



Interface-driven soft matter systems: from 2D particle crystallization and light-responsive assemblies to magnet-guided fluid transport

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Jacopo VIALETTA. Interface-driven soft matter systems: from 2D particle crystallization and light-responsive assemblies to magnet-guided fluid transport. Theoretical and/or physical chemistry. Sorbonne Université, 2018. English. NNT : 2018SORUS358 . tel-02865514

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Sorbonne Université

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Interface-driven soft matter systems: from 2D particle crystallization and light-responsive assemblies to magnet- guided fluid transport

Par Jacopo VIALETTO

Thèse de doctorat de Chimie

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Soutenance publique prévue pour le 24 octobre 2018

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*Solo dopo aver conosciuto la superficie delle cose,- conclude - ci si può spingere a cercare
quel che c'è sotto. Ma la superficie delle cose è inesauribile.*
— I. Calvino, *Palomar*

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Preface and Outlook

Soft materials are fascinating structures, subject of interest in the scientific community for understanding their, sometimes surprising, behaviours, and, on more general terms, for the preparation of both commonly used and innovative materials. Throughout this thesis, I am interested in soft matter systems to study new phenomena and behaviours, such as actuation and organization of small objects, for possible future applications as novel materials with responsive properties. More precisely, the objective is two-fold: i) identifying new triggers for useful operations, and ii) exploring emerging properties in stimulus-driven systems.

Soft matter is a field dealing with soft materials, by which we mean materials that are flexible, readily deformable and modifiable by a small energy input of the order of the thermal energy of the system. The father of the field is probably Pierre-Gilles de Gennes, Nobel laureate in physics in 1991, “for discovering that methods developed for studying order phenomena in simple systems can be generalized to more complex forms of matter, in particular to liquid crystals and polymers”. This statement introduces the second characteristic of a soft material after flexibility, which is complexity. Their complexity originates from the concurring interactions among the constituting components, interactions all of strength comparable to thermal energy. Since such interactions are weak, these types of materials are macroscopically “soft” – unlike metals for examples – easily modifiable by small variations in the environment. A direct consequence are their non-intuitive behaviours and highly adaptive properties upon external stimulation. Interestingly, on the other hand such materials can be “hard” too, that is resistant to specific variations in the surrounding that do not affect their structure. One example, reported by de Gennes in his Nobel lecture*, is indicative: the sap from the hevea tree is a liquid that, when in contact with the oxygen from the air, builds few bridges between the polymer chains switching from liquid to a hard network structure, now resistant to tension, a rubber. A mild chemical reaction brings about a drastic change in mechanical properties. Polymers are one of the constituting components of soft matter systems; other building blocks are liquid crystals, colloids, surfactants and particles. Bridging between the microscopic world of molecules and the macroscopic world of what surrounds us, those building blocks belong to the mesoscopic world, and its peculiar physics. In this thesis I will focus mainly on solid particles (of micro or nano-size) to build and study various kind of systems.

*P.-G. de Gennes, *Nobel Lecture* **1991**, 1–7.

Interesting and unpredictable behaviours often arise upon assembly of the building blocks into hierarchical, complex structures. This introduces the second important argument treated in the thesis, which is self-assembly: the autonomous organization of components into patterns or structures*. The units can be viewed as mesoscopic Lego bricks; the scientist working to self-assemble them aims at finding the proper interactions and conditions so that all components of the system (thousands or millions) assemble together in an organized fashion, without having to add one piece at a time. The building blocks of soft matter can also be seen as the missing link between the endless number of small molecules, and the complex functions of, say, a living cell (which is a typical example of a self-assembled system). What makes biological materials – but also, to some extent, man-made ones – so complex and fascinating is that the constituting components join into larger structures, each of them with a precise identity and function. It is the controlled assembly of such building blocks that enables the emergence of novel properties that are not present in the original molecules or soft-matter units. A sub-field of self-assembly is dissipative self-assembly, the creation of systems that require a constant supply of energy to persist in a far-from-equilibrium state†, a concept that will be also explored within the thesis.

A third recurring component throughout the thesis is the fluid interface. A fluid interface is the separation region between two liquids, or a gas and a liquid, and own several physical properties (discontinuities in concentration, density, refractive index, surface tension, etc.). They are involved in countless processes in physics, chemistry and biology. They are constitutive components of several foods, milk and derivatives or mayonnaise are the most common examples, determining their taste as well as their texture. The compartmentalization in our cells is characterized by the presence of fluid interfaces, controlled by our organism in order to guarantee the correct exchange of ions and molecules. In soft matter fluid interfaces are commonly used as templates to self-assemble particles, or other soft matter units, because they are intrinsically soft. The weak forces governing self-assembly at a liquid interface generate adaptable and reconfigurable structures, with the possibility to repair errors during the structure formation, and to produce devices responsive to external stimuli. The particles will not clump together randomly; instead they will rearrange to find the structure that is a minimum in the energy space of the system. On the other hand, fluid interfaces are exploited to actuate floating objects, moving them on-demand, thanks to their peculiar properties such as interfacial flows or deformation.

In this thesis we are interested in novel phenomena and actuating principles involving particles, self-assembly and fluid interfaces. With the long-term goal that these approaches should be robust and easy to use in a variety of applications, I am looking for new yet simple methods where neither complicated chemical modification nor use of complex devices is necessary. The PhD project is divided into three main parts, in which internal (chemical

*G. M. Whitesides, *Science* **2002**, *295*, 2418–2421.

†E. Mattia, S. Otto, *Nat. Nanotechnol.* **2015**, *10*, 111–119.

composition) or external (magnetic or light stimulation) triggers are employed to control either the organization (structure) or the motion (dynamics) of various soft-matter systems (drops, liquid marbles, particles) at the air/water interface. On one hand, the focus is on the adsorption and (self)organization of colloids (small solid particles) at the interfacial boundary between air and water, where colloids exhibit a number of interesting features not found in the bulk. Both static systems, in which particles organization is dictated by the chemical composition of the liquid mixture, and dynamic systems, where light stimulation is used to tune responsive particles systems, are studied. On the other hand, a novel magnetic actuation method is proposed for the controlled actuation of non-magnetic droplets floating at an air/liquid interface, exploiting the “softness” of the liquid surface.

This work lies in the domain of basic science, not aiming at implementing ready-to-use applications, but trying to discover, study and understand something new. In more literary words*, we can compare the world’s mysteries – and, perhaps, future scientific discoveries – to unknown tricks such as a rabbit pulled out of a hat by a magician. The rabbit can be compared to the whole universe; we who live here are microscopic insects existing deep down in the rabbit’s fur. To look for a new discovery is like trying to climb up the fine hairs of the fur in order to stare right into the magician’s eyes, instead of snuggle down comfortably. You will not know what you are going to see before climbing the last hair. This somehow summarizes the spirit of our research.

*This paragraph is rephrased from the beautiful book *Sophie’s world* by Jostein Gaarder, where the microscopic insects trying to climb up the rabbit’s fur are philosophers moved by their sense of wonder, and willing to answer the questions of life. I believe this metaphor can be somehow applied to scientists too; at the end, throughout history the difference between the two communities is not very pronounced.

Thesis Outline

The outline of the thesis is the following. The thesis is divided into three parts: **Part I** particles at the air/water interface, **Part II** dynamic photocontrol of particles organization at the air/water interface, **Part III** magnetic actuation using deformable liquid interfaces. Each part is composed of three chapters; the first one is bibliographic, introducing each specific subject, summarizing the main scientific literature and emphasizing advances and challenges; the two following chapters describe the results I obtained throughout my PhD thesis, with a discussion on the main findings. Specifically, **Chapter 2** introduces a novel method that I developed to adsorb colloidal particles at an air/water interface in a controlled manner, by means of adding exceptionally small amount of surfactant. The method is used both to study the characteristics required to the mixture for spontaneously adsorb particles from the bulk solution to the fluid interface, and to successively control the organization of the adsorbed particles into various two-dimensional (2D) structures (*i.e.* amorphous aggregates, crystals or gels). In **Chapter 3** I explore the breadth of applicability of the method, either by using particles having different sizes and surface properties, or by replacing surfactants with various salts. The ultimate focus is to obtain macroscopic 2D crystals composed of nanoparticles of different characteristics (shapes, chemical composition, etc.).

After understanding the properties of our system, as a step forward I devised two different methods (reported in **Chapters 5** and **6**) to implement precise, contactless and fast control of the organization of the adsorbed particles, using light as external stimulation. By this means, I could switch from static systems to dynamic, responsive, ones. To our knowledge, this is the first time that light is used to control the organization of large ensembles of particles at a fluid interface. In **Chapter 5** light-absorbing particles are employed to build reconfigurable 2D crystals; starting from ordered structures, I show how to tune particle-particle spacing in 2D crystals, and how to kinetically control melting of the system, as well as subsequent re-crystallization upon stimulus removal. In **Chapter 6**, photosensitive surfactant and common particles are mixed to obtain a, surprising, dissipative system. The particles organization is amorphous at rest, while arranges in an ordered fashion upon light stimulation. Experiments show that such 2D crystals are an example of dissipative out-of-equilibrium structures, which can be maintained only if energy, throughout light stimulation, is supplied to the system.

During my PhD work I was interested also by other phenomena involving soft matter systems at fluid interfaces. Specifically, we developed a novel magnetic actuation method of drops and liquid marbles using a deformable paramagnetic liquid substrate, which will be the subject of **Chapter 9**. Not relying on magnetosensitive particles added in the liquids, which is a commonly developed strategy, it consists instead in using a paramagnetic liquid as a substrate and exploits the deformation of the free air/water interface induced by an approaching magnet as the driving force for the motion of non-magnetic drops. **Chapter**

8 reports preliminary studies on the surface tension variation of paramagnetic and diamagnetic liquids in homogeneous magnetic fields; an information that is required for a precise understanding of the magnetic actuation mechanism.

This thesis was possible thanks to a close collaboration with several other people; in particular, regarding the experimental findings reported here, I am grateful to Manos Anyfantakis for preliminary results on particles/surfactant mixtures and for particle contact angle measurements at the air/water interface (Chapter 2), Masayuki Hayakawa for building the setup to measure the surface tension of drops in a homogeneous magnetic field (Chapter 8), and Nikita Kavokine for writing the analytical model in Chapter 9.

Part I

Particles at the air/water interface

The first part of the thesis is dedicated to the study of micro- (and nano-) particles at the air/water interface. It is now well established that solid particles adsorb on a liquid surface, stabilizing it and creating novel, interesting materials that expand over two dimensions (the liquid surface area, that could be μm to dm), with the third dimension being only one particle diameter (nm to μm). The liquid interface acts as a template for the design of soft materials having various geometries (from plane to highly curved), that are adaptive and with the possibility to repair errors during the structure formation. As a consequence, highly ordered long-range structures can be formed. Two main questions will be addressed in this first part: how to adsorb particles dispersed in the bulk phase at liquid interfaces (in particular air/water), and how to direct their subsequent collective arrangement into predetermined structures, being it amorphous, crystals or gels.

The **1st Chapter** reviews recent and past literature about particles at fluid interfaces (either at the boundary between immiscible liquids, or between a liquid and air). Considering the vastness of the topic, only few points will be addressed in order to introduce the main findings that are related to my experiments, which will be described successively in Chapters 2 and 3. The main points concern: i) interactions between a particle and the liquid interface, as well as interactions among adsorbed particles; ii) applications of particle-covered liquid interfaces; and iii) main methods used to disperse particles on fluid surfaces.

Chapter 2 reports our studies on mixtures of negatively charged colloidal microparticles and oppositely charged surfactant. We show for the first time that an ultra-low amount of conventional surfactant, typically three orders of magnitude smaller than the critical micellar concentration, induces the adsorption of various types of particles (polystyrene, silica) at the air/water interface. This phenomenon is exploited for the formation of two-dimensional colloidal assemblies with different structures, depending on surfactant and particle concentrations.

In **Chapter 3** I will expand the applicability of our method, on one hand by varying size, surface and bulk chemistry of the particles used, on the other hand looking for surfactant-free approaches. I will show how to control the adsorption and organization of nanoparticles with the goal to build polycrystalline assemblies showing intense structural colouration. In addition, I will introduce preliminary results on surfactant-free approaches, by using salts or positively charged particles, opening new directions for further research.

Ultimately, these results pave the way to prepare, in a direct, practical and well controlled manner, two-dimensional ordered colloidal assemblies on a liquid surface. The findings presented here will also be the starting point of the studies described in part two, where an external optical stimulation for the control over particles assemblies will be introduced.

Particles at fluid interfaces: properties, preparation and applications

1.1 Abstract

In this bibliographic chapter, properties and applications of particle-covered liquid interfaces are discussed, together with techniques for their preparation, *i.e.*, how to accumulate and organize particles at a fluid interface. It starts with a brief introduction on liquid interfaces, and how colloids affect their stability; successively, interactions between a particle and the liquid interface will be discussed, and the existence of an adsorption barrier for particles coming from the bulk liquid to the surface will be introduced. The last part of this section presents the most usual attractive and repulsive interactions between adsorbed colloids, which ultimately dictate their two-dimensional organization. The following section is devoted to the uses of particles-covered liquid interfaces: from industrial applications to the design and construction of novel devices, including some more fundamental studies on their use as model systems for the study of phase transitions. Finally, the two main methods currently used to disperse particles at a fluid interface will be discussed, namely: spreading them using a volatile solvent directly on the interface, or controlling their adsorption from the bulk liquid. Main advantaged and drawbacks will be evidenced.

1.2 Liquids and interfaces

When two non-miscible fluids touch each other, or simply when a liquid comes in contact with air or with a solid substrate, an interface is created between the two fluids or between the liquid and air or the substrate. Such interface is not simply a boundary between two media; instead it has some remarkably interesting and useful properties on its own.

A liquid is a condensed phase where the constituting molecules interact between each other through attraction forces comparable or higher than the thermal agitation. In such a state, molecules have both cohesion forces and a high degree of freedom that prevents the formation of frozen, solid structures. While a molecule in the bulk liquid will have strong cohesion with its neighbours, another molecule on the surface will experience less cohesion due to the decrease of neighbouring molecules. It is due to this decrease in the number of attractive interactions at the surface, and consequent decrease in cohesive energy, that the liquid will adjust its shape attempting to reduce its surface over volume ratio. And it becomes obvious that the system will need energy to extend its surface area, in order to pay off the loss of internal cohesive forces. For those reasons a liquid surface is characterized by a surface tension (when in contact with air, while it is called interfacial tension if the boundary is between two liquids or a liquid and a solid), that is «the free energy cost of increasing the surface area of the system^[1]».

The higher the cohesive forces between molecules of the liquid, the higher the energy needed to increase the surface area, therefore the higher its surface tension. Water, whose molecules interact through strong hydrogen bonding, will have a high surface tension value ($\gamma \approx 72 \text{ mN/m}$); while for most oils, that are held together through van der Waals interactions, the surface tension is much lower ($\gamma \approx 20 \text{ mN/m}$). In everyday life this explains why water spilled on a pan will form drops on the surface, while oil, due to the lower surface tension that doesn't hold the drop shapes, will tend to spread in a thin film (Figure 1.1A). Since the surface tension precludes the liquid to increase its surface area, it can be viewed as a force too: a force that act to decrease the interface area and to prevent its rupture. Insects walking on water exploit this phenomenon (an example is reported in Figure 1.1B); the surface tension of a pond can sustain the animal if its weight is low enough. However if the pond is polluted with surfactants – molecules that lower the surface tension of the liquid interface where they adsorb – the insect will sink due to the decrease of the surface force, not able to overcome its weight any more.^[2]

1.3 Particles at interfaces: scientific background

1.3.1 Particles (and surfactants) as surface stabilizers

We saw that high energy is associated to the formation of air/liquid and liquid/liquid interfaces. Therefore creating bubbles in a pure water solution, by increasing the total surface

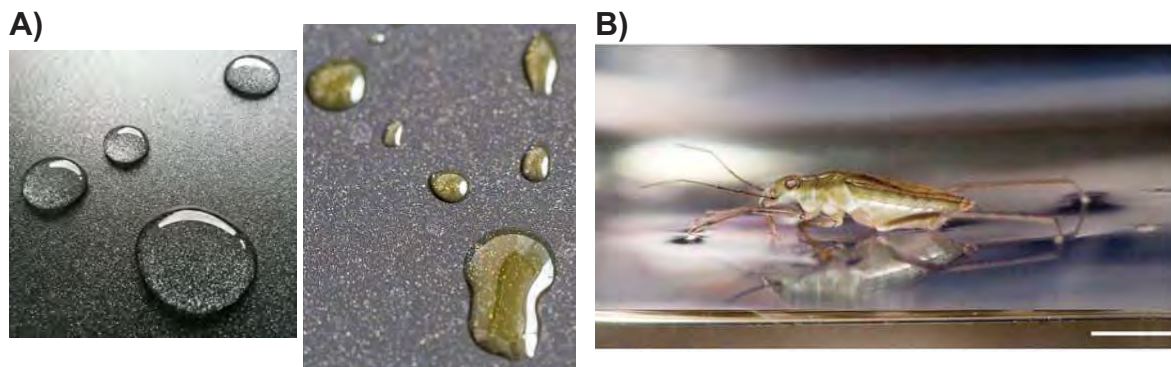


Figure 1.1: Surface tension dictates liquid surface deformability and strength. A) Water and oil drops on a surface have different shapes, depending on the cohesive forces between molecules in the liquid, and interaction with the solid underneath. B) A water treader *Mesovelia*, held on top of the liquid surface by surface tension that overcomes its weight.^[3] Scale bar: 3 mm.

area, gives a system that is in a higher energy state. Such system will seek to reach an equilibrium in a lower energy state, and the bubbles will quickly brake. A common way to support the bubbles is to add surfactants: lowering the surface tension, together with other reasons (*e.g.* electrostatics), stabilize the system decreasing its energy. Colloidal (solid) particles of nano or micron size can act as surface stabilizers too*. Under the word colloid are included a great variety of objects, not necessarily solids: from the small fatty droplets in milk, to the tiny grains of sand and clay in muddy water. The common point of colloidal dispersions is the presence of a medium and of small objects dispersed in it. Both medium and objects can be gaseous, liquids or solids; the only combination that cannot be found are gas-in-gas systems. According to the IUPAC definition, a colloidal system «refers to a state of subdivision, implying that the molecules or polymolecular particles dispersed in a medium have at least in one direction a dimension roughly between 1 nm and 1 μm , or that in a system discontinuities are found at distances of that order^[4]».

The use of solid particles to stabilize interfaces have been first reported by Ramsden in 1903 and later, in 1907, by Pickering,^[5] from whom the name Pickering foams and emulsions (respectively for air/liquid and liquid/liquid interfaces) comes from. An example of Pickering emulsion formation is reported in Figure 1.2A. As extensively reviewed,^[6–8] the adsorption of particles at a liquid interface has some similarities with common surfactants, and many differences.

A typical surfactant molecule is amphiphilic: it is composed of a hydrophilic part (being anionic, cationic or neutral) and a hydrophobic one. The hydrophilic moiety will prefer contacts with water while the hydrophobic one no; as a consequence the molecules will tend to accumulate at the interface with one part hydrated by water and the other in air or solvated by the second liquid. Moreover, at a given surfactant composition and concentration, those

*The word “colloid” comes from the ancient Greek words $\kappa\acute{o}\lambda\lambda\alpha$ (“glue”) and $-\epsilon\tilde{\iota}\delta\omicron\varsigma$ (“resembling”) and has been used the first time in 1861 by the chemist Thomas Graham, although they have been first discovered by the toxicologist Francesco Selmi.

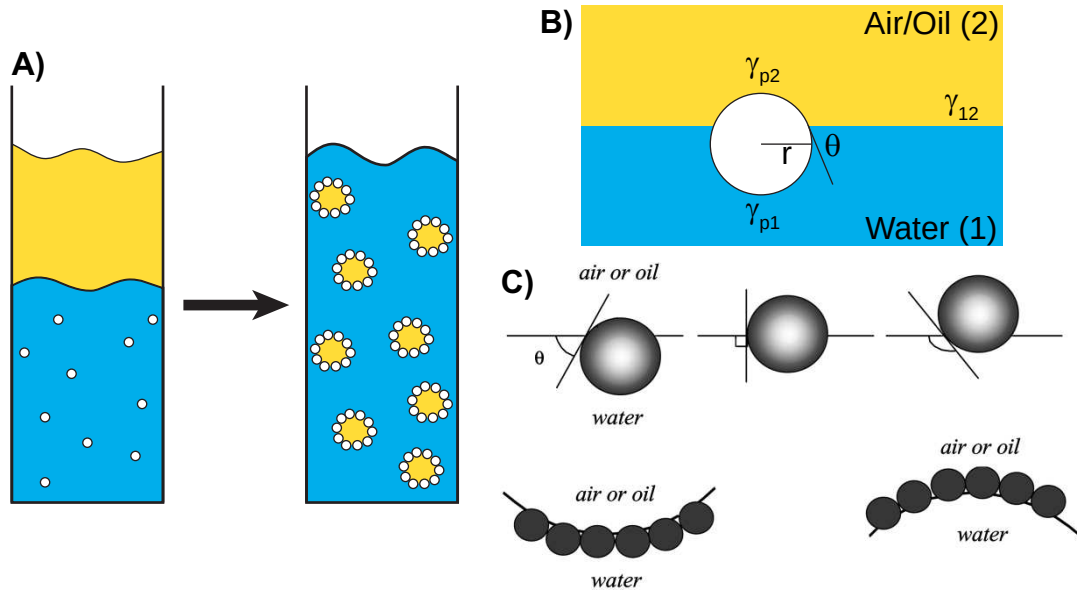


Figure 1.2: *Particles as surface stabilizers. A) Example of an emulsification process. A bifasic system composed of oil and water with properly chosen particles dispersed in it is shaken or mixed. As a result the particles wrap the oil drops stabilizing them in the water phase, creating a Pickering emulsion. B) Schematic of the positioning of a spherical, smooth, particle on a planar liquid interface (where liquid(2) can be air or oil, liquid(1) is water). γ_{12} is the liquid-liquid interfacial tension, γ_{p2} the particle-liquid(2) interaction, γ_{p1} the particle-liquid(1) interaction, r the particle radius and θ its contact angle measured through the water phase. C) Top: particle at a liquid interface having $\theta < 90^\circ$ (left), $\theta = 90^\circ$ (centre) and $\theta > 90^\circ$ (right). Bottom: for $\theta < 90^\circ$, particle-stabilised aqueous foams or emulsions may form (left); while for $\theta > 90^\circ$, particle-stabilised aerosols or emulsions may form. Image from ref.^[6]*

molecules can aggregate in the bulk liquid forming micelles and other interesting structures, such as vesicles and bilayers, in cooperative processes.^[9]

Particles normally used to stabilize foams and emulsions, on the contrary, are isotropic and with a homogeneous surface. An exception are Janus particles, particles with surface heterogeneities, that can be amphiphilic; but this is not a requirement for surface stabilization. In addition, particles do not have the tendency to cooperatively aggregate in complex structures in the bulk liquid solution. Their efficiency in stabilizing liquid interfaces arises from thermodynamic considerations – the gain in energy of the system upon particles adsorption to the interface – not due to amphiphilicity, but because of their wetting properties. Wetting refers to the study of how a liquid deposited on a solid, or liquid, surface spreads out; it depends on the balance between cohesive forces within the liquid, and adhesive forces with the substrate.

Considering two liquids (1 and 2) in contact, they will have an interfacial area with an associated interfacial tension γ_{12} . A particle coming from the bulk of one of the two liquids piercing the liquid interface will create a new particle-liquid(2) surface area of interaction (γ_{p2}) that will replace the former particle-liquid(1) interface (γ_{p1}), but, most important, will reduce the total contact area between the two fluids (see Figure 1.2B for a sketch of a particle

1. PARTICLES AT FLUID INTERFACES: PROPERTIES, PREPARATION AND APPLICATIONS

adsorbed at a liquid interface). Since the energy of the liquid interface is γ_{12} times the area, this “hole” will decrease its energy. The area of the hole will depend on where the particle will place itself with respect to the interface, and this is quantified in terms of the particle contact angle (θ , or particle wettability). For particles with radius r that are small enough to neglect the effect of gravity (r typically lower than few microns), the gain in energy E upon particle adsorption can be quantified as:

$$E = \pi r^2 \gamma_{12} (1 \pm \cos\theta)^2 \quad (1.1)$$

where the sign depends on which liquid the particle comes from. The extent of the interactions γ_{p2} and γ_{p1} are important as well; following Young’s law, they are included in the contact angle value at equilibrium:

$$\cos\theta = (\gamma_{p1} - \gamma_{p2})/\gamma_{12} \quad (1.2)$$

defining it. The contact angle is defined if $|\gamma_{p1} - \gamma_{p2}| < \gamma_{12}$. In other words, the particle will pierce the liquid surface reaching a given contact angle if the interaction energy between the particle and the fluid with higher surface energy is smaller than the decrease in free energy associated with reducing the surface area of the two liquids. For contact angles measured in the water phase, if the value is lower than 90° the particle will stay immersed more in water (as in Figure 1.2B), while if θ is higher than 90° it will stay more in the other phase (Figure 1.2C).

