaces). Three experimental works were developed and showed applicability of oil-based ferrofluid either in active or passive approaches. tSPRing and ferrofluid channel were considered as active approaches and micro-structuring of polymeric surfaces with dried ferrofluid spikes as a passive approach. The main conclusions from the mentioned works are as below:

Water droplets, within a wide range of volume, move in a programmable and controllable manner with tSPRing method. Spike shape instabilities of ferrofluid self-organize as a cupcake assembly around the water droplet and moving the magnet underneath manipulates the droplet on the surface. The ringed droplets show repulsion forces between the surrounding spikes and other ringed droplets, therefore a stable array of water droplets can be formed by using tSPRing method. Likewise a droplet on an upside surface, pendant droplets on a upside-down surface (against the gravity) can be manipulated robustly without falling from the surface by tSPRing approach.

An oil-based liquid channel can form on a surface by using the oil-based ferrofluid and a polymer- bonded magnet shaped as a channel. The formed liquid channel is switchable and dynamic, which means it can be manipulated on the surface by moving the magnet. The channel can be filled with water or multiple droplets can be introduced inside it manipulated. The multiple droplets can be mixed inside the liquid channel in a controllable and programmable manner.

A polymeric surface (PDMS) with spike-shape patterning can be fabricated by molding of ferrofluid instabilities. The regular spike pattern seen in liquid phase ferrofluid can be replicated on PDMS by drying the spikes and using solidified spikes as a mold. This approach introduce a bench-top technique to microstructure a polymeric surface in order to manipulate the interaction of droplets with the surface.

The overall conclusion of presented works summarises that the ferrofluid has great potential to be used in digital microfluidics. All three experimental chapters presented in this thesis are novel works that were not reported in literature and were proven to be used without the need of any complex tool or knowledge. Therefore, throughout demonstrated methodologies, this work offers applicable approaches of using ferrofluid for digital microfluidics purposes to be used by multidisciplinary researchers or engineers.

The impact of presented works can be expected either in applied or fundamental studies for futuristic works. Therefore, for applied studies:

- The manipulation of water droplets by tSPRing and liquid channel can be taken further to fabricate automatic manipulation device by means of proper engineering.
- The soft matter interaction of ferrofluid with water droplets in small volumes, notably in the case of tSPRing, can be investigated as a micro environment for bio-reactor applications.
- The pendent droplet manipulation by tSPRing is a novel observation that can open an avenue in upside-down droplet manipulation in which gravity can serve for manipulation of constituents inside the pendant droplet.

- By smart engineering the spikes pattern can be fabricate large surface area and therefore be applied in industrial scales.

and in the case of fundamental studies:

- liquid-liquid interaction of ferrofluid instabilities with polar liquids than water can be studied.
- The interfacial interaction of liquids such as blood can be investigated in the case of tSPRing. Blood is a liquid containing many different constituents that may show certain interaction with ferrofluid.

are foreseen to provide knowledge and offer numerous possible applications.

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BIOGRAPHICAL SKETCH

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Publications/Dissertations related to thesis work

- Nasirimarekani, V.; Benito-Lopez, F.; Basabe-Desmonts, L. Tunable Superparamagnetic Ring (tSPRing) for Droplet Manipulation. Advanced Functional Materials 2021, 2100178. (Cover Article)
- Nasirimarekani, V.; Benito-Lopez, F.; Basabe-Desmonts, L. Dried Ferrofluid Spikes – Stable Micron-sized Cone-shape Pillars for Molding Applications. (under preparation)
- Vahid Nasirimarekani; Benito-Lopez, F.; Basabe-Desmonts, L. "Open surface droplet manipulation and mixing by ferrofluid instabilities", MicroTAS 2020 - 24th International Conference on Miniaturized Systems for Chemistry and Life Sciences, 2020, pp. 132-133. (Poster Presentation)
- Vahid Nasirimarekani; Benito-Lopez, F.; Basabe-Desmonts, L. "TUNABLE SUPERPARAMAGNETIC RING (TSPRING) FOR DROPLET MANIPULATION", MicroTAS 2021 - 25th International Conference on Miniaturized Systems for Chemistry and Life Sciences, 2020, pp. 132-133. (Oral Presentation)
- Vahid Nasirimarekani, Peter Dunne, Bernard Doudin, F. Benito-Lopez, L. Basabe-Desmonts, "Benchtop Ferrofluid Lithography of Micron Size Cone-shape Pillars", International Conference on Magnetic Fluids – ICMF 2019, Paris, France, 2019. (Poster Presentation)

Awards

- Best Poster Presentation, awarded by Sorbonne University at International Conference on Magnetic Fluids – ICMF 2019, Paris, France, 2019. (Certificate and cash prize)