Putting numbers into equation (1.1) shows that, for a particle with $r = 50$ nm at the air/water interface ($\gamma_{12} = 72$ mN/m), the higher energy required to remove such particle is reached when $\theta = 90^\circ$ (particle equally immersed in both phases), and such value is equal to 2750 times $k_B T$. For contact angle values that are not extremely low (close to 0°) or high (180°), an energy value E much higher than the thermal energy $k_B T$ means that a particle, once adsorbed to the liquid interface, is almost irreversibly attached there. This very strong, and in many cases irreversible, adsorption is fundamental for understanding the properties of particles at liquid interfaces, as well as for practical application; and it is in strong contrast with the behaviour of adsorbed surfactant molecules, which have a quite fast dynamic of exchange between the surface and the bulk solution because their energy of adsorption is close to $k_B T$.

While thermodynamics explain why particles are so strongly held at liquid interfaces, and why ultimately their adsorption is energetically favourable for the system, the process of adsorption is somewhat more complex.

1.3.1.1 Particle-interface interactions

It is experimentally established^[10] that it can exist an adsorption barrier that has to be overcome to quantitatively adsorb particles from bulk solution to a liquid interface; but the correct

conditions for particles adsorption are not properly understood yet.^[11] The eventual adsorption barrier that a colloid has to overcome can arise from several contributing components, including van der Waals and electrostatic interactions.

A particle dispersed in a phase 1 approaching the interface with phase 2 can be considered as a particle of radius r interacting with a flat surface 2 through the medium 1. The van der Waals interaction energy between a spherical particle and a flat surface, in terms of their Hamaker constant A , can be expressed as:^[12]

$$W_{vdW} = \frac{-Ar}{6D} \quad (1.3)$$

where D is the particle (surface)-to-surface distance. If the absorption frequencies of all three media are assumed to be the same, the following approximate expression for the nonretarded Hamaker constant for two macroscopic phases p and 2 interacting across a medium 1 can be used:

$$A_{tot} = A_{\nu=0} + A_{\nu>0} \approx \frac{3}{4}kT \left(\frac{\varepsilon_p - \varepsilon_1}{\varepsilon_p + \varepsilon_1} \right) \left(\frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_2 + \varepsilon_1} \right) + \frac{3h\nu_e}{8\sqrt{2}} \frac{(n_p^2 - n_1^2)(n_2^2 - n_1^2)}{(n_p^2 + n_1^2)^{1/2}(n_2^2 - n_1^2)^{1/2}[(n_p^2 + n_1^2)^{1/2} + (n_2^2 - n_1^2)^{1/2}]} \quad (1.4)$$

where ε is the static dielectric constants of the three media, ν_e the main electronic absorption frequency, and n the refractive indices of the media in the visible. The first term in equation (1.4) gives the zero-frequency energy of the van der Waals interaction and includes the Keesom and Debye dipolar contributions; its value is normally low. The second term gives the dispersion energy and includes the London energy contribution. The sign of the Hamaker constant is very important and will result in attractive (for $A > 0$) or repulsive ($A < 0$) van der Waals interactions. A few relevant conclusions^[12] can be extracted from the above expression, depending on the refractive indices of the three media. While the van der Waals force between two identical object in a medium is always attractive – causing, for example, the aggregation of non-charged particles in water –, in the case of two different interacting objects this force can be either attractive or repulsive. Specifically, a positive value of A will be obtained if the refractive index of the medium 1 is smaller or larger than those of both the interacting media. Entering in the details of our systems described in the following chapters, in case of a polystyrene particle ($n_p = 1.55$) – or of a silica particle, $n_p = 1.44$ – interacting with air ($n_2 = 1$) through water ($n_1 = 1.33$), A will be negative. Therefore we can conclude that the van der Waals interaction between a particle in water and the air/water interface is repulsive.

Electrostatic interactions between a particle approaching a liquid interface and the interface itself arise from the experimental finding that both the air/water and oil/water interfaces are negatively charged. Although the existence of this negative surface charge and its origin are still a matter of debate,^[13] it has been evidenced by several experimental results. Indication of such negative charge arises from studies on the stability of thin water films on substrates coated with polyelectrolytes carrying negative or positive charge; in the latter case

rapid rupture was observed.^[14] The oil/water interface was found to be charged as well by means of measures of the electrophoretic mobility of pure – surfactant free – oil drops dispersed in water.^[15] Finally, following the deprotonation of a carboxylic acid by nebulization of the aqueous solution and analysis of the surface of the resulting droplets by electrospray ionization mass spectrometry (ESI–MS), evidences of the presence of hydroxide ions on the surface of water were reported.^[16]

Early works on the aggregation of colloidal particles dispersed in water at the air/liquid interface as a function of the ionic strength of the solution revealed the presence of an adsorption barrier in certain conditions.^[17;18] William and Berg,^[17] in particular, demonstrated that by increasing the ionic strength of the suspension (from a starting NaCl concentration of 2 mM), the adsorption rate of negatively charged polystyrene particles to the interface could be increased. Correlation between particles surface charge and charge of the liquid interface arises from studies on foams stabilization. It was found that positively charged stabilized polystyrene particles easily adsorb at the air/water interface at pH at which their surface remain positive, while negatively charged polystyrene particles bearing negative charge in all the pH range did not form any noticeable foam.^[19] Anionic particles with pH dependent surface groups were found to be good stabilizers upon charge suppression or inversion.^[20] It has to be bear in mind, however, that the supply of mechanical energy required for the formation of foams and emulsions can surmount the eventual adsorption barrier.^[21]

The precise value of the negative charge accumulation at the water interface in various experimental conditions is still unknown, and an accurate theoretical description of the electrostatic interactions between particle and interface is still lacking.

1.3.2 Interactions between adsorbed particles

The attachment of particles to fluid interfaces, in terms of adsorption barrier and final contact angle, together with their mutual interactions on the liquid surface, depends on the physicochemical parameters of the colloid itself, such as size, chemical nature, surface roughness, and wettability. The various materials and surface modifications of the particles that are currently available will be discussed in the following sections. The properties of the liquid media (*e.g.* dielectric constant, polarity) play a role as well. It is for this reason that the assembly of the same particles, in the same conditions, at the air/water or oil/water interface can give rise to diverse structures, for example^[22] close packed aggregate (in air) or open lattice with long range order (in oil). The interactions that dictate the organization of the adsorbed particles are manifold,^[23–25] therefore the final structure cannot always be easily predicted, depending on the balance between attractive and repulsive forces that can act at different length scales, concurrently with eventual external forces present in the system. The presence of the interface itself increases the complexity of the problem compared to the interactions normally considered in the bulk of a liquid.^[26] Several forces behave in a qualitatively

similar manner (like in the case of van der Waals or electrostatic) but the discontinuity between the two media in which the particles are dispersed makes the protocols for calculating such interactions even more complicated. Other forces, such as capillary interactions, are characteristic signatures of the presence of a liquid interface.

The interactions acting between particles at liquid interfaces can be broadly separated into attractive and repulsive, which will be now briefly summarized.

1.3.2.1 Attractive interactions

Van der Waals forces, interactions that occur between all molecules and particles, in case of identical objects, as described before, are attractive and lead to strong contact adhesion. It is due to van der Waals forces that uncoated particles will tend to aggregate irreversibly if this is not prevented, for example by steric or electrostatic stabilization. An approximate treatment to estimate van der Waals interactions between two particles at the liquid interface has been proposed.^[17] It is based on calculating an effective Hamaker constant A_{int} that depends on the fractional height f of the particles immersed in the medium 2.

$$A_{int} = A_{p1} + f^2(3 - 2f)(A_{p2} - A_{p1}) \quad (1.5)$$

where $f = (1 - \cos\theta)/2$. The interaction between two spherical particles is then given by:^[12]

$$W_{vdW} = \frac{-A_{int}r}{12D} \quad (1.6)$$

The deformability of the liquid interface accounts for attractive capillary interactions that can be established among adsorbed particles, which stems from the meniscus formation surrounding the particles itself (Figure 1.3A). The liquid surface tension will counteract the weight of the object adsorbed on it; the effect of the two forces – surface tension and gravity – acting on the object and the surrounding interface are measured by the dimensionless Bond number, defined as:

$$Bo = \frac{\Delta\rho gr^2}{\gamma} \quad (1.7)$$

with $\Delta\rho$ the difference in density between the adjoining fluid phases, and g the gravitational acceleration. A low value indicates that the system is governed mainly by surface tension. In case of smooth spherical particles adsorbed at a water surface, if their size is below 10 μm in diameter, their Bond number is usually $\ll 1$ and they are considered too small and light to deform perceptibly the interface. In case of heavier floating objects, instead, the deformation of the surrounding interface is perceptible, having a sign depending on the hydrophilic/hydrophobic properties of the objects, and capillary interactions are presents. Such interactions, sometimes called “the Cheerios effect”,^[27] will be attractive if the liquid deformation created by two interacting objects has the same sign, repulsive if the deformation of the two objects have different signs^[28;29] (as in Figure 1.3B). For small, smooth and spherical colloids, capillary interactions at liquid interfaces are absent between single particles, but

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become relevant when the collective behaviour of particles aggregates is considered. It has been demonstrated that a cluster of particles will collectively deform the surrounding interface,^[30;31] and this can be used to control collective interactions among groups of particles. Synthesized colloidal particles often have a rough surface; as a consequence the wetting at the interface could not be uniform, causing an irregular shape of the particle meniscus even for nanoparticles. Interacting particles will optimize such local surface deformation by adjusting their orientation and distance.^[32]

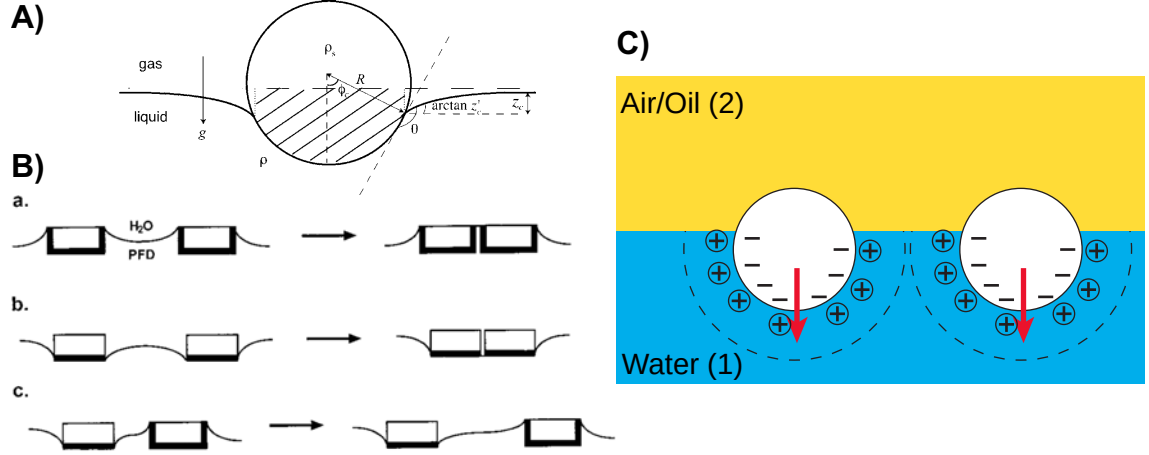


Figure 1.3: *Interactions between particles at a liquid interface. A) Deformation of the liquid interface surrounding a particle in the case that gravity overcomes surface tension.^[27] B) Capillary interactions among mm-sized objects arising from the shape of their menisci. The objects are made of PDMS having hydrophobic (thick lines) and hydrophilic sides (thin lines), and are placed at a water/perfluorodecalin interface. The arrows show the direction of spontaneous relative motion: attraction between similar menisci (a, positive menisci; b, negative menisci), repulsion between menisci of different sign (c).^[29] C) Sketch of two negatively charged particles adsorbed at a liquid interface; the accumulation of counterions around the particle surface and the consequent electric double-layer (dashed line), as well as the generated electric dipole (red arrow), are drawn.*

1.3.2.2 Repulsive interactions

Particles dispersed in water solution are normally stabilized by electrostatic interactions, being either naturally charged (as for silica particles), or after surface modification with charged or highly hydrated groups (as for polystyrene particles with grafted on them positive or negative surface groups). A sketch of two negatively charged particles at a liquid surface is depicted in Figure 1.3C. This charge will account for two repulsive interactions between adsorbed particles: Coulomb and dipolar interactions. Coulomb interactions between like-charged particles are always repulsive, they arise from the formation of the electric double-layer in aqueous solution, and scales as $e^{-\kappa x}$, where κ is the Debye length of the solution and x the particle surface-to-surface distance. It is a long-range repulsion – with a maximum value of about 680 nm due to the self-dissociation of water^[33] –, whose magnitude can be

easily tuned by changing pH, ionic strength or type of electrolyte (*i.e.* different valence or hydration properties) in solution.

Due to the interface discontinuity between the two different fluids, the surface charge of the particles can give rise to dipolar interactions as well. At an air/water interface, the ionic groups on the particle surface can only dissociate inside the water phase resulting in an asymmetric charge distribution around the particle^[34] (Figure 1.3C). The resulting dipoles on all particles are oriented parallel to each other and lead to a repulsive force with magnitude depending also on the contact angle of the particles, with a maximum for $\theta = 90^\circ$. To account for exceptional stability of polystyrene particles trapped at the air/water interface as a function of salt concentration, a second surface charge dipole on the particles above the water surface was hypothesized, arising from wetted surface groups in the air phase, beyond the influence of the ionic condition of the lower phase.^[35] The picture is somewhat similar at oil/water interfaces, where, instead, partial wetting by water drops of the particle surface in the oil phase is more likely and of longer stability in time due to the absence of evaporation. This additional dipole component at the oil/water interface results in stronger particle–particle repulsion compared to the same particles on the water surface.^[22]

A second way commonly employed to stabilize dispersed particles is to adsorb polymers on their surface. It can be done either through chemical – irreversible – grafting, or through physical modification. When two particles approach, the grafted polymer brushes in the gap are confined and exert an osmotic pressure that avoids the particles from aggregating, together with mechanical spring forces that arise from unfavourable decrease in configurational entropy due to compression and space restriction for the polymer chains.^[36] Those interactions are called steric repulsion; and their range is given by the brush thickness and the solvent quality. At a fluid interface the picture becomes more complicate because the brush thickness, that depends on the solvent characteristics, will be different between the two media.^[37] Interestingly, steric repulsion can be engineered to stabilize particles at very close distances, as required for the development of many collective properties.

1.3.2.3 External forces

In addition to the richness of interactions archetypical of particles at liquid interfaces, systems can be engineered to be responsive also to external forces for directing and increasing control over particles assemblies. Based on both solvent and particles properties, several external stimuli can be used, to name a few: temperature, electric and magnetic fields, or light. Mechanical manipulation can be applied too, as in the case of Langmuir–Blodgett troughs where a moving barrier compress or expand the floating particles inducing two dimensional phase transitions.^[22;38;39] The use of light stimulation as a trigger to control particles organization and assembly will be reviewed in Chapter 4, and will be experimentally applied in two different systems of particles at the air/water interface in Chapters 5 and 6.

1.4 Applications of particle-covered liquid interfaces

The interest in having particles at liquid interfaces is not only due to their ability to stabilize them. Particles have the unique characteristic of allowing a huge variety of bulk and surface properties; this is reflected in the different features that can easily be included and modified with such units, making them good building blocks to construct materials for diverse applications.

Colloidal particles with different composition can be synthesized with various, on demand, volumetric (bulk) and surface properties. Diverse materials are currently available, like: minerals, organic compounds, polymers, semiconductors and metals; giving building blocks with different sizes and densities, different magnetic, dielectric, conductive, plasmonic and light processing properties. Spherical colloids with dimensions from a few tens of nanometers up to several micrometers can be synthesized by diverse, extensively reviewed,^[40;41] methods: emulsion, dispersion, precipitation, inversion, swelling, suspension and seeded polymerization are commonly used for polymers, while precipitation reactions are usually used to obtain particles from inorganic materials. Nowadays such particles can be directly purchased from commercial companies in relatively large quantities. In addition, the spherical symmetry of the particles can be broken, and another level of anisotropic interactions can be explored.^[42] Thereafter, several post-synthetic approaches have been developed for afterwards modification of their surface characteristic and, as a consequence, of the interactions among them and with the environment. For example, particles carrying positive or negative surface charge can be obtained, as well as particles with different hydrophobicity – this subject will be discussed in more details in the following section. Binding of organic molecules allows to tailor molecular recognition and interaction in a highly selective fashion, using concepts similar to those developed in supramolecular chemistry,^[43] for precise arrangements and inter-particles specificity.^[44;45] To the above diversity an additional flexibility is offered by the use of “patchy”^[46] or Janus^[47] particles: particles made up of various domains with different properties, opening the way to atoms like colloids, with valence and directional bonding.

Mastering and engineering the adsorption of particles to liquid interfaces results in soft and adaptable structures – contrary to irreversible adsorption on solid substrates – with a plethora of applications: from every day materials to the understanding of fundamental physico-chemical problems.

1.4.1 Foams and emulsions

As already mentioned, particles are widely used for foams and emulsions stabilization^[48] (as in Figure 1.4A, 1.4B left, and Figure 1.4C). In this field, well established applications can be found in industry, medicine and engineering,^[8] where is of utmost importance to control the formation, stability and mechanical properties of the obtained foams or emulsions. Some

1.4 Applications of particle-covered liquid interfaces

applications will be listed below. The property of various particles to attach to air bubbles

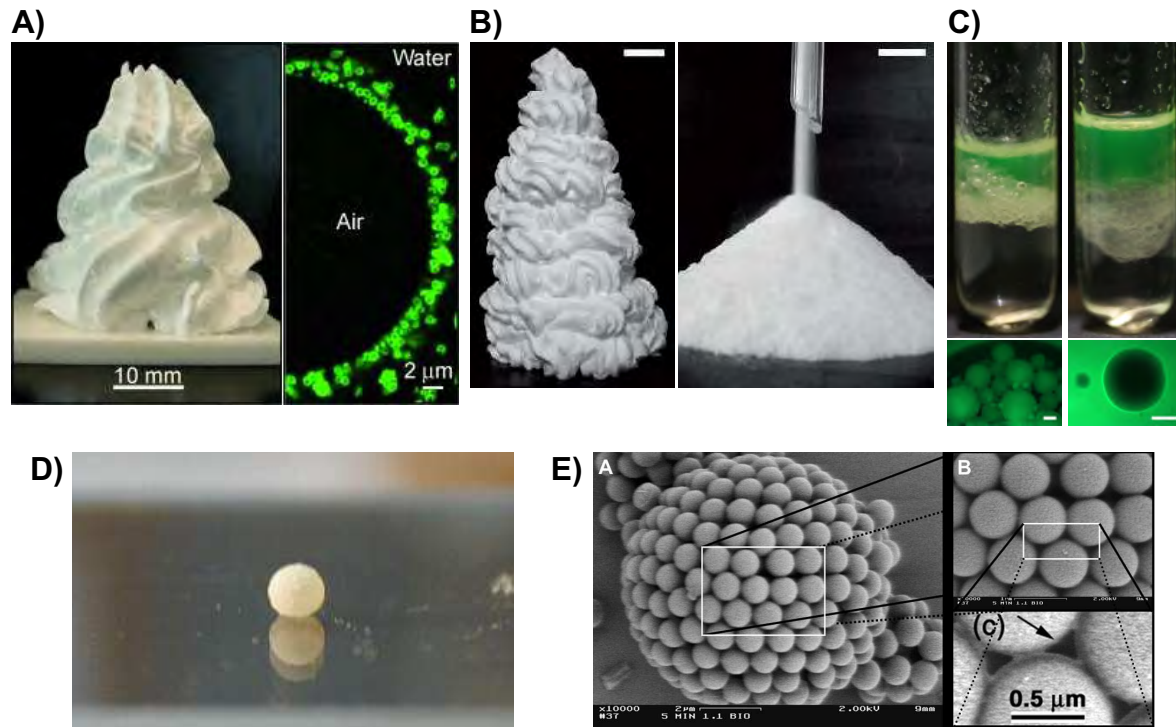


Figure 1.4: Particle-stabilized bubbles and drops. A) A particle-stabilized foam (left); on the right image of the particles (in green) adsorbed at the air/water surface after controlling their hydrophobicity with short amphiphilic molecules.^[49] B) Foam or “dry water” obtained aerating 5 g of silica particles and 95 g of water, depending on particles hydrophobicity. On the left a foam prepared using silica particles possessing 32% SiOH; on the right a free-flowing powder (“dry water”) made with silica particles possessing 20% SiOH.^[50] Scale bars = 1 cm. C) Images of oil-in-water (left) and water-in-oil (right) Pickering emulsions, from.^[51] Scale bars = 200 μm. D) A liquid marble^[52] prepared by covering a water drop with hydrophobic particles (silane-treated lycopodium grains). Drop radius: 1 mm. E) Scanning electron microscope (SEM) image of a dried, 10-μm-diameter colloidosome composed of 0.9-μm-diameter polystyrene spheres, from.^[53]

in water is used in froth flotation industry for mineral processing, paper recycling and wastewater treatment. For the scope, the solution is aerated and the forming froth is successively separated from the mother solution for materials recovery. With this method noble metals can be collected, or hydrophobic contaminants, such as ink, can be separated in order to recycle paper. For applications in medicine, Pickering emulsions can be used for drug delivery purposes.^[54] Solid colloids that are biocompatible and biodegradable, such as chitosan or starch particles, act as barrier for emulsion drops that can be engineered to break and release their content only in specific sites and with defined kinetics for controlled delivery. Their application is widespread not only in pharmaceutical industry, but also for personal care, detergency and food industry. Finally, foams, as well as emulsions, are used as intermediate structures to build macroporous materials for a diverse range of utilization,^[55;56] for example: in engineering to fabricate low-weight and insulating structures, in medicine to build scaffolds for tissue and bones with proper mechanical properties and biomimetic cellular environment.

In addition, novel, exotic, objects have been discovered, based on particle-covered liquid interfaces. Aussillous and Qu  r  ^[52] reported a method to stabilize water drops floating on water surfaces, calling such objects “liquid marbles” (Figure 1.4D) – liquid marbles will be protagonists of Chapter 9. They are obtained by wrapping the water drops with hydrophobic particles; the particles will separate the inside water from the outside keeping a thin layer of air in between. Such liquid marbles are in a perfectly non-wetting state, they have a dramatically reduced adhesion to solid or liquid surfaces, and behave like soft solids. Moreover, they can float on top of a surface of the same liquid, being stable until their content evaporates. Nowadays, several different liquids (*e.g.* ionic liquids, organic solvents) can be contained inside liquid marbles depending on the coating materials.^[57] Another interesting structure was described by Dinsmore et al.,^[53] which reported a particular type of particles stabilized emulsion droplets called “colloidosomes” (Figure 1.4E) in analogy to liposomes. As for liposomes, and in contrast to Pickering emulsions, the liquid phase inside a colloidosome is the same as that on the outside. Such capsules have a controlled permeability, which is achieved by varying the size of the particles or by sintering them together. Colloidosomes responsive to external stimulation can be obtained, for example using microgel particles whose size depend on temperature.^[58] Finally, control over the phase inversion of particle-stabilized air/water systems has been described by Binks and co-workers,^[50] and has been used to switch from air-in-water foams to water-in-air powders, called “dry water” (as the one showed in Figure 1.4B). Control on the air/water surface curvature, and subsequent stabilization of air-in-water or water-in-air is obtained by varying particle hydrophobicity or by addition of charged surfactant.^[59]

1.4.2 Two-dimensional highly ordered materials

Top-down approaches (such as laser and electron beam lithography,^[60;61] dip-pen lithography^[62] or the newly published bubble-pen lithography^[63]) for micro and nanoscale patterning of functional materials are very well developed, being able to form precise architectures with a variety of substrates. But the need of complex facilities, the low throughput and the impossibility to scale up the process opens the way to the development of different techniques. Micro- and nano-particles, thanks to their broad range of bulk and surface properties, sizes and shapes, and ease of synthesis, are suitable building blocks for the manufacturing of materials with the desired electric, magnetic and optical properties. Liquid interfaces can be used as a template for a bottom-up approach to the synthesis of 2D materials, where the weak forces governing the self-assembly allows to obtain adaptable and reconfigurable structures, with the possibility of scaling up the synthesis, using at the same time comparably simpler equipment than common top down techniques.^[64–66]

The high degree of positional long-range order that can be achieved with colloidal self-assembly makes such strategy optimal for the formation of two-dimensional crystals: ordered arrays along two dimensions that easily span several hundred particles (an example, after

1.4 Applications of particle-covered liquid interfaces

transferring the colloids from the water surface to a solid substrate, is shown in Figure 1.5f), with the particle diameter as third dimension. Particles size, shape and type of material, as

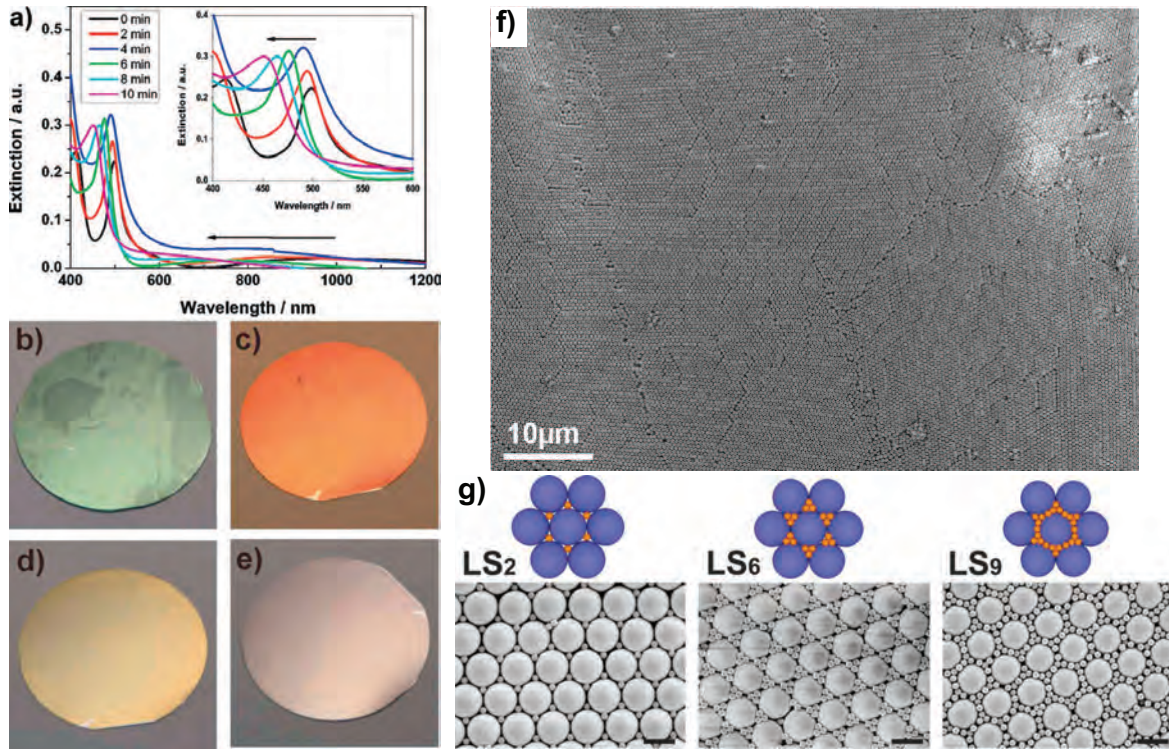


Figure 1.5: *Highly ordered 2D particles arrays and their optical properties. Colloidal monolayers prepared at the air/water interface and transferred to silicon wafers. a) UV-Vis-NIR transmission spectra of monolayers where particles are reduced in size by oxygen plasma treatment for 2–10 min. Arrows indicate the extinction maxima shift toward shorter wavelength for longer etching times. b-e) Photographs of monolayers (on a 2-inch wafer) illuminated normal to the wafer surface, showing colour variation for different particles spacing: b) initial monolayer, c-e) after oxygen plasma treatment for 4 min (c), 6 min (d) and 8 min (e). f) SEM image of the monolayer in b). a-f) from ref.^[67] g) Co-crystallized binary monolayers composed of spherical particles having different diameters, at different stoichiometries.^[68] Scale bar: 1 μm. The procedures for monolayers preparation are in Figure 1.8B for (b-f) and 1.8C for (g).*

well as solvent properties, influence the forces governing their assembly.^[65] If attractive and repulsive forces are well balanced, long-range order structures will be obtained, whose symmetry will be directly related to the shape of the colloids employed. Monodisperse spheres, for example, favour hexagonal crystal packing, as the bigger spheres in Figure 1.5g. Interestingly, it has been shown that, if the assembly conditions at the liquid interface are properly controlled, mixing of bidisperse particles at different stoichiometries leads to the crystallization of binary monolayers with various arrangements^[68] (Figure 1.5g).

Depending on the balance of the interactions among particles, either close-packed, dense structures, or non-close-packed lattices can be obtained (an example already mentioned being the assembly of the same particles at an air/water or at an oil/water interface, where repulsive components are maximized). Other symmetries are commonly achieved using other particles shapes; for example monodisperse cubes tend to yield square lattices,^[69] while anisotropic,

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ellipsoidal particles gives more complex, chain-like, structures.^[70] Precise particles surface modifications into specific binding sites^[46;71] (patchy particles) and defined regions possessing different properties^[72] (Janus particles) provide a higher level of control over their assembly. Recently, more complex, non-hexagonal phases with spherical building blocks dispersed at a liquid interface, have been demonstrated assembling the microspheres in the presence of poly(N-isopropylacrylamide) (PNIPAM) microgels. A phase diagram of different arrangements (*i.e.* hexagonal close-packed or non-close-packed, square and chain phases) is obtained upon compression and expansion of the system.^[73]

One of the main applications of such materials depends on the way they interact with visible light. From the way light is scattered and diffracted by random or periodic structures, various colours can arise. This interaction creates structural colours: the production of colours by microscopically structured surfaces, fine enough to interfere with visible light. In nature, belongs to this category many of the brightest and most vivid colouration existing, such as the iridescent colours of opals, beetle scales, butterfly wings and the feathers of some birds.^[74] Iridescence*, often created by structural colouration, is an optical phenomenon of certain surfaces in which hue and colours are changeable in nature, depending on the angle of observation and of illumination. More specifically, periodically ordered particles, and their interstitial voids, act as diffraction gratings for visible light waves when the interstices size are of the same order of magnitude as the incident wavelength. The resulting colours originate from diffraction and constructive interference according to Bragg's law, in a way analogous to the scattering of X-rays in crystalline solids. For this reason, such colours are often called Bragg reflections. An example of the different colours arising from monolayers having different particles spacing is reported in Figure 1.5a-e.

Photonic crystals, structures with periodic features having different dielectric constants at the scale of the wavelength of incident light,^[75] are nowadays made up by assembling ordered colloidal particles for various light processing applications. A photonic crystal can influence photon propagation in a way similar as a semiconductor does for electrons. Thanks to the possibility to confine, control and manipulate photons, various technological applications can be envisioned, in principle, for the production of light-emitting diodes (LEDs), diode lasers, and to enhance the performance of many other types of optical or electronic devices.^[76] Coatings having mirror behaviour, colouration or reflectivity dependent on the wavelength of the incident radiation can be engineered. In addition, periodic changes in density and mechanical moduli give rise to vibronic bandgaps, and the possibility to control phonon propagation as well as photons.^[77] Although more effort has been put in fabricating 3D photonic crystals,^[78] their 2D counterparts have similar applicabilities, with the possibility to build vast, planar, structures.

*The word comes from the Latin *iris*, or the ancient Greek *ἵρις*, meaning rainbow; and also refers to Greek goddess Iris, which is the personification of the rainbow and a messenger to the gods.

1.4 Applications of particle-covered liquid interfaces

Two-dimensional ordered arrays find applications also as masks for subsequent lithographic techniques.^[79;80] This method, known as nanosphere lithography,^[81] exploits nanostructured monolayers for etching or deposition of a material on the substrate underneath the areas that are not protected by the particles. The ordered features that can be obtained are about one seventh of the diameter of the colloidal spheres. Electrochemical deposition of metals in the interstices among the particles layer allows for the construction of highly ordered metal spots on solid substrates, in a parallel and efficient manner.^[82] Complex architectures can be obtained, including multilayered structures with optical characteristics similar to the one that can be found in nature.^[83]

Liquid interfaces are used either as a template for colloidal organization, in which case successively the structures are “fished” out and permanently fixed, or they can be directly used to construct “liquid devices”. An example of a “liquid device” are highly reflective metal liquid-like films (as the ones showed in Figure 1.6), for adaptive optics applications, where a layer of metal particles is adsorbed to the interface (normally between water and an organic phase) giving materials that are metallic, meaning that they maintain metallic properties such as reflectivity, but at the same time exhibits rheological properties of liquids, they can flow and sustain waves.^[84] The nanoparticles surface coverage is crucial for optimal

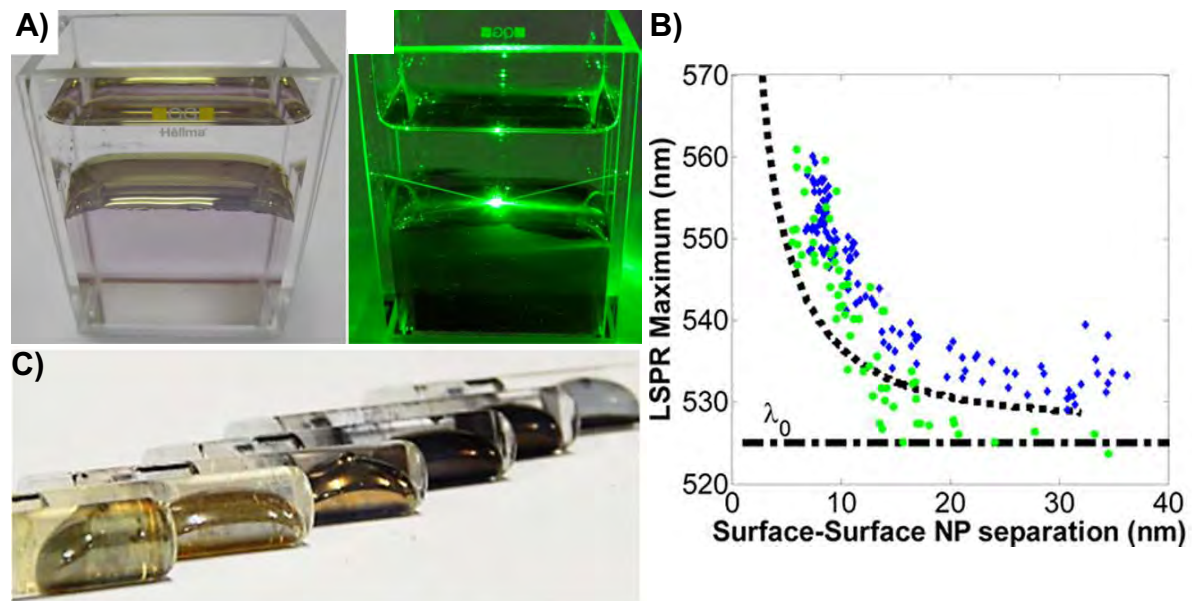


Figure 1.6: 2D materials on liquid surfaces: metal liquid-like films. A) Optical images of Au nanoparticle (60 nm in diameter) films at the [heptane + dichloroethane]/water interface, adapted from.^[85] In the right image the liquid interface is irradiated with a laser ($\lambda = 532$ nm) and reflection of the light beam is clearly visible. B) Demonstration of a “plasmonic ruler” at the liquid interface, from.^[86] The localized surface plasmon resonance (LSPR) maximum versus the particles separation is plotted as a function of both particles added to the liquid interface (green dots) and of NaCl in the water phase and consequent decrease of the interparticles distance (blue dots). C) Metallic liquid layers at water/oil interfaces obtained using various particles by means of “promoters” (hydrophobic salts) added in the oil phase to direct particles adsorption at the liquid interface.^[87]

reflectance; this can be achieved either by controlling the amount of added particles,^[85] or

by acting on the repulsion between particles tuning pH and electrolyte concentration in the water phase.^[86] This allowed Eled and co-workers to design a “plasmonic ruler”, where the localized surface plasmon resonance maximum can be directly correlated to the interparticles distance, as shown in Figure 1.6B. Ultimately, a unique property of liquid/liquid interfaces can be exploited: hydrophobic ions can be added in the oil phase – and not only in the water phase – to both promote and control adsorption of various particles coming from pure water solutions^[87] (Figure 1.6C).

Having precise control over surface coverage and particles spacing allows to tune the plasmonic properties of the monolayer for applications such as a sensor for surface-enhanced Raman spectroscopy (SERS) at the liquid interface. By amplifying the Raman scattering from analyte molecules captured by the nanoparticles from the water or oil phase it is possible to detect trace levels of several substances.^[88]

1.4.3 A model system for fundamental studies

Colloidal particles, forming crystals and other phases, are excellent model systems for the study of the mechanisms of phase transitions^[89] because their motion can be directly visualized with optical microscopy techniques, and their positions can be precisely tracked by image processing.^[90] They can be viewed as counterparts of atomic and molecular systems, whose motion is instead difficult to resolve in space and time, with customized size, shape and interactions. Jean-Baptiste Perrin (Nobel prize in physics in 1926) was the first to realize that colloidal suspensions could be examined by microscopy to determine their structure and dynamic. In this way he could verify the origin of Brownian motion – as originating from collisions of solvent molecules with the colloids – and estimate Avogadro’s number from the equilibrium distribution of colloids in suspension.^[91]

As atoms, colloidal particles experience strong thermal motion; in time they can explore their phase space and form thermally equilibrated phases – but contrarily to atoms, a liquid solution is needed otherwise they form powders without any possibility of motion or rearrangement. While the interaction energy between atoms far exceeds the thermal energy, the surface forces acting between the mesoscopic building blocks of soft materials are comparable to thermal energy ($k_B T$). Moreover, their diameter is much bigger; as a consequence, the energy density and elastic moduli of a colloidal crystal are much smaller than those of atomic crystals. It is for such reason, interaction energy among colloidal particles comparable to $k_B T$, that they form “soft” materials,^[91;92] which are, as mentioned in the preface, easily deformable and modifiable by a small energy input.

While common colloidal particles have no specific bond directionality, therefore being only a crude model of atoms and molecules, “patchy”^[46;93] particles can be considered as colloids with a defined valence and specific directional bonding, being a more proper model for molecules. In addition, completely new interactions and phenomena can be studied with

1.4 Applications of particle-covered liquid interfaces

colloidal particles: while atoms are “passive”, particles can be made “active”, able to convert energy into systematic movement, self-propelled motion.^[94–97]

Nevertheless, the microscopic mechanisms of phase transitions of even simple, isotropic, colloidal systems give useful insight into how condensed phases arise and collectively organize; and their self-assembly can be linked to how ordered structures are built in biological systems. Particles adsorbed at liquid interfaces are, therefore, a valid model system for the understanding of two-dimensional phase transitions. Pieranski, in his seminal paper on two-dimensional interfacial colloidal crystals^[34] published in 1980, was the first to report the ordering of polystyrene particles at an air/water interface (an example of a typical ordered monolayer is displayed in Figure 1.7A). Since then, extensive studies have been performed

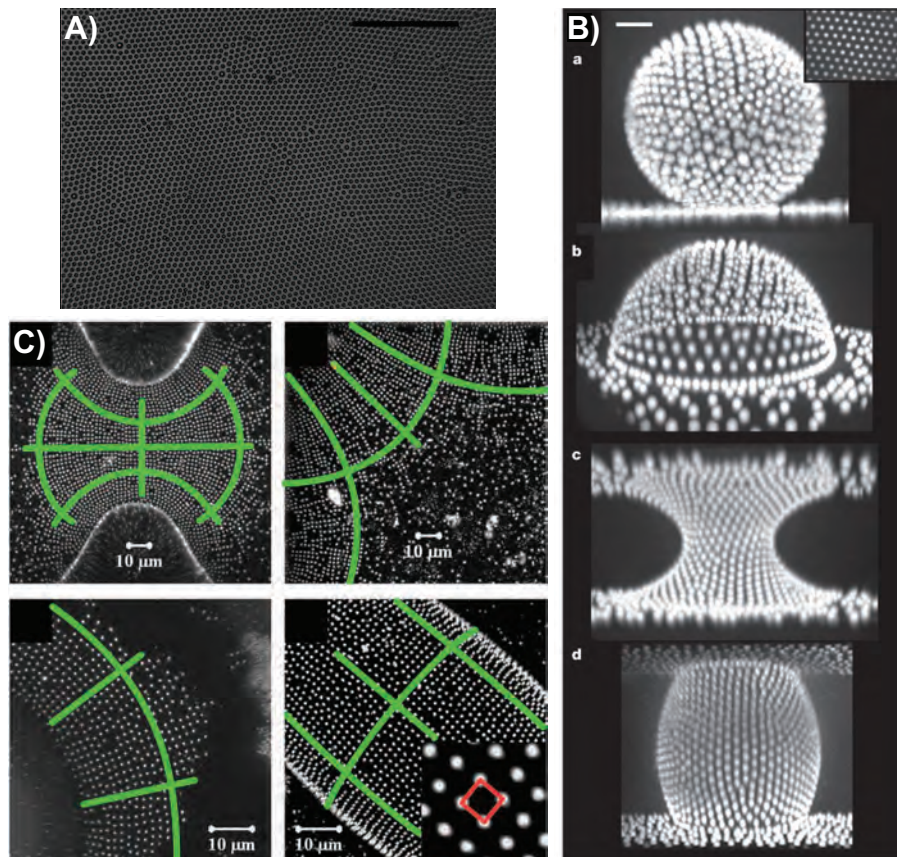


Figure 1.7: Organizing particles at flat and curved liquid interfaces. A) Example of an ordered monolayer of microparticles at a flat oil/water interface, from.^[38] Scale bar: 100 μm. B) Fluorescent particles bound to various curved oil/water interfaces in the form of: spheres (a), domes (b), waists (c) and barrels (d). C) Organization of particles at oil/water interfaces having different shapes dependent on patterned hydrophobic patches on the solid surface. Green lines indicate the directions of principal curvature.

both on how to crystallize particles having different properties and shapes in two dimensions, and on gaining control over aggregation or melting of the obtained monolayers.^[22;35;98;99] Together with macroscopically ordered monolayers, micrometer-size polystyrene particles have been shown to form, in a less controlled fashion, clusters and mesostructures of circular, chain and soap-froth type at the air–water interface.^[100] Several explanations have been suggested

for the formation of such anisotropic structures: from the presence of oil contaminants on the interface,^[101] to the existence of attractive components in the interaction potential due to rugged contact line arising either from surface roughness,^[32] or from spatially heterogeneous distribution of dissociable groups on the colloids.^[102]

In addition, the well controlled deformability of a liquid interface allows for studying how matter organize on surfaces having different curvatures. The assembly of particles at the interface of water-in-oil drops permits to follow crystal growing on spherical surfaces.^[103;104] Several shapes and curvatures can be obtained by depositing drops on a solid surface (domes), or by stretching capillary bridges between two plates (waists and barrels)^[105] (Figure 1.7B). Alternatively, geometrically more complex interfaces derive from depositing drops on patterned hydrophobic (or hydrophilic) patches,^[106] as in Figure 1.7C. Crystal growth, defect patterns and non-intuitive particles positional ordering are among the features that can be engineered on curved liquid interfaces.

1.5 Preparation of particle-laden interfaces

Two techniques are typically used to cover liquid interfaces with particles: particles can be added to the liquid surface either in a direct manner, or their adsorption can be controlled from the bulk of one of the two fluids in which they are suspended. Belong to the first category the widely used method of spreading drops of a concentrated suspension of particles in a volatile solvent (usually isopropanol or ethanol) onto an already prepared liquid interface (see Figure 1.8). A variant of this technique consists in spreading drops of the mixture in the volatile solvent onto a hydrophilic substrate placed at an angle of around 45° touching the target liquid surface^[108] (Figure 1.8B, C). After drop deposition, the volatile solvent will quickly evaporate while most of the particles will remain attached to the interface forming a Langmuir monolayer. In this way particles can be spread even on top of a liquid where they cannot be suspended. This method is typically adopted for the formation of large, ordered arrangements at air/water or oil/water interfaces: the particles can be kept charged and well dispersed, and prone to organize as a consequence of interparticle interactions and external forces.

Spreading at the air/water interface usually results in the formation of close packed crystalline structures.^[67;109] Transfer of the colloidal crystal on a solid substrate can be obtained using two strategies. The substrate can be immersed in the liquid before or after addition of the particle suspension, placed below the monolayer, and lifted off after crystal formation,^[110] as in Figure 1.8B, C. Otherwise the substrate can be inserted into the water across the particle film and lifted up vertically at a steady speed as in Langmuir–Blodgett-type deposition, in this case leaving colloidal arrays on both sides of the substrate.^[111] Non-close-packed monolayers can be obtained either dispersing the particles at the oil/water interface, due to stronger repulsive forces present,^[80] or by subsequent plasma reduction of the particles

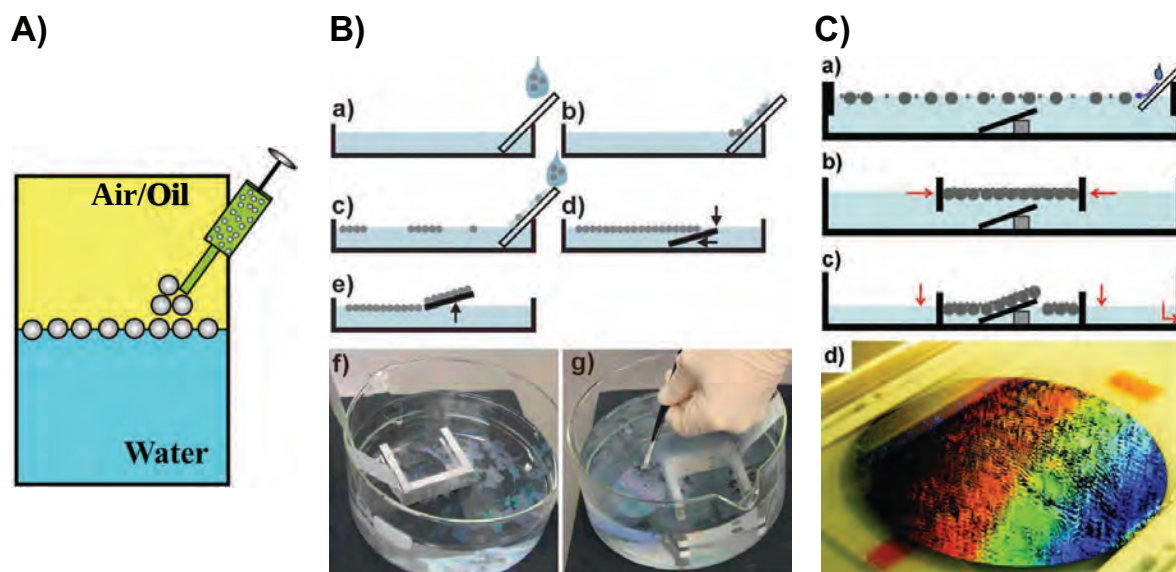


Figure 1.8: Direct deposition of particles on liquid interfaces. A) Sketch of the spreading method: a syringe containing a high concentrated particle solution in a volatile solvent is placed close to the liquid interface (being either with air or oil), where the solution is injected. Adapted from.^[107] B) Schematic illustration and photographs of the fabrication of a particle monolayer on a solid substrate.^[67] The particle suspension in a volatile solvent is spread on the water interface through a partially immersed hydrophilic glass slide (a,b); the required particles concentration for the formation of a close-packed monolayer is obtained by several addition cycles (c). The substrate is inserted in the water phase (d and f) and carefully lifted up (e and g). The particle monolayer at the interface is clearly visible by their light reflection. C) Schematic illustration of the formation of a monolayer, composed of particles having two diameters, by spreading the particles mixture and subsequent compression of the interface with moving barriers^[68] In (d) image of the particles crystal on the substrate prior to lifting the substrate from the solution.

deposited on the solid substrate^[67] (Figure 1.5a-e). The precise handling of those techniques allows obtaining single crystalline domains over several square centimetres both on the liquid interface and on the solid surface.

Crystallization at the liquid interface is achieved either increasing the number of adsorbed particles by several additions of spread drops (Figure 1.8B), or by compressing the monolayer with moving barriers (Langmuir–Blodgett trough, Figure 1.8C). Tunability of the floating colloidal structures is ensured by adjusting the pH of the subphase, allowing for a further increase in long-range order, with single crystal domains reaching macroscopic dimensions;^[112] or using the Langmuir–Blodgett method for compression-relaxation cycles.^[113]

Although this method is very powerful both for studying properties of particles at interfaces^[38] and for material science applications, some disadvantages exist.^[11] The use of an external solvent could cause contaminations, a complete adsorption of all the particles cannot always be considered, and for continuous monolayer formation it could not be the most practical method for industrial applications.

An alternative for the formation of particles monolayers consists in controlling their ad-

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sorption from the bulk suspension of one of the two liquids, forming, in this way, a Gibbs monolayer. As already described, three key parameters control spontaneous adsorption of particles to a liquid interface. One is the wettability of the particle, quantified by the contact angle it makes with the liquid/liquid interface; another is the eventual adsorption barrier that prevents a particle to reach the interface; finally, particles need to diffuse from the bulk to the surface.

For thermodynamic reasons – a decrease in the free energy of the liquid interface – spontaneous adsorption is possible in cases in which a contact angle can be defined. The gain in stabilization energy will be maximized for $\theta \approx 90^\circ$, while it will be much lower for too low or high contact angle values; in particular, completely hydrophilic or hydrophobic particles will prefer to be dispersed in one of the two phases. Therefore, especially for foams and emulsions stabilization, in order to prevent mechanisms of destabilization (*e.g.* coalescence, coarsening or disproportionation), particles with intermediate wettability are preferred. Several methods exist for desired modification and precise control of particles wettability. Their surface can be modified prior to dispersion in one of the liquid phases. Surface reactions are used especially for silica particles, which can be coated by silanization reaction of the surface silanol groups (SiOH) with various hydrocarbon chains,^[114] and for polystyrene particles with carboxyl surface groups (COOH), which can be modified by coupling reactions.^[115] Alternatively, surface active modifier can be added successively to destabilize the particles and tune their wettability *in situ*. For this purpose acids or bases,^[20] long-chain^[116;117] or short-chain surfactants,^[49;118] short-chain alcohols^[119] and various functionalized amphiphilic molecules^[120] have been used. Whichever the method employed, controlled wettability of the particles in solution allows not only to strongly stabilize liquid interfaces, but also to invert the dispersed phase in the system. As in the example in Figure 1.4B, it is possible to switch from air-in-water foams to water-in-air powders, which means from air bubbles dispersed in water, as in normal foams, to water drops dispersed in air. Phase inversion is possible because the curvature of an air/water or oil/water interface stabilized by particles is determined by their contact angle (as reported in Figure 1.2C). For more hydrophilic particles ($\theta < 90^\circ$), for which a larger area of their surface will stay in water, the interface will curve in a way that the larger area of the particle surface remains on the external side, therefore resulting in air or oil-in-water dispersions. The opposite happens for more hydrophobic particles ($\theta > 90^\circ$).

A second component preventing adsorption of particles is the presence of an adsorption barrier. As already mentioned, the charge of the particles is an important parameter determining if particles will spontaneously adsorb or not. To overcome such a barrier, as well as to cope with the third problem pointed before – the diffusion from bulk toward the surface – externally delivered energy can be exploited. Mechanical energy can be provided by agitation, as in the emulsification process, otherwise sonication^[21] or centrifugation^[86] can be used. Furthermore, an addition of electrolytes, which can decrease the adsorption barrier, has found to be a prerequisite for complete particles adsorption.^[86] Interestingly, in liquid/liquid

systems the particles can be added in one phase, while the electrolytes in the other phase;^[87] usually with hydrophobic ions carrying an opposite charge to the particles. Surfactants too have been used to control particles surface charge. The electrostatic binding of the oppositely charged surfactant to the particle surface allows tuning their surface charge from negative to neutral and positive (for negatively charged particles) as a function of their respective concentration.^[117;121] Charge reversal is attributed to the formation of surfactant double-layers on the particle surface.

While spontaneous adsorption can be adapted for a complete uptake of particles from suspension, and can be used for continuous monolayers formation as well as for particles stabilized foams and emulsions, it has still some drawbacks. The conditions in which particles adsorb to liquid interfaces in a well-controlled and complete manner are still poorly understood.^[11] In many experiments, the surface-active molecules added, or the particles surface modification used, render the particles themselves less stable and prone to uncontrollably aggregate instead of rearrange in an organized fashion as required for crystals formation. As a consequence, the spreading technique is commonly preferred for the construction of perfectly ordered monolayers since the weak forces acting among highly stabilized particles allow for self-repairing until a minimum energy state (the crystalline phase) is reached.

1.6 Conclusions

In this chapter I introduced the scientific background foundation, in general terms, of the entire thesis, successively focusing on the first two parts of it, whose main subject is particles at liquid interfaces. Entering in this subject, I reviewed the related literature in order to position our work. I underline that the main differences between the scientific literature presented here and our work are more precisely outlined in the introductions of the next chapters.

The control and understanding of particle-interface interactions, *i.e.*, how to adsorb particles dispersed in the bulk solution to the liquid interface, and how to direct their assembly into large 2D ordered structures, will be of great importance in the following chapters of Part I. They are the basis for understanding the novelty of our method to adsorb particles to liquid interfaces using minute amount of surfactants, and how to successively control their organization into predefined structures depending on the amount of particles and surfactant in the mixture (Chapter 2). They are also a starting point to describe the large 2D structures made of nanoparticles, and are required to explain their properties under light irradiation, *i.e.* their intense structural colouration showed (Chapter 3).

The concept of self-assembly, of great importance for the construction of 2D structures at liquid interfaces, will be resumed and extensively discussed in the bibliographic Chapter 4 (where the focus will be not only on particles assemblies on liquid interfaces, but also in the bulk of the liquids). In addition, for a broader interest, in this chapter I described several

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exciting experiments related to particles at liquid interfaces, even though not necessarily directly connected to my experiments. Among them, the adaptive 2D structures at liquid interfaces presented here will also be a starting point for the results reported in Chapters 5 and 6, where external and contactless optical stimulation will be used to control particles interactions and organization.

Adsorption and crystallization of particles at the air/water interface induced by minute amounts of surfactant^{*}

2.1 Abstract

Controlling the organization of particles at liquid/gas interfaces usually relies on multiphasic preparations and external applied forces. Here, we show that micromolar amounts of conventional cationic surfactant induce, in a single step, both the adsorption and crystallization of various types of nanometer- to micrometer-sized anionic particles at the air/water interface, without any additional phase involved nor external forces other than gravity. Contrary to conventional surfactant-induced particle adsorption through neutralization and hydrophobization at a surfactant concentration close to the critical micellar concentration (CMC), we show that in our explored concentration regime (CMC/1000-CMC/100), particles adsorb with a low contact angle and maintain most of their charge, leading to the formation of two-dimensional assemblies with different structures, depending on surfactant (C_s) and particle (C_p) concentrations. At low C_s and C_p , particles are repulsive and form disordered assemblies. Increasing C_p in this regime increases the number of adsorbed particles, leading to the formation of mm-sized, highly-ordered polycrystalline assemblies due to the long-range attraction mediated by the collective deformation of the interface. Increasing C_s decreases the particle repulsion and therefore the inter-particle distance within the monocrystalline domains. A further increase in C_s ($\pm$ CMC/10) leads to a progressive neutralization of particles accompanied by the formation of disordered structures, ranging from densely packed amorphous ones to loosely packed gels. These results emphasize a new role of surfactant to mediate both adsorption and crystallization of particles at liquid/gas interfaces and provide

^{*}This chapter is adapted from “Adsorption and crystallization of particles at the air-water interface induced by minute amounts of surfactant”, paper under review.

a practical manner to prepare two-dimensional ordered colloidal assemblies in a remarkably robust and convenient manner.

2.2 Introduction

Controlling the adsorption and the two-dimensional organization of particles at a fluid interface is a crucial process^[122] that is directly involved in numerous industrial, environmental and technological applications.^[65;123] From a fundamental viewpoint, particles at interfaces also provide both a rich playground for studying physical phenomena in two dimensions^[34;73;98;106;124–129] and an invaluable technological platform for the development of functional materials with tunable properties.^[11;64;130;131] In this study, we describe a new and remarkably simple way to induce the adsorption of colloidal particles at an air/water interface and further control their two-dimensional organization. We show that, when a minute amount of cationic surfactant is added to a dilute aqueous suspension of anionic microparticles, a significant number of the particles adsorb at the air/water interface. Depending on both surfactant and particle concentration, we find that the adsorbed particles can organize into various two-dimensional structures, from close-packed colloidal crystals to loosely packed gels.

Our strategy markedly differs from what has been reported so far regarding the two-dimensional self-assembly of colloidal particles at a fluid interface, in the following aspects. First, in our approach, the particles are transported from the bulk of the suspension to the air/water interface where they directly adsorb. This is in contrast to most studies, where a small amount of an external suspension of particles in an organic solvent is spread on the surface of an aqueous solution (usually exempt of particles). This forces the particles to stay at the air/water interface after the evaporation of the organic solvent.^[65] This spreading methodology has been widely used to study the behavior of particle monolayers at the air/water interface, especially during compression or expansion in Langmuir troughs.^[22] Second, we report an effect of surfactant at concentrations 100 to 1000 times lower than what has been investigated so far. Indeed, oppositely charged surfactants have been extensively exploited to alter the surface properties of particles and therefore to mediate their interaction with a fluid interface.^[132] More specifically, surfactants at high enough concentrations are known to electrostatically adsorb on oppositely charged hydrophilic particles, thus altering their wettability. At the surfactant concentration regime where particles become hydrophobic enough, the latter could adsorb at the air/water interface.^[116] This very efficient approach has been exploited to stabilize foams^[133] and emulsions,^[134] or for other applications such as the suppression of the coffee-ring effect.^[121;135] However, achieving such a level of hydrophobization typically requires a sufficiently large amount of adsorbed surfactant typically leading to particle neutralization. Compared to the critical micellar concentration (CMC), such effects

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are usually achieved with a concentration of the order of $\text{CMC}/10$ for ionic surfactants adsorbing on hydrophilic surfaces.^[136–138] As a result, the neutralized particles become barely repulsive and thus poorly prone to crystallization. Velikov et al. could produce colloidal crystals in that surfactant concentration regime in the particular geometry of microparticles confined in thinning foam films.^[139] The conjunction of surfactant-induced particle hydrophobization and application of mechanical force led to particle adsorption at both the top and bottom interfaces, as well as long-range hexagonal ordering of the interfacial particles upon stepwise compression of the films.

Here, for the first time, we demonstrate that, without applying any additional external force, a strikingly smaller amount of a cationic surfactant is enough to induce the adsorption of negatively charged particles to a static air/water interface without modifying the particle surface properties. At these concentrations, which are typically 3-4 orders of magnitude lower than the CMC, surface tension effects are negligible. Furthermore, by means of zeta potential measurements we demonstrate that there is no significant surfactant adsorption on the particle surface. As a result, the adsorbed particles at the interface maintained most of their initial charge, being able to organize and eventually crystallize there. We suggest that it is the preferential adsorption of the surfactant at the air/water interface that diminishes the electrostatic barrier for particle adsorption on the like-charged interface and therefore facilitates the adsorption of anionic particles there.^[17] To our knowledge, such an “electrostatic shielding” effect, which is reminiscent of the role of salts in mediating particle adsorption at the air/water interface,^[17;18] has never been described using surfactants. A striking advantage of surfactants over simple salts is their inherent ability to accumulate at the interface, therefore increasing their local shielding efficiency. As a result, we show that particle adsorption and crystallization can be induced at micromolar concentrations of surfactant, which are at least three orders of magnitude smaller than typical electrolyte concentrations used to promote particle adsorption.

We exploit this new principle and describe two practical ways to induce the adsorption of anionic particles at the air/water interface without neutralizing them. Through a combination of wide-field transmission and confocal reflection microscopies, we analyse the adsorbed particle monolayers and explain how both surfactant and particle concentrations control the way particles organize at the interface. We establish a phase diagram evidencing a wide range of conditions where extended two-dimensional colloidal crystals can be obtained in a reproducible way. Finally, we demonstrate that this same principle can be applied to crystallize two different types of microparticles (anionic polystyrene and silica) as well as nanoparticles (see Chapter 3), suggesting that the approach is operational irrespective of specific physicochemical particle properties. Overall, our findings provide both a new look at particle behaviour at fluid interfaces and a useful guideline for the rational design of functional two-dimensional materials in a novel and strikingly robust manner.

2.3 Experimental results and discussion

2.3.1 Particle adsorption and two-dimensional organization at the air/water interface

This section begins with a description of the preliminary results obtained by the laboratory. Figure 2.1 shows a schematic representation of the experiments, which consisted in mixing a dilute aqueous suspension of anionic polystyrene (PS) microparticles (cross-linked particles with both sulphate and high density of carboxyl functional groups on their surface, diameter $5.1\ \mu\text{m}$) with an aqueous solution of cationic surfactant dodecyltrimethylammonium bromide (DTAB) in an Eppendorf tube. The concentration of microparticles and surfactant in the final

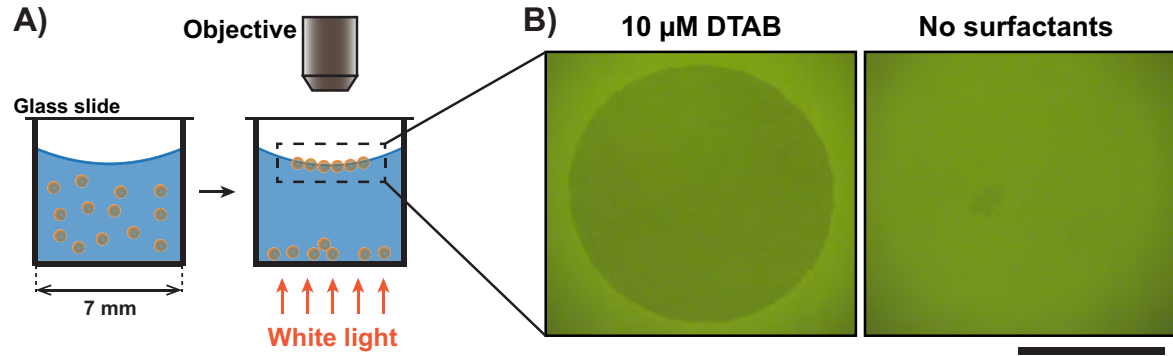


Figure 2.1: Cationic surfactant (dodecyltrimethylammonium bromide, DTAB) induces the adsorption of negatively charged PS microparticles (diameter = $5.1\ \mu\text{m}$) at the air/water interface leading, at concave interfaces, to circular 2D colloidal assemblies. A) The “straight method”: the surfactant/particle mixture is placed in a cylindrical cell (diameter 7 mm) covered with a glass slide to avoid evaporation and is left unmoved overnight. A 2D patch of particles spontaneously forms at the center of the concave air/water interface while non-adsorbed particles sediment at the bottom of the cell. B) Brightfield transmission microscopy image of the air/water interface with a particle concentration of $C_p = 5\ \text{mg/mL}$, in the presence (left) and absence (right) of DTAB, $C_s = 10\ \mu\text{M}$. Scale bar: 1 mm.

mixture was $C_p = 5\ \text{mg/mL}$ and $C_s = 10\ \mu\text{M}$, respectively ($\text{CMC} = 13.4\ \text{mM}$ at 25°C ^[121]). We then transferred $200\ \mu\text{L}$ of the mixture to a cylindrical chamber (diameter 7 mm) and we placed a glass coverslip on it to prevent water evaporation. The aqueous mixture partially wetted the walls of the chamber (contact angle $\approx 80^\circ$), resulting in a slightly concave air/water interface. The sample was placed on the stage of a home-built upright microscope and was left unmoved overnight at room temperature ($22 \pm 2^\circ\text{C}$). We called this process, which did not involve any manipulation of the sample cell, the “straight method” (Figure 2.1A). Inspection of the sample with brightfield transmission microscopy revealed that, whereas most of the microparticles accumulated at the bottom of the chamber due to sedimentation, a significant number of particles were spontaneously adsorbed at the liquid-gas (LG) interface. These interfacial particles formed a two-dimensional (2D) colloidal crystal at the center of the air/water interface, *i.e.* at the middle of the chamber (Figure 2.1B, left). A representative movie, recorded shortly after loading the surfactant/particle mixture in the chamber, reveal

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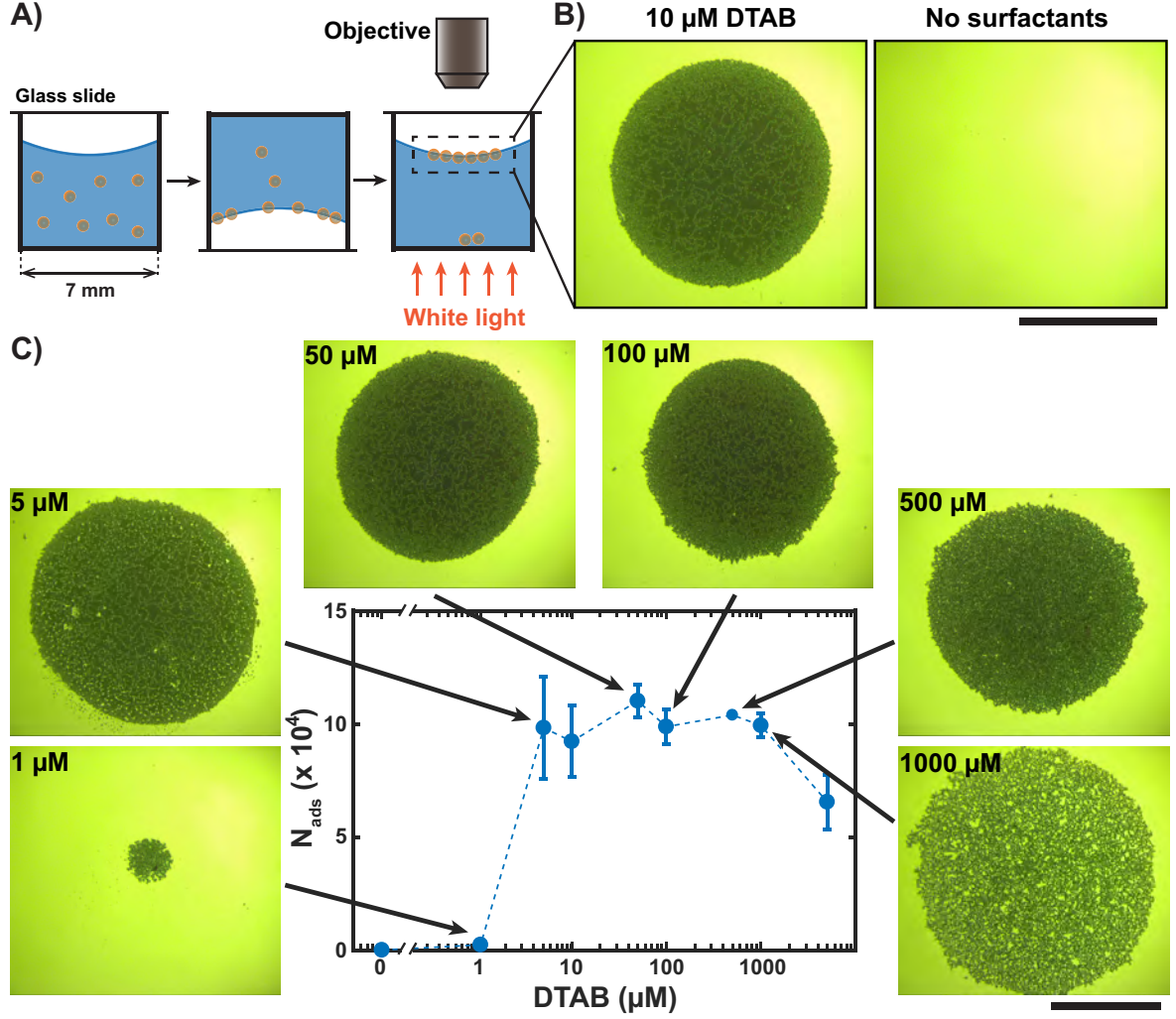


Figure 2.2: Controlled negatively charged particles adsorption and organization at the air/water interface mediated by cationic surfactant DTAB, using the “flipping method”. A) The surfactant/particle mixture is placed in the cell prior to flipping it upside down so that gravity brings the particles to the air/water interface. After 2 h, the sample cell is flipped back to its original position. Adsorbed particles accumulate at the center of the concave interface to form a 2D colloidal patch. B) Bright-field transmission microscopy image of the air/water interface with a particle concentration of $C_p = 0.05 \text{ mg/mL}$, in the presence (left) and absence (right) of DTAB, $C_s = 10 \mu\text{M}$. C) Number of particles adsorbed at air/water interface, N_{ads} , as a function of DTAB concentration using the flipping method. Brightfield transmission microscopy images show the corresponding 2D colloidal assemblies: disordered ($C_s = 1 \mu\text{M}$), densely packed and polycrystalline ($C_s = 5 - 100 \mu\text{M}$), densely packed and disordered ($C_s = 500 \mu\text{M}$) and loosely packed gels ($C_s = 1 \text{ mM}$). Symbols and error bars show mean values $\pm$ sd from three individual experiments. All scale bars are 1 mm.

that particles are present at the air/water interface since the beginning of the video; in around 5 h they collect in the centre of the chamber and form the 2D crystal. We hypothesized that DTAB was responsible for promoting the adsorption of particles to the air/water interface and their subsequent crystallization in two dimensions. To test this hypothesis, we repeated the same experiment in pure water (no surfactant) and we found that almost no particles were adsorbed at the air/water interface (Figure 2.1B, right). We attributed the transport of

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the particles to the free interface to convection. Flow visualization experiments revealed that convective flows were always present in our samples, presumably due to unavoidable small variations in ambient temperature (of the order of 0.1°C).

In order to study the system in a more precise and controlled way, I devised another simple method to realize a controlled transport mechanism that would bring particles to the air/water interface in a fully controllable fashion. We called it the “flipping method” (Figure 2.2A). After loading the chamber with the surfactant/particle mixture, I inverted the chamber and left it in this position for two hours. Note that the capillary forces prevented the liquid from flowing out of the chamber. I kept the surfactant concentration the same as for the straight method ($C_s = 10\text{ }\mu\text{M}$), however I employed a much lower particle concentration, $C_p = 0.05\text{ mg/mL}$. I chose this C_p because i) it should yield a surface coverage similar to that in the straight method (assuming that all particles adsorb to the free interface) and ii) the absence of sedimented particles at the bottom of the chamber would allow for better transmission imaging due to the absence of strong scattering. After 2 h, I inverted the chamber once again to bring it to its initial position (Figure 2.2A). Similar to the straight method, I observed the formation a two-dimensional polycrystalline patch of circular shape (Figure 2.2B, left), having a diameter of $1.8 \pm 0.1\text{ mm}$ composed of monocrystalline domains (dark zones inside the patch) separated by boundaries (bright lines inside the patch). I analysed the crystallization process of particles adsorbed at the air/water interface by recording their behaviour soon after the second flipping process. I observed that, similar to the “straight method”, particles first accumulated at the center of the chamber where the interface curvature was maximum, prior to progressively crystallizing from the center of the patch to its edge. The whole process (particle assembly and crystallization) took about 5 h. A control experiment using the same colloidal suspension but without surfactant yielded no particle adsorption at the air/water interface, and thus no 2D structure was formed (Figure 2.2B, right).

I conducted further experiments mixing the particle suspensions with anionic (sodium dodecyl sulfate, Figure 2.3A) or nonionic surfactant (triethoxy mono-octylether, Figure 2.3B), and I found that almost no particles were adsorbed at the interface. All these findings indicate that a micromolar amount of DTAB cationic surfactant induced the adsorption of anionic particles at the air/water interface. Once adsorbed, these particles accumulated at the center of the concave interface where they self-organized into a mm-sized, two-dimensional polycrystalline colloidal crystal.

2.3.2 Influence of surfactant concentration on particle adsorption and inter-particle interactions at the air/water interface

To elucidate the role of surfactant in the adsorption and further crystallization of the suspended particles at the air/water interface, I used the “flipping method” at a fixed particle concentration ($C_p = 0.05\text{ mg/mL}$) and varying DTAB concentration. In Figure 2.2C, I report the measured number of particles adsorbed at the air/water interface (N_{ads}) as a function of

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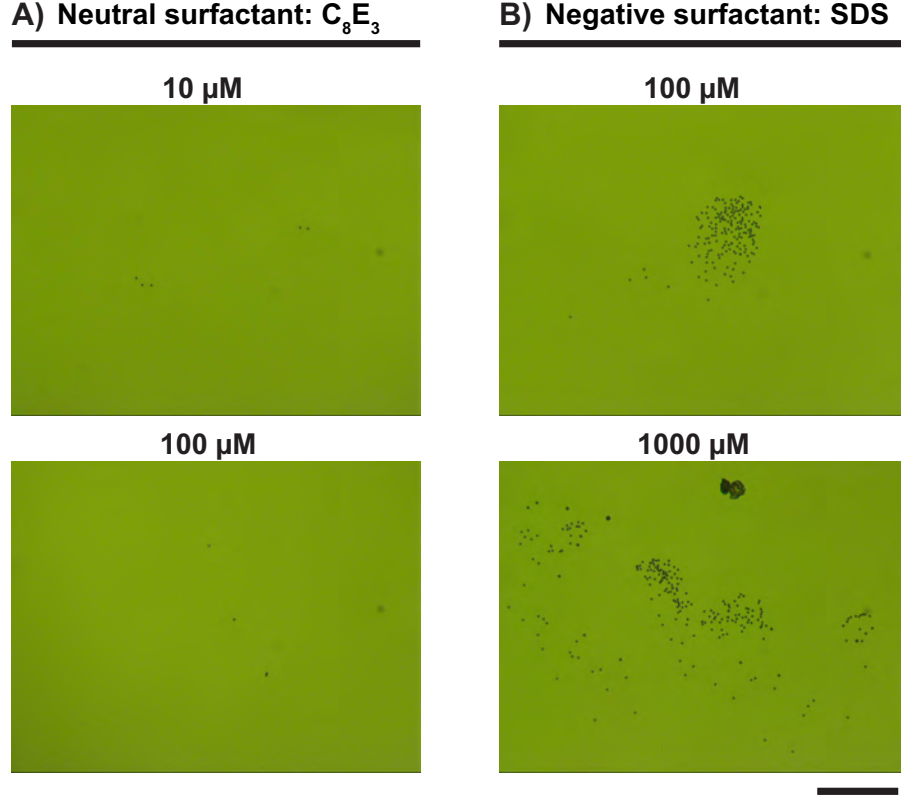


Figure 2.3: Brightfield transmission microscopy images of the air/water interface for a suspension of anionic PS particles ($C_p = 0.05$ mg/mL) and different amounts of the negatively charged surfactant sodium dodecyl sulfate (SDS) A) or of the neutral surfactant triethoxy mono-octylether (C_8E_3) B). The “flipping method” was used. $C_s = 1$ mM or 100μ M are, respectively, the maximum amount of surfactants that could be added as larger concentrations led to the depinning of the contact line while turning the well upside down. Scale bar: 200μ m.

C_s . As mentioned earlier, there was no particle adsorption for the surfactant-free dispersions. For $C_s = 1\mu$ M, only a small amount ($N_{ads} \approx 2.3 \cdot 10^3$) of particles was adsorbed to the free interface. These particles formed a small disordered patch of roughly circular shape. Raising the DTAB concentration to $C_s = 5\mu$ M led to a dramatic increase in the number of adsorbed particles, with N_{ads} reaching a value of about 10^5 and the formation of a dense circular patch with a diameter of 1.8 ± 0.2 mm. Further increasing the DTAB concentration, in the range $C_s = 10\mu$ M – 500μ M, did not result in an increase of N_{ads} , which remained of the order of $\sim 10^5$ particles. Strikingly, this N_{ads} was very close to the total number of particles in suspension ($1.4 \cdot 10^5$), confirming that using the “flipping method” at this particle concentration, the majority of suspended particles adsorbed at the air/water interface. Although particles always formed circular patches of approximately constant diameter, the microstructure of the colloidal assemblies was dependent on C_s . For $C_s = 5 - 100\mu$ M, all patches displayed a polycrystalline structure except at their edges where particles were less ordered. For $C_s = 500\mu$ M, particles were organized in a dense but amorphous circular patch. For $C_s = 1$ mM, whereas N_{ads} remained unaltered ($N_{ads} \approx 10^5$), the adsorbed particles formed a loosely packed circular patch of increased diameter of ~ 2.2 mm. Notably, the number of adsorbed

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particles decreased with further increasing DTAB concentration, reaching $N_{ads} = 6.5 \cdot 10^4$ for $C_s = 5$ mM.

To investigate the evolution of the microstructure of the 2D colloidal assemblies as a function of surfactant concentration, I examined the central part of the patches by means of high magnification transmission microscopy (Figure 2.4A). I quantified the observed structural

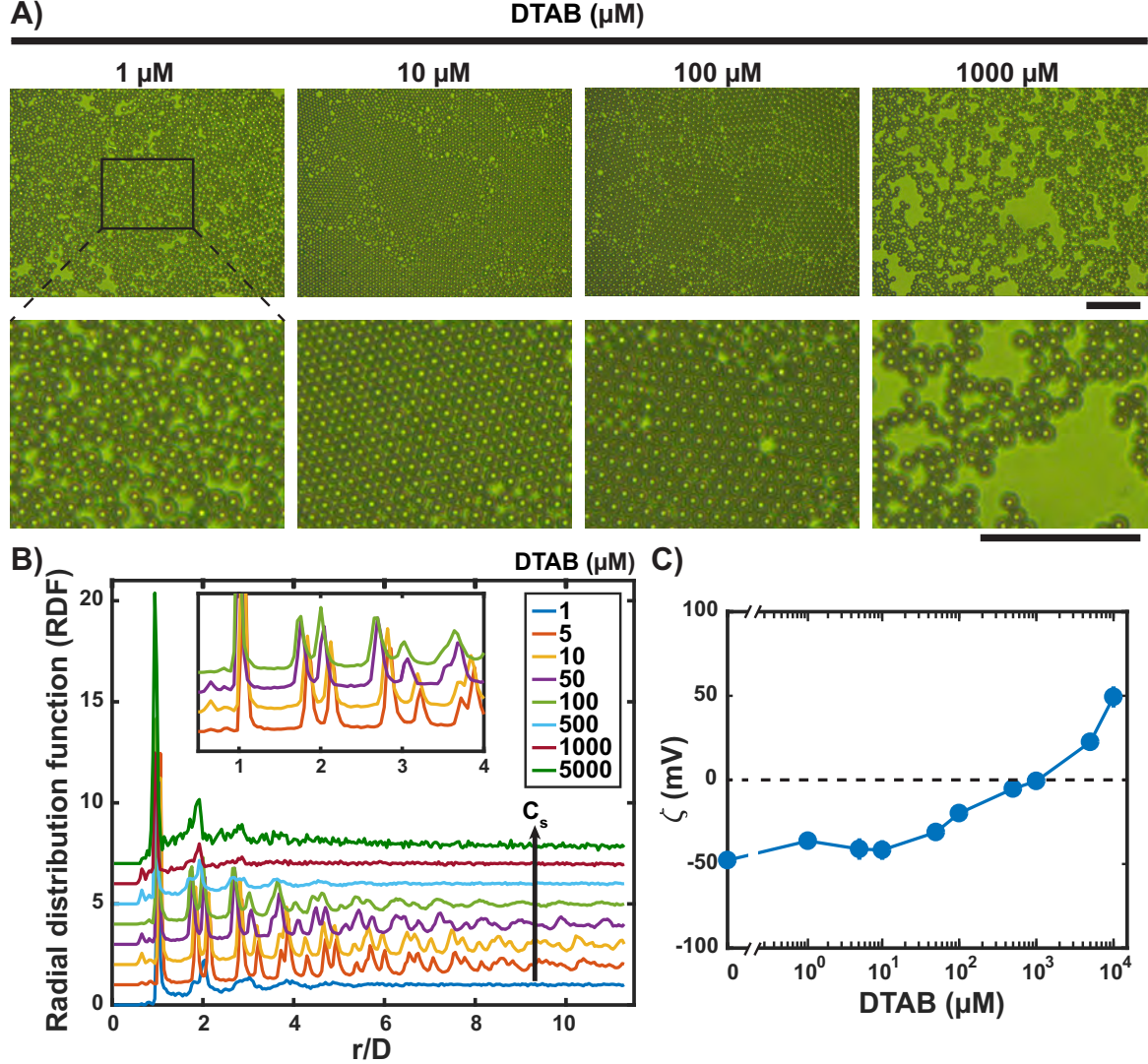


Figure 2.4: DTAB concentration tunes the organization of particles adsorbed at the air/water interface using the “flipping method”. A) Representative brightfield transmission microscopy images of the 2D colloidal assemblies as a function of DTAB concentration (given), at a fixed particle concentration $C_p = 0.05$ mg/mL. Zoomed images of the central area of the assemblies (indicated by a black rectangle) are shown in the bottom row. The scale bars are 50 μm . B) Radial distribution function (RDF) computed from images as in (A) top row, as a function of DTAB concentration (C_s); r is the inter-particle distance, D is the particle diameter. The RDFs are vertically offset for the ease of comparison. The inset shows a magnified view of the first peaks, revealing a shift towards shorter inter-particle distances upon increasing surfactant concentration. C) Zeta potential (ζ) measurements of mixtures of PS particles ($C_p = 0.05$ mg/mL) with varying concentrations of DTAB. Symbols represent mean values of six independent measurements. The error bars (standard deviation, not shown) are smaller than the symbol size.

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evolution by computing the radial distribution function (RDF) from these images (Figure 2.4B). For $C_s = 1 \mu\text{M}$, the particles were organized in a relatively dense arrangement but with no long-range order (Figure 2.4B, blue curve). In striking contrast, for $C_s = 5 - 10 \mu\text{M}$, particles were arranged in a close-packed hexagonal lattice with only a few defects (Figure 2.4B, red and yellow curves). The corresponding RDF confirmed the long-range positional order, showing clear peaks up to distances (r) normalized with respect to the particle diameter (D) of $r/D = 10$. This increased positional order was maintained for $r/D = 6$ for higher DTAB concentrations, up to $C_s = 100 \mu\text{M}$. For $C_s = 500 \mu\text{M}$, most of the long-range order was lost, while for $C_s \geq 1 \text{ mM}$ the structure was disordered with patches adopting a 2D gel-like morphology. A video recording the process (at $C_s = 1 \text{ mM}$) showed that particles collect in the centre of the chamber and stick to the neighbouring particles as soon as they encounter them, without having the possibility to rearrange. Moreover, in the region where crystallization occurred ($C_s = 5 - 100 \mu\text{M}$), the RDF analysis showed that the positions of the first peaks were shifted to lower r/D values upon increasing C_s , indicating repulsive particles assembling at a closer distance to each other with an increase in C_s (inset of Figure 2.4B). In particular, the position of the first peak decreased progressively from $r_1/D \approx 1.1$ to nearly 1.0, showing that particles were very close but not in absolute contact when they crystallized.

The role of surfactant concentration was thus shown to be instrumental in controlling both the adsorption and organization of particles at the air/water interface. Adding a small amount of surfactant promoted particle adsorption but adding too much resulted in amorphous gel-like structures of “sticky” particles. Crystallization thus occurred at a specific C_s range where particles repelled each other with an inter-particle distance that decreased with an increase in C_s .

2.3.3 Role of the electrostatic surface properties of the particles

To investigate how the electrostatic properties of particles were affected by the presence of DTAB, we measured the zeta potential (ζ) of the aqueous particle suspensions under the conditions used in Figures 2.4A and 2.4B, by keeping $C_p = 0.05 \text{ mg/mL}$ and varying C_s (Figure 2.4C). The PS particles displayed a negative surface potential of $\zeta = -50 \text{ mV}$ in pure water, as a result of their dissociable surface groups (being mostly carboxylic acid). For DTAB concentrations up to $C_s = 10 \mu\text{M}$, ζ retained this value, indicating that in this C_s range there was no significant surfactant adsorption on the surface of the particles. With increasing DTAB concentration, the magnitude of the zeta potential started to decrease, assuming values of $\zeta = -31 \text{ mV}$ and $\zeta = -20 \text{ mV}$ for $C_s = 50 \mu\text{M}$ and $C_s = 100 \mu\text{M}$, respectively. Further addition of DTAB led to the neutralization ($C_s = 0.5 - 1 \text{ mM}$) and then to the sign reversal ($C_s = 5 - 10 \text{ mM}$) of the zeta potential, attributed to the formation of a monolayer and then a bilayer of DTAB molecules on particle surfaces, respectively.^[121] Particles adsorbed at the air/water interface thus significantly crystallized, *i.e.*, displayed a long-range order,

only when they remained highly negatively charged and thus repulsive ($5 \leq C_s \leq 100 \mu\text{M}$). In this C_s range, the correlation between the slight decrease in $|\zeta|$ and the decrease in the inter-particle distance (Figure 2.4B, inset) shows that the surfactant concentration tuned the inter-particle distance in crystal domains through the modulation of the electrostatic repulsion potential between the particles. Similarly, amorphous and gel-like structures were obtained when surfactant neutralized the particles ($C_s = 0.5 - 1 \text{ mM}$).

All these results show that short-range inter-particle repulsion was necessary for crystallization to occur, which occurred at a surfactant concentration significantly lower than that necessary to neutralize particles.

2.3.4 Effect of particle concentration on two-dimensional crystallization

We observed that, at a very low surfactant concentration, particles did adsorb while keeping a highly negative surface, but they did not crystallize. For instance, no crystallization occurred at $C_s = 1 \mu\text{M}$ and $C_p = 0.05 \text{ mg/mL}$ (Figure 2.4A) despite a highly negative zeta potential ($\zeta = -36 \text{ mV}$). Interestingly, this situation corresponded to the case where only a few particles were adsorbed to the air/water interface (Figure 2.2C). To assess whether crystallization could occur for a higher number of adsorbed particles at this surfactant concentration, I used the “flipping method” to prepare colloidal patches for various particle concentrations at a fixed $C_s = 1 \mu\text{M}$. For very dilute suspensions ($C_p = 0.01 \text{ mg/mL}$), almost no particles were present at the air/water interface ($N_{ads} = 290$). A gradual increase in N_{ads} was observed with increasing particle concentration from $C_p = 0.05 \text{ mg/mL}$ to $C_p = 1 \text{ mg/mL}$, with the respective values being $N_{ads} = 2.3 \cdot 10^3$ and $N_{ads} = 8 \cdot 10^3$. Further raising C_p to 5 mg/mL resulted in a more drastic increase in N_{ads} , which assumed a value of $2.3 \cdot 10^4$ (Figure 2.5B).

The number of interfacial particles had a profound effect on the microstructure of the 2D colloidal assemblies, as demonstrated by the corresponding RDF shown in Figure 2.5B (microscopy images are shown in Figure 2.5A). For the lowest particle concentration ($C_p = 0.01 \text{ mg/mL}$) and hence the minimum number of adsorbed particles, the resulting structure was relatively closely packed but lacked any long-range order. For $C_p = 0.05 - 0.5 \text{ mg/mL}$, the degree of order increased as shown by the emergence of sharp peaks at $r/D = 2$ and $r/D = 3$ in the RDF. Interestingly, further increasing the number of adsorbed particles by using more concentrated suspensions drastically improved the degree of two-dimensional order, which extended to distances $r/D = 7$ and $r/D = 9$ for respectively $C_p = 1 \text{ mg/mL}$ and $C_p = 5 \text{ mg/mL}$, corresponding to $N_{ads} = 8 \cdot 10^3$ and $N_{ads} = 2.3 \cdot 10^4$, respectively. Note that a similar evolution from disordered to more ordered structures with increasing C_p was also observed at a higher C_s ($10 \mu\text{M}$, Figure 2.6) but required lower values of C_p .

All these results show that a sufficiently high number of adsorbed particles is necessary for crystallization to occur and that the range of crystalline order increases with increasing N_{ads} , a parameter that is directly controlled by C_p . We attribute this effect to the long-range attraction between adsorbed particles driven by the deformation of the interface induced

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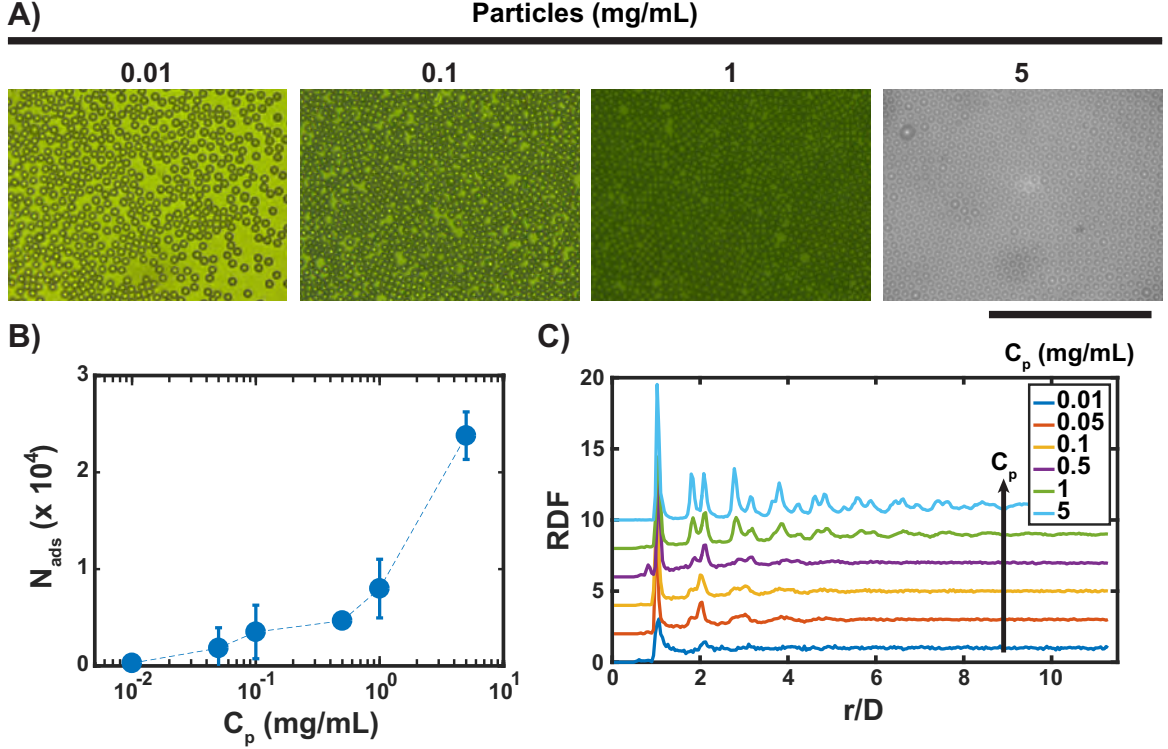


Figure 2.5: Raising the particle concentration C_p increases the number of particles adsorbed at the air/water interface and promotes 2D colloidal crystallization in patches prepared at a fixed DTAB concentration ($C_s = 1 \mu\text{M}$) using the “flipping method”. A) High magnification images of the centre of the interfacial assemblies obtained using brightfield transmission microscopy ($C_p = 0.01 - 1 \text{ mg/mL}$). Reflection microscopy was used at $C_p = 5 \text{ mg/mL}$ because excess of deposited particles at the bottom of the cell led to blurring of the transmission image. Scale bar: $100 \mu\text{m}$. B) Number of adsorbed particles (N_{ads}) at the air/water interface as a function of particle concentration. Symbols and error bars show mean values $\pm$ standard deviations from 3 individual experiments. C) Radial distribution function (RDF) computed from the images of the colloidal assemblies for different values of C_p . The RDFs are vertically offset for clarity. The RDF were calculated from larger fields of view ($253 \mu\text{m} \times 192 \mu\text{m}^2$) than the images in A.

by the weight of the particle ensemble. Due to the so-called ‘collective sinking effect’,^[31] increasing C_p and therefore N_{ads} results in a higher curvature that increases the long-range attraction potential between particles.

2.3.5 Comparison between “straight” and “flipping” method experiments

In this section I compare the results obtained previously in the laboratory (“straight” method), and the results I obtained successively (“flipping” method). As mentioned earlier (Figure 2.1 and 2.2), the adsorption and the self-organization behaviour of the particles at the air/water interface were qualitatively similar for the “straight” and the “flipping” methods. It is interesting at this point to scrutinize in more detail the microstructural properties of the interfacial colloidal assemblies resulting from these two methods. We begin by discussing the assemblies formed with the “straight” method using a fixed particle concentration ($C_p = 5 \text{ mg/mL}$)

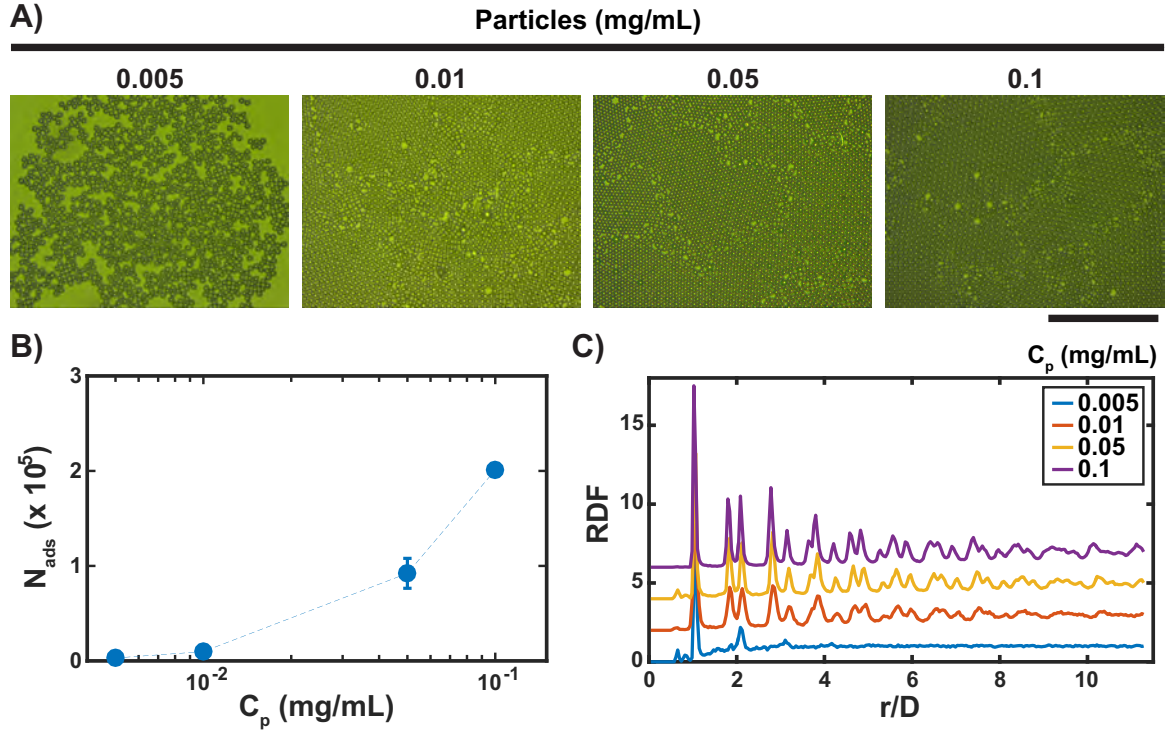


Figure 2.6: Evolution of the microstructure of the 2D colloidal assemblies obtained with the “flipping method” versus particle concentration at a fixed DTAB concentration ($C_s = 10 \mu\text{M}$). A) High magnification images of the centre of the interfacial assemblies obtained using brightfield transmission microscopy. B) The number of adsorbed particles (N_{ads}) at the air/water interface versus particle concentration (C_p). Symbols and error bars show mean values $\pm$ standard deviations from 3 individual experiments. C) The radial distribution functions (RDF) computed from the images in A). The RDFs are vertically offset for clarity. Scale bar: $100 \mu\text{m}$.

and varying C_s . A researcher of the laboratory utilized white light-based reflection confocal microscopy to visualize the structure of the assemblies with higher lateral resolution, as well as to quantitatively map the vertical positioning of single particles at the air/water interface, as discussed later in more detail. The height images corresponding to particle monolayers formed at different surfactant concentrations are shown in Figure 2.8A, and the respective RDFs are presented in Figure 2.8B. Highly organized polycrystalline patches were formed for all DTAB concentrations in the range $C_s = 1 - 100 \mu\text{M}$. However, the long-range order of the interfacial structures was dependent on the value of C_s . Well-ordered crystals for distances up to $r/D = 9$ were observed for $C_s = 1 - 50 \mu\text{M}$, with the inter-particle distance decreasing with increasing C_s . The range of order considerably decreased for $C_s = 100 - 500 \mu\text{M}$ while largely disordered particle monolayers were observed for $C_s \geq 1 \text{ mM}$. These results are in accordance with the ones obtained with the “flipping” method at the much lower particle concentration $C_p = 0.05 \text{ mg/mL}$, except for the extreme cases of very low and very high C_s . With the “straight” method, well-ordered crystals were obtained for $C_s = 1 \mu\text{M}$, whereas the “flipping” method led to the formation of an amorphous close-packed colloidal patch. This dissimilarity can be explained by the difference in the number of adsorbed particles, which

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was larger with the straight method due to the much higher C_p (Figure 2.7, to compare with Figure 2.2C). This is also in agreement with the fact that crystals were obtained at $C_s = 1$

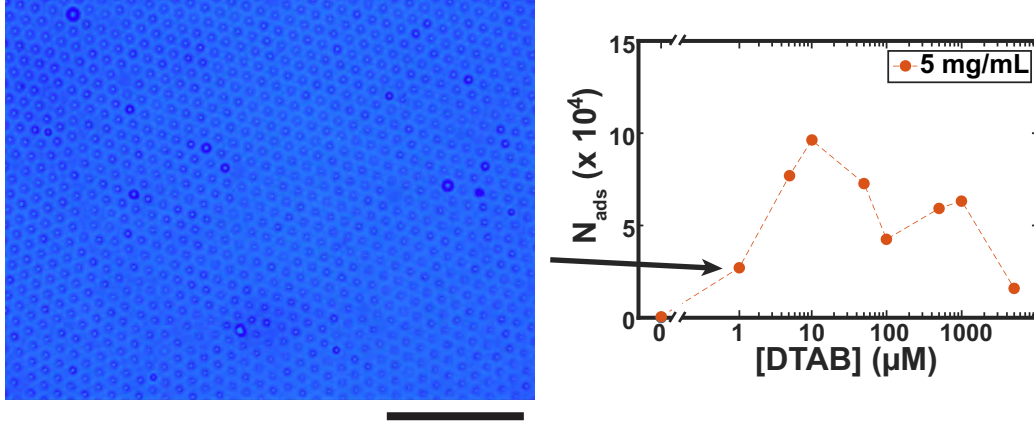


Figure 2.7: The number of adsorbed particles (N_{ads}) at the air/water interface versus DTAB concentration, at a fixed particle concentration ($C_p = 5 \text{ mg/mL}$), as obtained from the “straight method”. On the left high magnification image of the centre of the interfacial assembly at $C_s = 1 \text{ } \mu\text{M}$ obtained using reflection microscopy, showing a microstructure composed of particles arranged in a close-packed hexagonal lattice ($N_{ads} \approx 2.7 \cdot 10^4$). Scale bar: $50 \text{ } \mu\text{m}$.

μM using the “flipping” method by increasing C_p (Figure 2.5). For $C_s = 5 \text{ mM}$, the number of adsorbed particles obtained with the “straight” method was very low (Figure 2.8A) while it remained significant with the “flipping” method (Figure 2.2C). This difference may be attributed to the different mechanisms that transport particles to the free interface. With the “flipping” method, gravity was able to bring both single particles and aggregates formed in the bulk liquid to the air/water interface, while with the “straight” method convection more selectively transported single particles.

The results from both the “straight” and “flipping” methods show that a DTAB concentration of the order of μM induced the adsorption of particles at the air/water interface, regardless of the mechanism of transport (convection and sedimentation, respectively). Adsorbed particles crystallized only when they remained charged and, in that regime, surfactant concentration tuned the inter-particle distance in the colloidal crystal. For the “flipping” method, where the mechanism responsible for transporting particles to the interface was well controlled, increasing the particle concentration in the suspension led to a larger number of interfacial particles, which in turn favoured particle ordering.

2.3.6 Elucidating the role of particle contact angle at the liquid-gas interface

From the confocal images of the particles at the air/water interface (Figure 2.8A), we measured the maximum height (h) protruding in the air for each particle. This allowed us to calculate the contact angle (θ) measured through water that each individual particle made

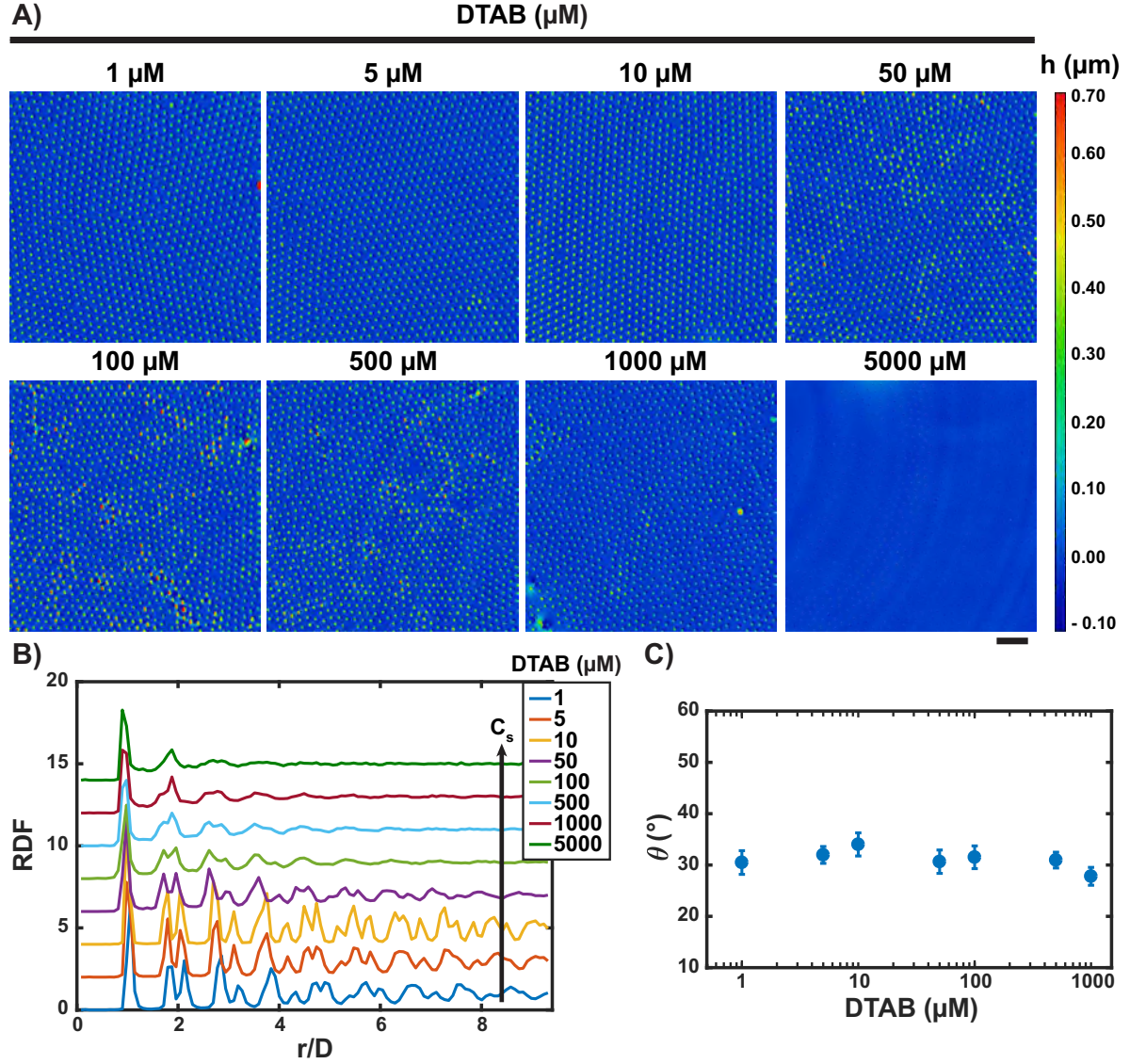


Figure 2.8: *In-situ* confocal microscopy experiments reveal the exact positioning in three-dimensions of the PS microparticles at the air/water interface obtained using the “straight” method. A) Height images of the interfacial particle assemblies obtained by varying C_s (given) at $C_p = 5$ mg/mL. h is the height protruding into air. The scale bar is $20\ \mu\text{m}$. B) Radial distribution function (RDF) corresponding to the height images shown in (A). The RDFs are vertically offset for ease of comparison. C) Average value of the contact point angle that each PS particle forms with the air/water interface as a function of C_s . There is no point at 5 mM because the images were not analysable due to the very small h values. Details of these measurements are included in Figure A.5.

with the air/water interface, $\theta = \arccos((D - 2h)/D)$ (the method I used is reported in Annex A.4). Confocal microscopy was used in the past and shown to extract reliable values of the contact angle of single particles.^[140] Here, we expanded this principle to measure *in-situ* the contact angle of a large number of individual microparticles at the air/water interface. Figure 2.8C shows the evolution of θ , averaged from about 10^3 individual particles, as a function of C_s for $C_p = 5$ mg/mL. Interestingly, the contact angle that the particles made with the air/water interface did not depend on DTAB concentration for $C_s = 1\ \mu\text{M} - 1$ mM,

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assuming a value of $\theta \approx 30$. This constant value of θ shows that changes in the wettability of the particles was not at the origin of the marked evolution of particle organization at the air/water interface, from highly crystalline to amorphous structures when C_s increased from 1 μM to 1 mM. Moreover, the value of $\theta \approx 30$ corresponds to a protruding fraction of the particle diameter into air of only $P = h/d \approx 6\%$. This strong immersion of particles in the water phase shows that the short-range electrostatic repulsion between adsorbed particles was mostly affected by the surface charge of particles in water. The zeta potential evolution measured in bulk (Figure 2.4C) was thus a good estimation of how this surface charge was affected by the concentration of surfactant and how in turn it directly controlled the organization of adsorbed particles.

2.3.7 Proposed explanation for particle adsorption at a very low cationic surfactant concentration

First, we have discovered that an amount of DTAB cationic surfactant of the order of $C_s = 1\text{--}10\ \mu\text{M}$ (*i.e.* three to four orders of magnitude lower than the CMC = 13.4 mM) induced the adsorption of anionic PS microparticles at the air/water interface. It is known that ionic surfactants adsorb onto oppositely charged particles and can in turn induce their adsorption to fluid interfaces, by significantly decreasing their charge and/or increasing their hydrophobicity.^[116;141] This is however not the mechanism explaining particle adsorption at such a low C_s observed in our experiments. As we demonstrated by zeta potential measurements in bulk (Figure 2.4C) and in-situ measurements of the particle contact angles at the air/water interface (Figure 2.8C), particles adsorbed at C_s where their wetting and electrostatic properties were almost unaffected by the presence of surfactant. We suggest instead that the main role of surfactant was through their adsorption at the air/water interface. We propose that the amount of adsorbed cationic surfactant at the liquid surface, although very small, was enough to reduce the energy barrier between adsorbing anionic particles and the air/water interface, which is the result of both the repulsive van der Waals and electrostatic interactions between them.^[16;17] An effect qualitatively similar to the surfactant-driven effect described here has been reported in similar PS latex suspensions, where the addition of simple electrolytes resulted in enhanced particle adsorption to the air/water interface.^[17;18] In addition, organic salts with hydrophobic ions have been used for promoting the adsorption of oppositely charged nanoparticles to oil/water interfaces.^[87] The height of the adsorption barrier, described by the classical DLVO theory after considering the effects of the solvation zone around the particles and the air/water interfacial regions, decreased with increasing ionic strength of the suspension.^[18] We believe that the surfactant cations have an action similar to electrolytes (see Section 3.3.3), however they are more effective than the latter as they can work at very low concentrations due to their preferential accumulation at the air/water interface, acting effectively as ‘super-salts’. Our suggested mechanism is confirmed by our

observation that using anionic instead of cationic surfactant did not induce particle adsorption (Figure 2.3B) presumably because they increase the electrostatic adsorption barrier for anionic particles.

2.3.8 Proposed mechanism and phase diagram of interfacial particle organization

Based on our results, we can propose a general mechanism for the adsorption and subsequent organization of anionic particles at the air/water interface, in the presence of a small amount of cationic surfactant. Cationic surfactant induced particle adsorption at a concentration C_s that was large enough to decrease the electrostatic barrier for particle adsorption at the interface but small enough for the particle charge to be preserved (Figure 2.4C), thus resulting in short-range electrostatic repulsion between adsorbed particles which were mostly immersed in the water phase (Figure 2.8C). Once adsorbed, the interfacial microparticles did not leave the free interface, which was due to the reduction of the total surface energy associated with the transport of the particles from the bulk to the partially wetted state at the interface,^[48] resulting in the ‘capillary trapping’ of particles at the interface in agreement with earlier work. The contact angle of the particle-surfactant aqueous mixture with the walls of the sample cell was always less than 90° , resulting in a concave meniscus (see Figure A.6 in Annex). As a result, all adsorbed particles were subjected to a curvature-driven gravity transport toward the center of the air/water interface, resulting in a long-range attractive potential toward the center of the patch. The combination of this long-range attraction with the short-range electrostatic repulsion at low C_s led to particle organization into polycrystalline patches. We can thus discuss how both surfactant (C_s) and particle (C_p) concentrations controlled the way particles organized once adsorbed at the air/water interface. The general trend was that increasing C_s , by promoting surfactant adsorption both at the air/water interface and onto the surfaces of the particles, decreased the electrostatic potential between particles. This first resulted in a decrease in the inter-particle distance within the colloidal crystals accompanied by a progressive loss of the long-range order. At large C_s , particles were not repulsive anymore and formed amorphous gels. Increasing C_s , by increasing the number of adsorbed particles, led to a stronger long-range attraction potential due to the collective deformation of the interface by adsorbed particles. It thus promoted crystallization for surfactant concentrations at which adsorbed particles remained repulsive. To analyse the synergistic role of these two parameters, we built a phase diagram where we represented the experimentally observed state, *i.e.* amorphous or crystal, as a function of C_s and C_p (Figure 2.9). In this phase diagram, four zones were qualitatively distinguished. At low C_s and C_p , the number of adsorbed particles was very small, resulting in a too weak long-range attractive potential: the particles thus formed a disordered phase (zone 1). At a given C_s , increasing C_p promoted particle crystallization by the ‘collective sinking mechanism’, an effect becoming weaker when the number of adsorbed particles induced by surfactant increased, *i.e.*

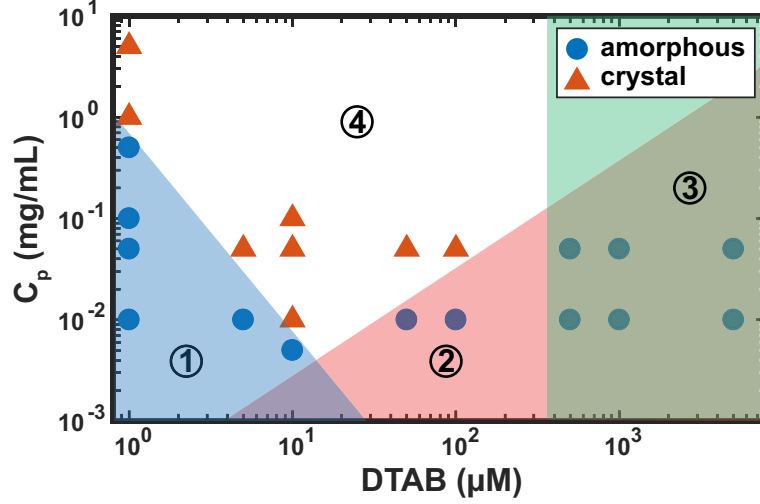


Figure 2.9: Phase diagram of the patch organization as a function of PS particle and DTAB surfactant concentrations. Symbols are experimental data depicting an amorphous (blue circle) or a polycrystalline (orange triangle) state. The background colors qualitatively depict 4 zones (see main text for details).

by increasing C_s . The slope between zones 1 and 4 was thus negative. At a moderately higher C_s but low C_p (zone 2), particles did not crystallize because they were partially neutralized by surfactant. Increasing C_p at constant C_s again promoted crystallization, but this effect became stronger with a decrease in particle charge, *i.e.* when C_s increased. The slope between zones 2 and 4 was thus positive in that case. With a further increase in C_s , particles became almost fully neutralized by surfactant, leading to sticky particles within the patches. The adsorbed particles thus formed amorphous gels, most probably regardless of particle concentration (zone 3). Zone 4 thus corresponds to the situation where both C_s and C_p allowed the adsorption and organization of a large number of repulsive particles into 2D polycrystalline patches.

2.3.9 Generalization of 2D crystallization method with other surfactants and particles

We hypothesized that our 2D crystallization method should be applicable to different anionic particle/cationic surfactant systems. To assess its breadth of applicability, I first kept the same PS anionic particles but replaced DTAB with a more hydrophobic cationic surfactant, hexadecyltrimethylammonium bromide (CTAB). As expected, CTAB induced particle adsorption and crystallization at the air/water interface in a way similar to DTAB (Figures 2.10 and 2.11). Particle adsorption was however promoted at a lower C_s (Figure 2.10 *cf.* Figure 2.2), which we attribute to the higher surface activity of CTAB ($\text{CMC} = 0.92 \text{ mM}^{[121]}$), implying that a lower amount of surfactant was enough to efficiently decrease the adsorption barrier. Interestingly, the formation of gels was also observed at C_s corresponding to particle neutralization (Figures 2.10 and 2.11).

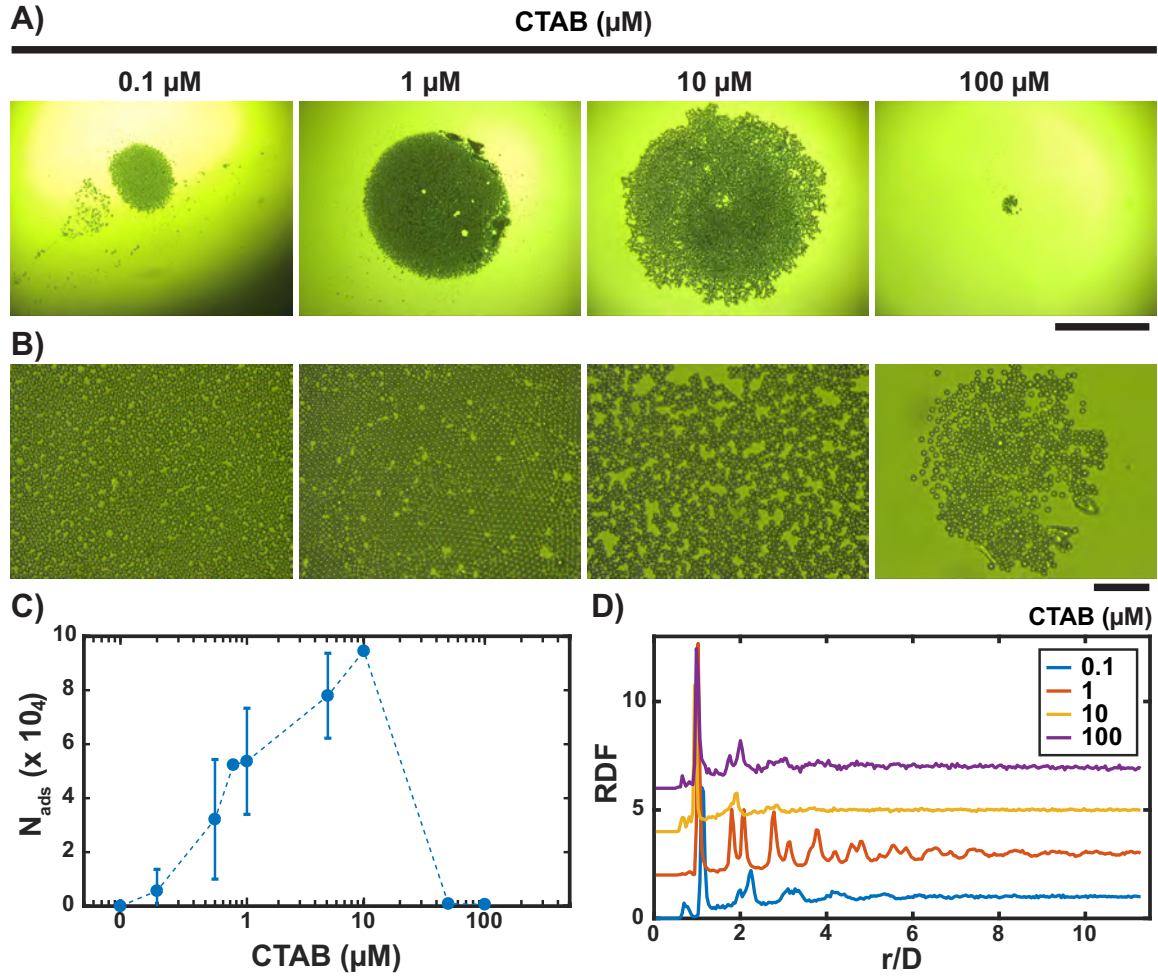


Figure 2.10: Evolution of the adsorption and organization of PS particles at the air/water interface as a function of CTAB concentration, at a fixed particle concentration ($C_p = 0.05 \text{ mg/mL}$), obtained using the “flipping method”. A) Representative brightfield transmission microscopy images of the patch structure. Scale bar: 1 mm. B) High magnification images of the centre of each assembly displayed in (A), evidencing the 2D organization. Scale bar: 50 μm . C) Number of particles adsorbed at the air/water interface, N_{ads} , as a function of CTAB concentration, using the “flipping method”. D) Radial distribution function (RDF) computed from images as in (B), as a function of CTAB concentration. The RDFs are vertically offset for the ease of comparison.

Next, I kept DTAB as the cationic surfactant but used hydrophilic anionic silica particles (diameter 4.6 μm , possessing surface silanol groups) instead of anionic PS particles. Because silica particles (1.85 g/cm^3 according to the manufacturer) are denser than PS particles (1.06 g/cm^3), I used the “flipping” method to study their adsorption and crystallization behaviour at the air/water interface. In the case of surfactant-free dispersions, I observed no particle adsorption at the air/water interface. On the contrary, 2D crystals were obtained when DTAB was added to the suspension at the same concentration ($C_s = 10 \mu\text{M}$) as in the case of PS particles (Figure 2.12). Interestingly, the entire colloidal assembly was crystalline in the case of silica particles, a feature never observed in the case of PS particles. Additionally, due to their higher density, the silica particles quickly accumulated at the center of the

2. ADSORPTION AND CRYSTALLIZATION OF PARTICLES AT THE AIR/WATER INTERFACE

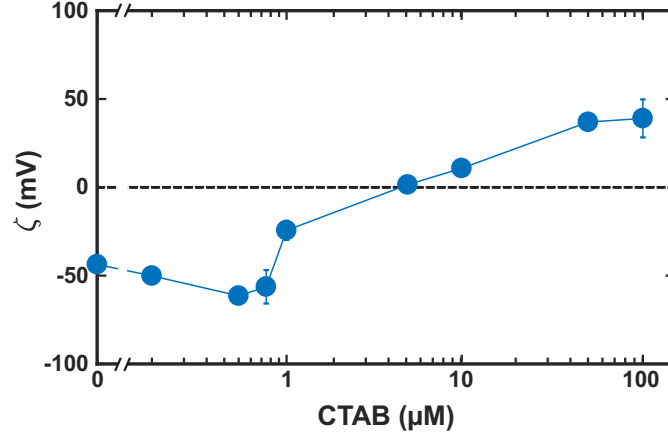


Figure 2.11: Zeta potential (ζ) measurements of mixtures of PS particles ($C_p = 0.05$ mg/mL) with varying concentrations of CTAB. Symbols represent mean values of six independent measurements. The error bars (standard deviation), if not shown, are smaller than the symbol size.

air/water interface, resulting in a much faster crystallization kinetics compared to the case of the PS particles of similar size. Under our experimental conditions, crystallization occurred simultaneously with particles gathering at the center of the air/water interface, resulting in the whole patch being formed and fully crystallized in typically 20 minutes after the second flipping of the cell. We believe that those aspects are a direct consequence of the “collective sinking effect”,^[31] which was more pronounced in the case of silica microparticles due to their higher density. Finally, we observed that the monocrystalline domains were generally composed of a higher number of particles compared to the PS case, presumably due to the lower size polydispersity of the silica particles. Interestingly, the highly ordered organization of silica particles led to structural optical properties. With a lateral white light illumination, the patches displayed selective reflection, allowing one to distinguish adjacent monocrystalline domains through the color shift induced by the abrupt change in domain orientation (Figure 2.12B).

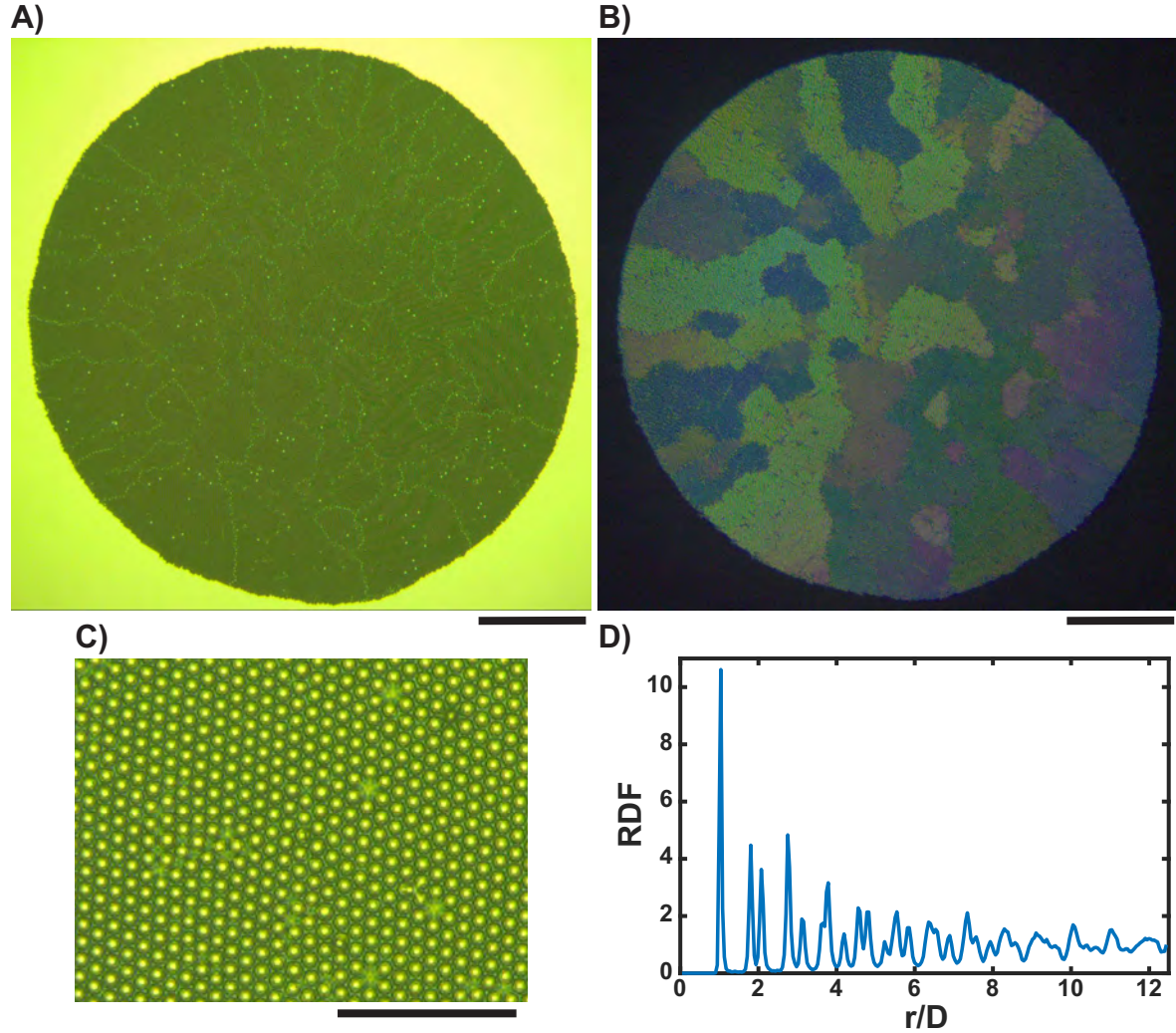


Figure 2.12: DTAB induces the adsorption and subsequent crystallization of negatively charged silica microparticles (diameter $4.6 \mu\text{m}$) at the air/water interface. A) Transmission microscopy image of a 2D polycrystalline patch obtained with the “flipping” method at $C_s = 10 \mu\text{M}$ and $C_p = 0.05 \text{ mg/mL}$. B) Reflection image of the same sample as in A) obtained using white light illumination from the side of the chamber. The emergence of structural colors allows one to distinguish adjacent monocrystalline domains. C) High magnification image of the central region of the colloidal patch in A). D) RDF computed from an area of $250 \mu\text{m} \times 190 \mu\text{m}^2$ of the colloidal crystal. The scale bars are $300 \mu\text{m}$ (A, B) and $50 \mu\text{m}$ (C).

2.4 Conclusions

We have shown that cationic surfactants induced the adsorption of anionic particles at the air/water interface at concentrations typically 10^3 smaller than their CMC. At such concentrations, surfactant could decrease the adsorption barrier of particles at the air/water interface but did not significantly affect the charge of particles. Particles thus adsorbed with a low contact angle and remained stabilized (*i.e.*, they did not aggregate) mostly through electrostatic repulsions operating in the water phase. I demonstrated that when the number of adsorbed particles was high enough, the combination of inter-particle electrostatic repulsion and the long-range gravity-driven attraction *via* the collective deformation of the interface led to the formation of highly-ordered polycrystalline assemblies. I showed that inter-particle repulsion and long-range attraction was directly controlled by surfactant and particle concentrations, respectively, making it possible to control not only the type of organization (disordered, densely-packed crystalline, densely-packed amorphous, loosely packed gel) of the two-dimensional colloidal assemblies, but also the inter-particle distance.

With these findings, we have critically expanded the potential of surfactants to control the behaviour of particles at interfaces. Widely used to increase particle hydrophobicity or to modify interfacial energies, we have shown here that surfactants can also directly govern colloidal crystallization at the air/water interface.

The next chapter will be dedicated to broaden our approach for scientific and, possible, industrial interest. A large variety of nanoparticles, forming two-dimensional structures bearing interesting properties, will be tested, ranging from silica to metals with diverse surface modifications. At the same time surfactant-free approaches for various user needs will be presented. The results here described will also be the starting point for the experiments reported in Chapters 5 and 6, where precise and contact-less control over two-dimensional particles organization will be provided by means of external light stimulation.

Expanding 2D colloidal organization: surfactant-induced assembly of nanoparticles and surfactant-free approaches

3.1 Abstract

The previous chapter opened two different directions: on one hand, can we apply our method to assemble in one step 2D structures of nanoparticles at the air/water interface? On the other hand, can we explore the system from another point of view, *i.e.*, achieving surfactant-free adsorption and organization of particles, to open future directions of the study and new perspectives? In the previous chapter we reported a simple method to adsorb in a complete manner negatively charged particles from bulk solution to the air/water interface by addition of micromolar amounts of oppositely charged surfactant, using only gravity as external force. As a next step, I explore here how to achieve adsorption and organization of micro to nano-size particles having different bulk and surface chemistry (silica and metal particles with different coatings), showing how to control their assembly into mm-sized 2D crystals having intense structural colouration. At the same time, I investigate how to remove surfactants from the system. For this scope, two possibilities are addressed: i) salt-induced adsorption of anionic particles, investigating the effect of changing the counterion properties (*i.e.*, their valence and hydration properties); and ii) spontaneous adsorption of cationic particles in aqueous solution to investigate how particles bearing charge opposite to the one of the liquid surface adsorb, and eventually organize, on it. With these findings, I evidence that our method can be easily adapted to various user needs in terms of molecules and particles added in the aqueous mixture, thus allowing to obtain on-demand different 2D particles organizations.

3.2 Introduction

The first two sections examined the potentiality of our one-step method for adsorption and organization of particles at the water surface (Chapter 2) by adding small amount of cationic surfactant to solutions of colloidal particles having different size and composition. Two-dimensional materials made of colloidal particles, organized in a long range ordered fashion, find several applications in science and technology.^[65;122;142] Particularly, structures composed of building-blocks down to nano-size dimensions, are an important goal in material science due to their specific responses arising from collective interactions. For example, they can be used for the fabrication of sensors,^[88] surfaces with desired wettability^[143] and reflective responses,^[85] or for biomimetic materials.^[83] Among others, optical properties are an exciting feature of colloidal monolayers, which can exhibit structural colouration arising from the interaction of the incident light with periodic variations in refractive index. Due to their light processing properties, photonic crystals are extensively studied to control, diffract, transmit or amplify the incoming radiation.^[75] A well-defined periodic arrangement is required for the desired interaction with light, therefore precise control over the particles positioning and order is of utmost importance.

Liquid/liquid interfaces are a useful tool as template for the formation of self-assembled structures,^[64] with particles monolayers that spans over macroscopic dimensions, having an exceptionally high degree of positional order, up to single crystals of mm² size.^[112] If particles are deposited on a solid surface, they remain in fixed positions and in a defined arrangement. On the contrary, the weak forces governing their self-assembly at a liquid interface generate adaptable and reconfigurable structures, with the possibility to repair errors during the structure formation. The “softness” and flexibility of the liquid interface allows to produce responsive devices with tunable properties,^[86;131;144] where particles can rearrange following an external stimulation. Typically, particles are added to a liquid interface by means of spreading drops from a concentrated suspension in a volatile solvent, either close to the liquid interface, or onto a hydrophilic substrate touching the target liquid surface.^[108] Crystallization will be achieved either increasing the number of adsorbed particles by several additions of spread drops,^[67] or by compressing the monolayer with moving barriers (as in a Langmuir trough)^[68] – a more detailed description is provided in Chapter 1. Few one-step methods, with direct particles assembly on a liquid interface from a suspension in one of the two phases, have been studied, including emulsification^[87] or centrifugation.^[86] In both cases external energy has to be applied to favour particle-interface proximity; and addition of salt has found to be a requirement for complete adsorption.

In the following work I show that our method, using micromolar amounts of oppositely charged surfactant and only gravity as external force, can be extended to particles having different bulk composition (silica, silver and gold), surface chemistry, shape and sizes down

3. EXPANDING 2D COLLOIDAL ORGANIZATION: NANOPARTICLES AND SURFACTANT-FREE APPROACHES

to ~ 100 nm. Self-organization of the adsorbed particles results in the formation, for silica particles, of mm-sized two-dimensional crystals showing intense structural colouration. Varying the amount of surfactant in the mixture allows to assembly either light-processing ordered structures, or amorphous aggregates. Metal nanoparticles can be efficiently adsorbed at the air/water interface too, resulting in a variation of the reflective properties of the interface. Gravity is used both to bring the particles to the interface, and is involved in the “collective sinking effect”^[31] determining the close-packed arrangement within the aggregates. Nonetheless, we show that this does not hinder nanoparticles adsorption and the formation of mesoscopic crystals in a well-controlled manner. These results emphasize how such method can be a valid alternative to other methodologies for particles assembly, without the requirement of external solvents, nor millimolar amounts of salt, being extremely simple yet powerful.

The third section is dedicated on studying whether salts added in the particles mixtures could be employed, instead of micromolar-amount of surfactant, to reach similar adsorption and organization of the particles at the air/water surface. The role of salt addition to particles mixtures for promoting particles adsorption at air/water or oil/water interfaces as already been reported,^[17;18;145] and in many experimental formulations the presence of salt has found to be fundamental to reach substantial particles accumulation at liquid interfaces.^[22;114;128] Although the addition of salts is known to induce aggregation of pre-formed crystalline colloidal monolayers,^[22;38] a detailed description of the effect of different salts both on the adsorption of particles from bulk solution, and on their subsequent 2D collective organization is still lacking.^[11] Here, I will report the results on the spontaneous adsorption and controlled arrangement into various structures (crystals, gels) of particles at the air/water interface as a function of salt content in the mixtures, varying two important parameters: the counterion valence, and the counterion size and hydration properties.

Mixtures of particles and salts are extensively studied in bulk solution.^[146–150] Particles aggregation in bulk follows the Schulze–Hardy rule, which dictates that the salt concentration to promote aggregation decreases increasing the counterion valence. The classical DLVO theory of particles aggregation predicts a similar effect. A trend in particles aggregation as a function of the counterion size cannot be predicted by the classical DLVO theory since ion specificity is not considered, apart from their valence. However, the presence of counterion of different size and hydration properties affects particles aggregation as well. Specifically, the results can be rationalized following the Hofmeister series.^[149] The Hofmeister series^[151;152] was created from protein precipitation experiments, and it classifies ions according to their increasing stabilization power of protein solutions. Considering only the cations is as follows:

$$N(CH_3)_4^+ < NH_4^+ < Cs^+ < Rb^+ < K^+ < Na^+ < Li^+ < Mg^{2+} < Ca^{2+}$$

In the case of negatively charged particles aggregation, bigger and poorly hydrated counterions (left side) cause aggregation at a lower concentration than the small and strongly

3.3 Experimental results and discussion

hydrated ones (such as Na^+ or Li^+). The far right ions having higher valence should be excluded due to their effect following the Schulze–Hardy rule, that has a greater impact. It is important to note that the surface characteristics play a role as well; while this picture is true for hydrophobic particles (such as polystyrene), hydrophilic particles follow the Hofmeister series in the opposite direction.^[149] The preliminary results reported here investigate the effect of varying the counterion properties on the adsorption and organization of negatively charged particles at the air/water interface, and are qualitatively compared with the results in bulk water solutions.

Finally, the last section is dedicated to the study of mixtures of positively charged particles dispersed in water solution, to assess in which conditions they adsorb to the water surface from the bulk phase, and in which conditions they can form highly ordered 2D assemblies. In the previous chapter we proposed that the amount of cationic surfactant adsorbed at the air/water interface – or salt added in bulk solution –, by reducing the energy barrier between anionic particles and the water surface, a consequence of both van der Waals and electrostatic repulsive interactions between them,^[16;17] was fundamental to adsorb anionic particles at the air/water interface. On the contrary, cationic particles would not experience such electrostatic repulsion from a negative surface,^[19;20] but instead they would experience an attractive component. Therefore, they could readily adsorb to the interface from a dispersion in pure MQ water, if the electrostatic repulsion was actually the main cause preventing adsorption of anionic particles. Furthermore, if highly charged, a mechanism similar to the one responsible for promoting the crystallization of anionic particles is expected to hold also for adsorbed cationic particles; being independent on the actual sign of the particle charge. In the related section, I will show how cationic particles can be adsorbed at the air/water interface, and how particle-surface modification can be exploited to control their collective 2D organization.

3.3 Experimental results and discussion

3.3.1 Silica particles: from micro to nano

Our experimental system to adsorb particles to the air/water interface from bulk solution in a complete manner has been described in Chapter 2 (see Figure 2.2). We showed that positively charged surfactant (normally dodecyltrimethylammonium bromide, DTAB) at a concentration $C_s \geq 1 \mu\text{M}$ could induce complete adsorption of anionic particles. A slightly concave meniscus of the water solution permits all the adsorbed particles to collect in the centre of the experimental cell used, where they collectively organize. Such collective organization, for polystyrene particles, was found to be dependent on both particles and surfactant concentrations. Adsorption and crystallization was possible also for silica particles. In the following section I expand our method by studying mixtures of silica particles of different diameters with increasing amounts of positively charged surfactant.

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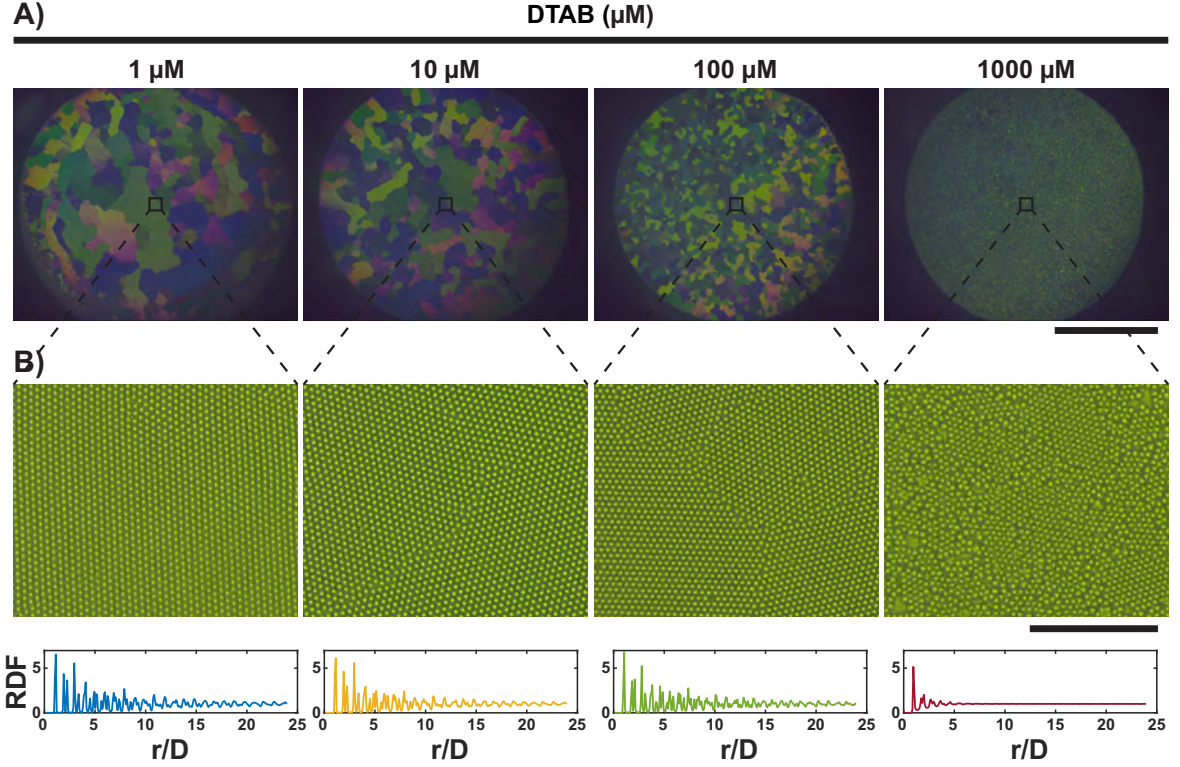


Figure 3.1: *Controlling the organization of silica microparticles adsorbed at the air/water interface. A) Representative optical microscopy images of the particles aggregates on the water surface. The samples are illuminated with a white light source normal to the liquid surface (see Annex A.2.1), and are composed of silica particles (diameter: $2.4\ \mu\text{m}$, $C_p = 0.05\ \text{mg/mL}$) mixed with various concentrations of cationic surfactant (dodecyltrimethylammonium bromide, DTAB). Scale bar: $1\ \text{mm}$. B) High magnification brightfield transmission microscopy images of the centre of the aggregates in (A). Scale bar: $50\ \mu\text{m}$. Bottom row: radial distribution functions (RDFs) calculated in a larger window of the same images, of size $253 \times 192\ \mu\text{m}^2$. D is the particle diameter, r the distance from a reference particle.*

Figure 3.1 shows the controlled organization of silica particles (having a diameter of $2.4\ \mu\text{m}$), at fixed concentration $C_p = 0.05\ \text{mg/mL}$, as a function of surfactant concentration. Optical microscopy images obtained with a white light source parallel to the water interface allow for a direct visualization of the macroscopic structure within the aggregate (Figure 3.1A. A sketch of the optical set-up is reported in Annex A.2.1). Each single-crystal domain reflects light with different colourations depending on its main directions and on the curvature of the overall crystal. We point out that, due to the weight of the whole structure (also described as “collective sinking effect”^[31]), the interface is lower from the centre to the edge. From the different colourations, the size of the domains in the crystal structure can be easily detected. Their size can be tuned depending on the DTAB content: from larger domains at $C_s = 1\ \mu\text{M}$, to smaller ones at $C_s = 100\ \mu\text{M}$. A further increase of C_s causes the particles to arrange in an overall disordered aggregate, with an almost complete loss of the structural colouration. High magnification brightfield transmission microscopy images of the centre of the aggregates in Figure 3.1A are showed in Figure 3.1B, allowing for a description of the microstructure

3.3 Experimental results and discussion

of the adsorbed particles monolayer, together with a precise characterization of the particles positional order by analysing their radial distribution functions (RDFs). A low concentration of surfactant corresponds to long range hexagonal packing, with an almost complete absence of defects in the field of view (left image, at $C_s = 1 \mu\text{M}$), with peaks in the RDF indicating a well-ordered arrangement exceeding 24 particles diameters. At $C_s = 10 \mu\text{M}$ a grain boundary arises in the zoomed image and, upon incrementing the surfactant concentration, more and more grain boundaries are formed. Finally, a different organization state is obtained at $C_s = 1 \text{ mM}$, where small crystallites are surrounded by particles arranged in a disordered fashion; the RDF reaches value 1 (disordered state) after less than 5 particles diameters.

Therefore, as for micrometer-size polystyrene particles (*cf.* Chapter 2), varying the amount of surfactant allows forming, in a fully controlled fashion, different structures also with silica particles. Interestingly, the inherent surface properties of the two different particles (hydrophobic for polystyrene, hydrophilic for silica) did not affect the range of oppositely charged surfactant concentration required. These results confirm, in contrast, that the process is mainly dictated by the particle charge, being negative for both particles. Because of the higher density of silica particles compared to polystyrene (1.85 g/cm^3 according to the manufacturer, compared to 1.06 g/cm^3 for polystyrene), and the consequent higher deformation of the air/water interface in the centre of the cell, the particles are always in close contact. Mm-size single-crystals are easily obtained at defined $C_s = 1 \mu\text{M}$, and the whole aggregate self-organize in an ordered fashion, from the centre to the edge. Moreover, in the presence of crystal domains, such structures display intense structural colouration.

In the method used, gravity play a role in bringing particles to the interface during cell flipping, and it is involved also in the sinking effect^[31] determining the close-packed arrangement within the aggregates. Nonetheless, I show in Figure 3.2 that it is also able to contribute to the formation of mm-size 2D crystals composed of nanoparticles, despite their reduced weight. For this purpose, I prepared samples containing silica nanoparticles of different size at a low ($C_s = 5 \mu\text{M}$) and high ($C_s = 1 \text{ mM}$) surfactant concentration. Due to the small size of particles and thus extended sedimentation time, I kept the same protocol as for microparticles (*cf.* Chapter 2), but I increaased the time with the cell upside down to 24 hours. After flipping back the cell, I found that 6 hours was enough for all particles to accumulate and organize at the centre of the cell. Representative images of the particles aggregates at the water surface, for different particles diameter and surfactant concentration, are showed in Figure 3.2. The intense structural colouration, for the samples at $C_s = 5 \mu\text{M}$, is an indication of the formation of long range ordered 2D crystals. On the contrary, the whitish structures for $C_s = 1 \text{ mM}$ indicates the presence of disordered particles aggregates, which scatter the incoming white light in a random fashion.

To ensure that the structural colours in Figure 3.2A were actually due to the formation of an ordered monolayer, I transferred the particles aggregate onto a solid substrate for further microscopic characterization with a scanning electron microscope (SEM). For this scope, I

3. EXPANDING 2D COLLOIDAL ORGANIZATION: NANOPARTICLES AND SURFACTANT-FREE APPROACHES

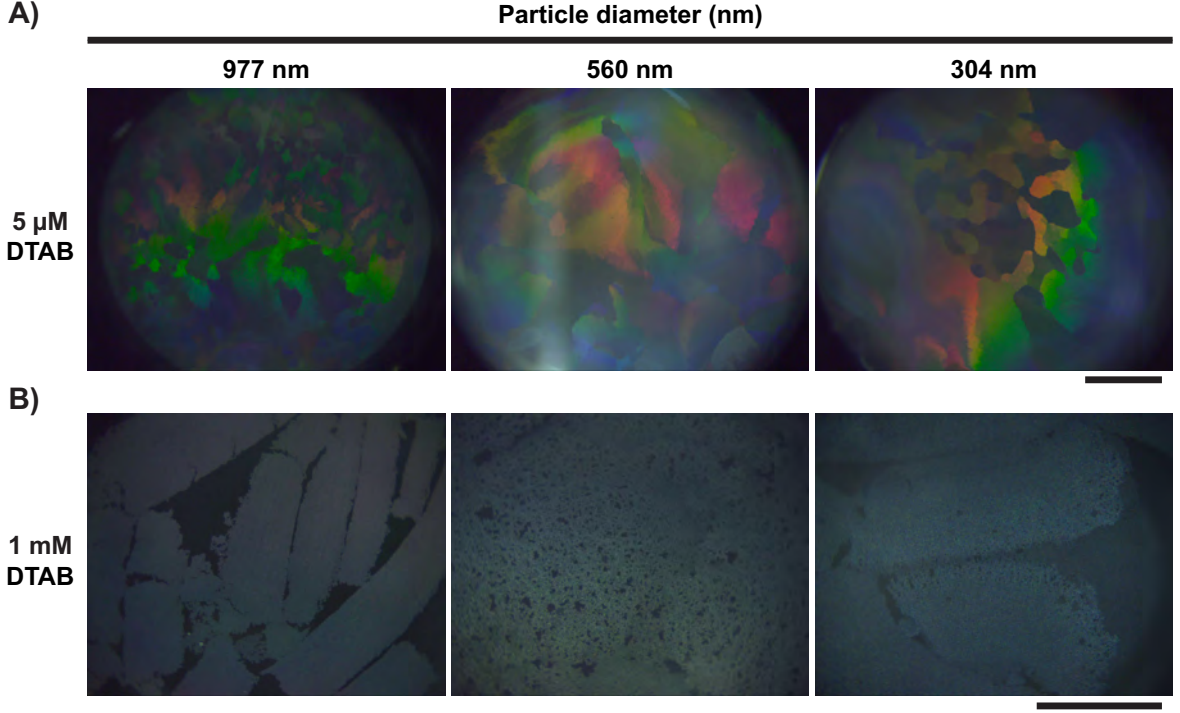


Figure 3.2: Tuning the structural properties of silica nanoparticles adsorbed at the air/water interface. Representative optical microscopy images of the particles aggregates at the air/water interface for silica particles ($C_p = 0.05 \text{ mg/mL}$) having different diameters: 977 nm (left column), 560 nm (middle column), 304 nm (right column). In A) $C_s = 5 \mu\text{M}$; in B) $C_s = 1 \text{ mM}$. Scale bars for all images: 1 mm.

used modified open chambers glued on glass slides (a description of the procedure is reported in Annex A.3). Following particles adsorption at the water surface, slow evaporation of the water solution was allowed. Complete evaporation ensured transferring of the particles structure to the solid substrate. Note that the last step of evaporation is non-homogeneous because water accumulates on the side of the cell, close to the meniscus with the side wall, leaving only a thin layer in the middle, where the adsorbed particles are. The thin layer is the first to evaporate, causing deposition of particles starting from the centre toward the edge of the aggregate. As a consequence of the non-homogeneous evaporation, we expect to slightly perturb the particles structure during deposition. Finally, the glued cells were removed, leaving glass slides with the aggregates prepared at the air/water surface transferred on them.

Representative images of the centre of the deposits on the solid substrate are displayed in Figure 3.3. In particular, Figure 3.3A shows the positional order achieved in case of a low surfactant concentration ($C_s = 5 \mu\text{M}$). Few grain boundaries and vacancies are present; nonetheless, overall the particles are placed in a hexagonally ordered, close-packed array, giving an indirect proof that the nanoparticles structures as in Figure 3.2A are two-dimensional crystals (presumably having a much broader long-range order). Conversely, for sample mixtures containing $C_s = 1 \text{ mM}$ (Figure 3.3B), the structures on the solid substrates are not

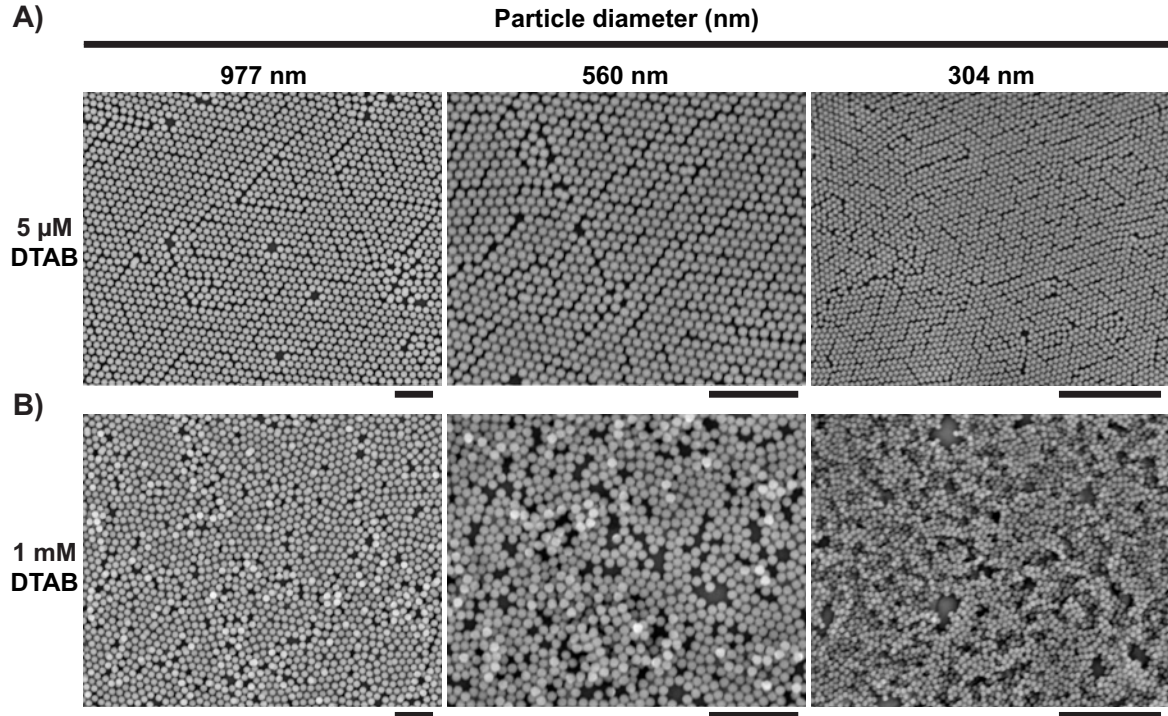


Figure 3.3: Microstructure of the particles aggregate adsorbed at the air/water interface and then transferred to a glass substrate, as imaged using a scanning electron microscope (SEM). Samples composed of particles ($C_p = 0.05$ mg/mL) having different diameters: 977 nm (left column), 560 nm (middle column), 304 nm (right column). In A) $C_s = 5$ μ M; in B) $C_s = 1$ mM. Scale bars for all images: 5 μ m.

ordered, and several particles are deposited on a second layer (or several layers in the case of particles having diameter of 304 nm). Being highly improbable that some of the particles adsorbed at the air/water interface were out of the water phase, we believe that the successive layers are due to the deposition of clusters of aggregated particles already present on the water surface. The images in Figure 3.3B give an indirect proof that the nanoparticles structures as in Figure 3.2B are amorphous aggregates. Therefore, as for microparticles, the concentration of surfactant added in the sample mixture permits a precise tuning of the organization state of nanoparticles adsorbed at the air/water interface: extended colloidal crystals at a very low C_s (~ 5 μ M) and disordered assemblies at significantly higher concentration.

We can conclude that both the controlled adsorption and the final 2D arrangement of the negatively charged particles as a function of the concentration of the cationic surfactant used (DTAB) is independent not only on the particle surface properties (polystyrene microparticles, Chapter 2; silica microparticles, Figure 3.1), but also on the particle size (up to diameter ~ 300 nm); thus rendering our method potentially valuable for a vast range of applications.

3.3.2 Silver and gold nanoparticles

Finally, I investigated if metal nanoparticles, commonly employed for the assembly of light processing 2D structures, such as photonic crystals^[131] or liquid mirrors,^[85] could be adsorbed

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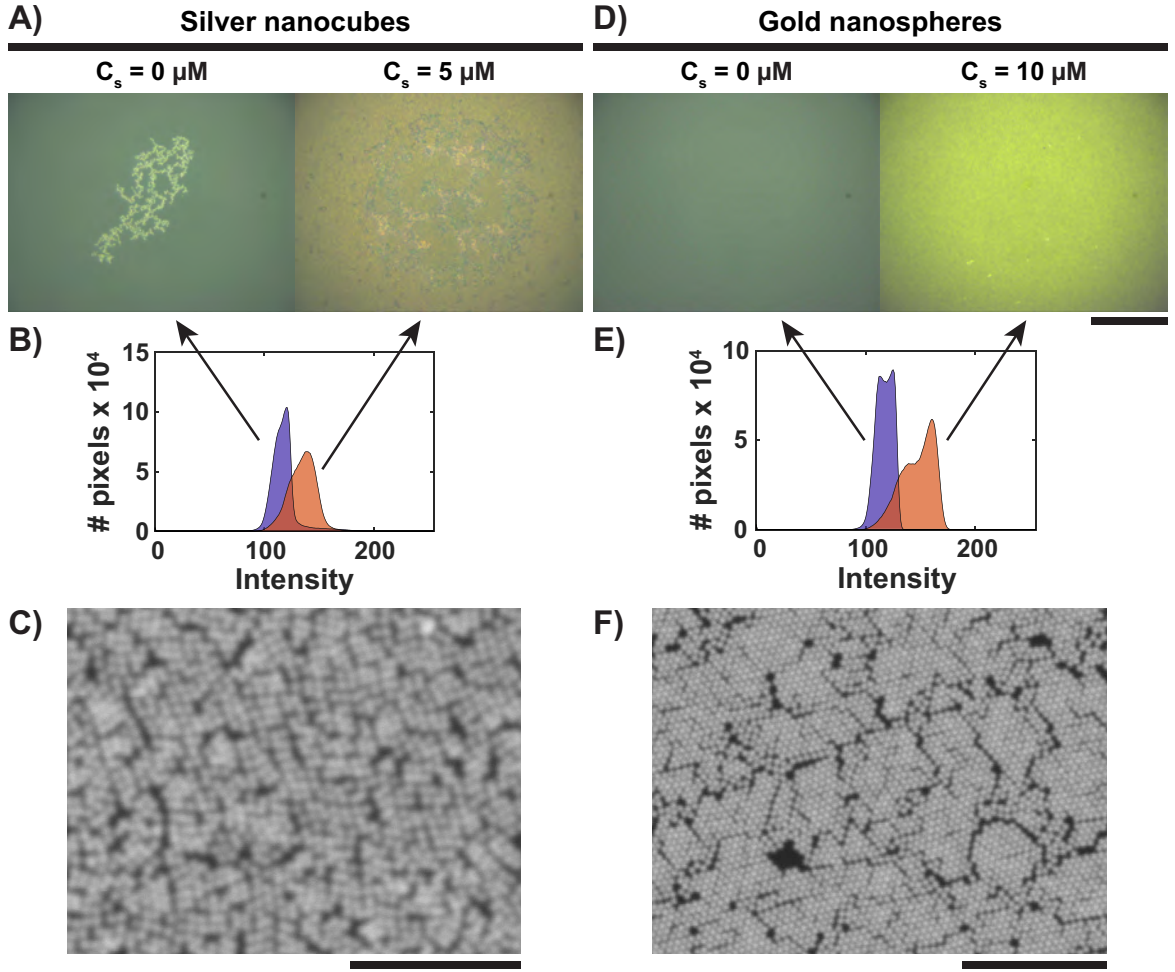


Figure 3.4: Surfactant-induced adsorption of silver and gold nanoparticles at the air/water interface. A; D) Representative reflection microscopy images of the air/water interface of samples containing $C_p = 8 \mu\text{g/mL}$ of silver cubes having a size of 100 nm (A); or gold spheres with a diameter of 100 nm (D) and various concentration of DTAB. Scale bars for all images: 100 μm . B) Pixel intensity distribution of the images in A): the blue curve correspond to $C_s = 0 \mu\text{M}$, the orange curve to $C_s = 5 \mu\text{M}$, showing an increase in light reflection from the interface in the presence of particles. C) SEM image of the microstructure of the particles aggregate in A), right image, adsorbed at the air/water interface and then transferred to a glass substrate. E) Pixel intensity distribution of the images in D): the blue curve correspond to $C_s = 0 \mu\text{M}$, the orange curve to $C_s = 10 \mu\text{M}$. F) SEM image of the microstructure of the particles aggregate in C), right image, adsorbed at the air/water interface and then transferred to a glass substrate.

at the air/water interface using our method. To assess, at the same time, a broader applicability of the method, and its independence on many particles characteristics, I tested particles having different surface chemistry, namely silver nanocubes coated with Poly(vinylpyrrolidone) (PVP) and gold nanospheres coated either with Lipoic acid, or with Poly(ethylene glycol) (PEG) with COOH termination. The absence of surfactant in the sample mixture, once more, resulted in no adsorption of particles at the air/water interface (Figure 3.4A and D). Note that, in the case of silver nanoparticles, a small aggregate could be observed in the centre of the cell, but otherwise the interface was exempt of particles. In contrast, adding the

same quantity of surfactant as for mixtures containing polystyrene or silica particles, resulted in a complete coverage of the air/water interface with particles. Figures 3.4A and D show high magnification images focused at the air/water interface in the centre of the chambers for samples containing $C_s = 5 \mu\text{M}$ for silver nanoparticles, and $C_s = 10 \mu\text{M}$ for gold nanoparticles, in direct reflection mode. In Figures 3.4B and 3.4E we quantified the amount of light reflected by an interface covered with particles, compared to the air/water surface without particles, by looking at the pixel intensity distribution of the images in Figure 3.4A and 3.4D respectively. The histograms corresponding to the images of the air/water interface of mixtures containing surfactant are showed with orange areas. A shift towards higher intensity of the orange areas indicates that the interface, when $C_s > 0$, reflects more of the incoming white light. We believe this is a preliminary indication that the surface was covered with metallic particles, thus allowing enhanced reflection of the incident light.

SEM images of the aggregates deposited on the solid substrate are showed in Figures 3.4C and F. As already mentioned, perturbation of the particles structure at the water surface is expected, especially for such small particles. For silica nanocubes, only small crystallites are visible in the SEM images (Figure 3.4C). It is important to note that they have a higher polydispersity (from producer: 6.7% coefficient of variation of diameter) that hinders the formation of a long-range ordered structure. In the case of gold nanospheres, on the contrary, SEM images reveal the hexagonal organization of the particles into several crystallites (Figure 3.4F).

We can conclude that, although we could not bring any direct evidence of the formation of highly ordered structures at the air/water interface, small (100 nm in diameter) metal nanoparticles could be efficiently adsorbed at the water surface using minute amount of cationic surfactants, independently on the particles bulk and surface properties (as proved by the different surface coatings), as soon as such particles are negatively charged. To our knowledge, this is the first time that such an effect is reported. Further experiments are required to fully characterize and control the structural organization of such nanoparticles.

3.3.3 Particle adsorption mediated by salt addition: the effect of varying valence and size of the counterion

In this section, I studied the effect of various salts first on the adsorption, and then on the organization, of negatively charged polystyrene microparticles (cross-linked particles with both sulphate and high density of carboxyl functional groups on their surface, diameter $5.1 \mu\text{m}$) at the air/water interface by using the “flipping method” (sketch of the method in Figure 2.2). Three salts were chosen in order to have a preliminary comparison on the two effects mentioned in the introduction for the case of bulk solutions: different counterion size and hydration properties, different valence. For this purpose, NaCl, tetramethylammonium bromide (TMAB) and MgCl_2 were employed. NaCl and TMAB are compared because the counterions (Na^+ and $\text{N}(\text{CH}_3)_4^+$, TMA^+) have both valence one, but are very far in the

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Hofmeister series; TMA^+ is much bigger and poorly hydrated. Even though they do not share the same anion, the difference between Cl^- and Br^- is considered to be much less relevant because of their similarities in the Hofmeister series of anions when interacting with hydrophobic, negatively charged particles.^[152;153] NaCl and MgCl_2 are compared because of the different valence of the counterions Na^+ and Mg^{2+} .

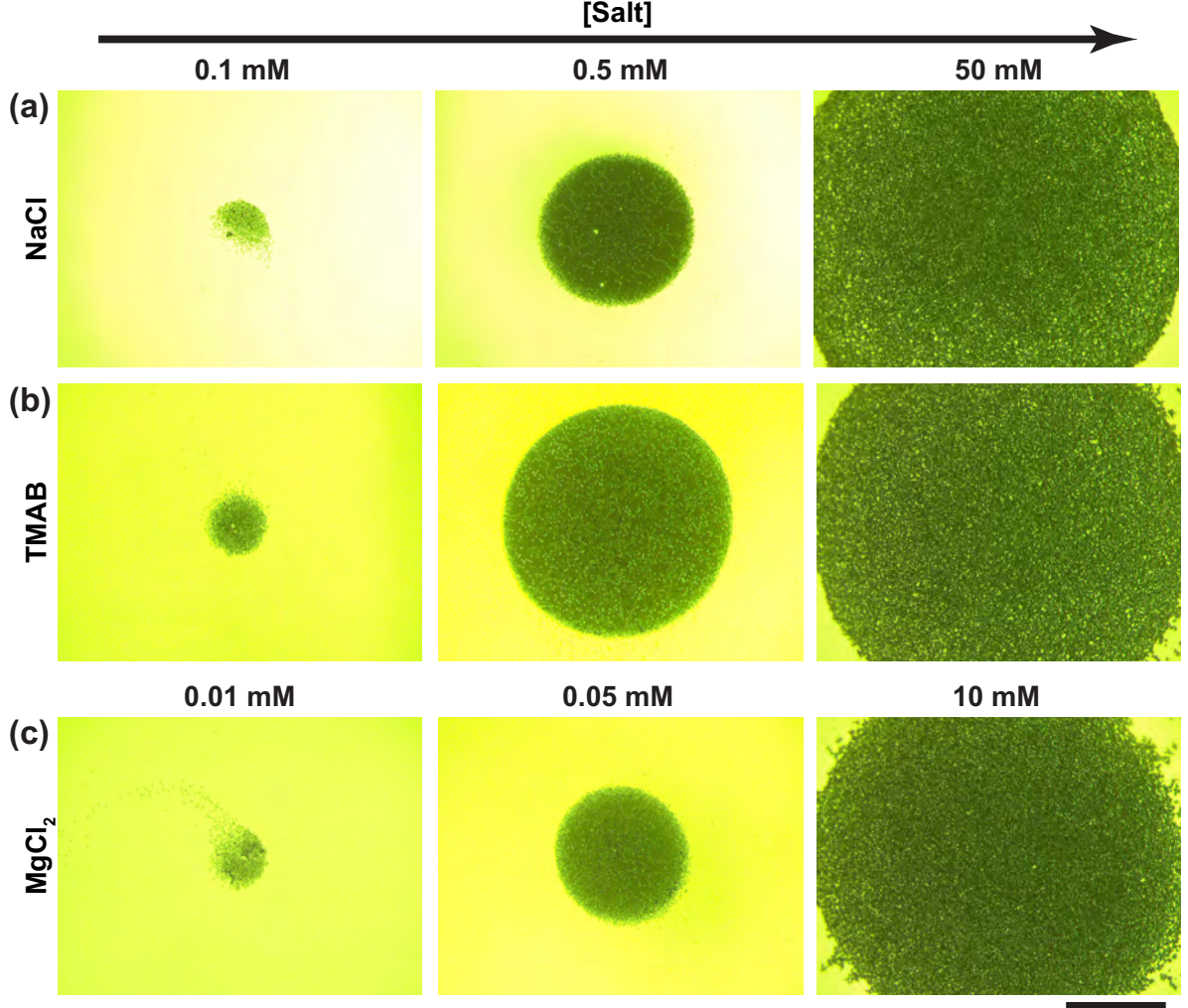


Figure 3.5: Controlled adsorption and organization of negatively charged particles at the air/water interface mediated by addition of different salts, using the “flipping method”. Brightfield transmission microscopy images of the air/water interface with a particle concentration of $C_p = 0.05$ mg/mL, as a function of salt concentration: NaCl (a), tetramethylammonium bromide (TMAB) (b) and MgCl_2 (c). 2D colloidal assemblies organize as a function of the salt concentration: disordered (left column), polycrystalline (centre), closely packed and disordered (right). See Figure 3.6 for a better view of the particle organization in the structures. Scale bar: $500\ \mu\text{m}$.

Figures 3.5 and 3.6 show the main results obtained mixing a fixed amount of particles ($C_p = 0.05$ mg/mL) with increasing concentration of salts. I will begin by describing the effect of adding NaCl to the particles mixtures; those results will be successively compared with the other salts analysed. Addition of 0.1 mM induces adsorption of a small amount of particles to the liquid surface, forming a disordered patch of roughly circular shape (Figure

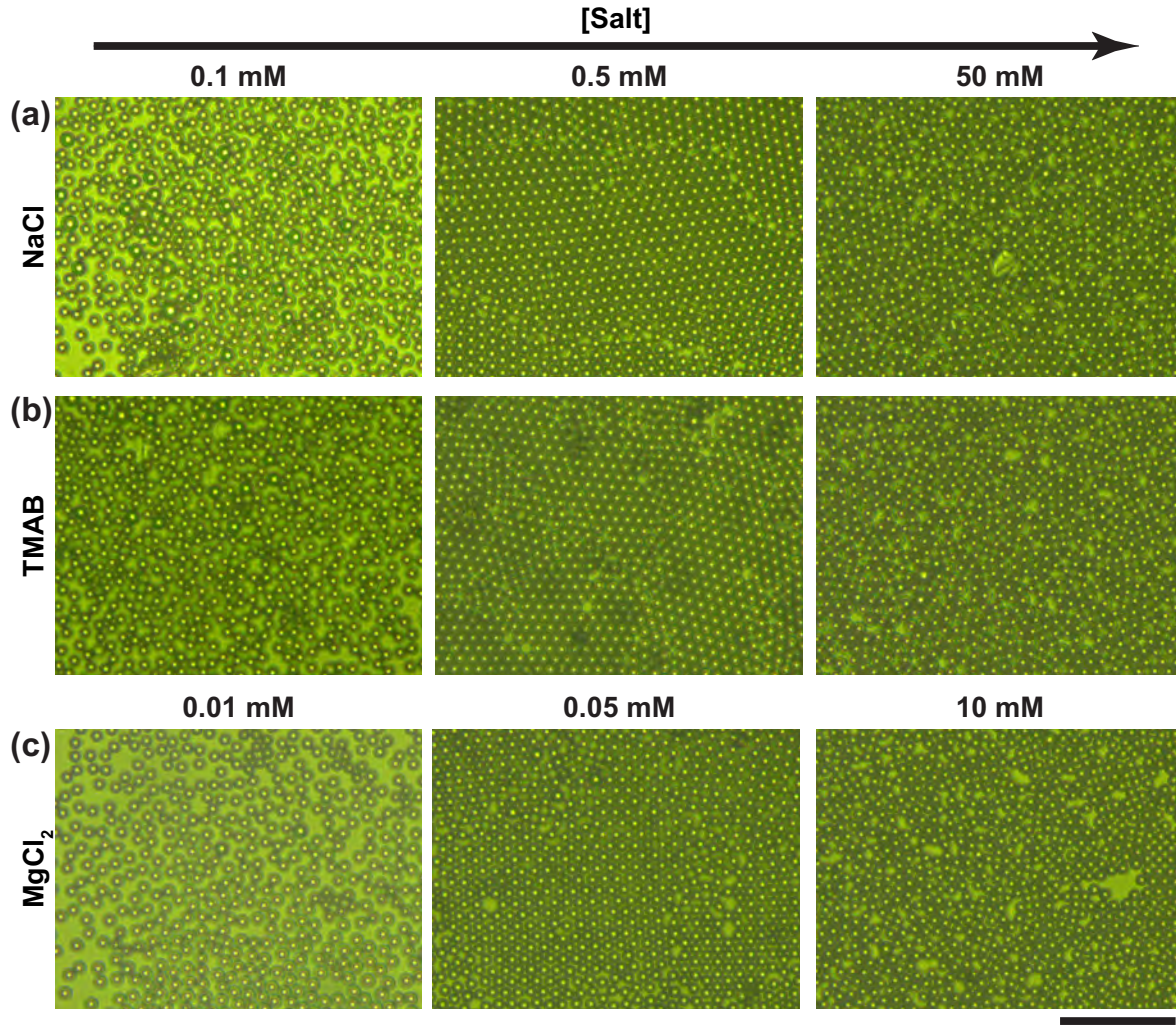


Figure 3.6: Salts concentration (increased from left to right) tunes the organization of particles adsorbed at the air/water interface, using the “flipping method”. High magnification brightfield transmission microscopy images of the 2D colloidal assemblies as in 3.5. Scale bar: 50 μm .

3.5(a), left). The arrangement is relatively dense (Figure 3.6(a), left), but the particles are free to move by Brownian motion. Increasing the NaCl concentration to 0.5 mM leads to a large increase in the number of adsorbed particles, and to the formation of a dense circular patch (Figure 3.5(a), centre). The particles arrange in a close-packed hexagonal lattice (2D crystal) with few defects and grain boundaries (Figure 3.6(a), centre). A further increase in NaCl concentration up to 50 mM causes the adsorption of an increased number of particles to the air/water interface. Now the adsorbed particles form a loosely packed, roughly circular, aggregate (Figure 3.5(a), right), where they do not show any Brownian motion, instead forming a gel-like structure of “sticky” particles (Figure 3.6(a), right).

As already reported, the onset of particles adsorption to the air/water interface following the addition of an electrolyte is due to the overcome of the electrostatic adsorption barrier.^[11] Once a large number of particles is adsorbed at the interface, the long-range attraction potential caused by the local deformation of the interface allows 2D crystallization of the

3. EXPANDING 2D COLLOIDAL ORGANIZATION: NANOPARTICLES AND SURFACTANT-FREE APPROACHES

particles; a requirement being that most of their charge is kept in order to ensure particle-particle short range repulsion. Further aggregation of colloidal monolayers by an increase of the bulk salt concentration has already been evidenced for monolayers at air/water^[22] or oil/water interfaces.^[38] The main difference with our experiments being that in their case particles were added externally to the liquid surface (through the spreading technique); the monolayer was at first formed, and successively perturbed by addition of salt in the subphase. In our case, instead, is the initial composition of the mixture, in terms of particle and salt concentration, that dictates how particles will organize on the water surface.

When TMAB is employed, the first significant adsorption of particles at the air/water interface is observed at the same salt concentration (0.1 mM) as the NaCl case. A similar small, disordered patch is formed (Figure 3.5(b) and Figure 3.6(b), left). Close-packed hexagonal arrangement of adsorbed particles starts forming at $[\text{TMAB}] = 0.5 \text{ mM}$, therefore at the same concentration of salt as using NaCl (Figure 3.5(b), centre). However, the domains contain, on average, a lower number of particles, and more vacancies and grain boundaries are present (Figure 3.6(b), centre). In addition, few particles are seen entering in and out the focal plane, therefore they seem to be not trapped at the air/water interface, but instead close to it, probably through interactions with the neighbouring, adsorbed, particles. Rising the TMAB concentration causes the formation of loosely packed aggregates of adsorbed particles from $[\text{TMAB}] = 50 \text{ mM}$; also in this case they form a gel-like structure of attached particles (Figure 3.5(b) and Figure 3.6(b), right).

Overall, both looking at particles adsorption to the air/water interface, and at their 2D organization, we can conclude that the trend as a function of NaCl and TMAB concentration is similar, with comparable structures at the same salt content. Particles adsorption, depending on the suppression of the adsorption barrier, is expected to happen at a lower salt content in the event that the salt employed tends to accumulate preferentially at the air/water interface (lowering the adsorption barrier). Both from experiments and simulations it has been observed a difference in the accumulation of various cations and anions to the air/water surface, and it has been concluded that such accumulation, or depletion, is ion specific.^[154] In our experimental system, such eventual effect has not been detected. If there is a difference in the accumulation of the cations, or anions, at the air/water interface, this difference is smaller than the one detectable, indirectly, by the accumulation of particles at a diverse salt concentration. Regarding the onset of particles aggregation, as explained previously, in bulk solution negatively charged polystyrene beads are expected to aggregate at a lower salt concentration when a salt on the left of the Hofmeister series is used. Contrarily, the similarity detected in our experiments at the liquid interface could be explained by considering all the components governing the final 2D ordering, which depends not only on the particle-particle interactions – governed by the amount of added molecules, being surfactants or salts – but also on the long-range attraction potential due to the collective deformation of the interface by the adsorbed particles. If the addition of equal amounts of NaCl or TMAB modifies only

3.3 Experimental results and discussion

slightly the particle-particle interactions, the presence of the other component – predominant if a number of particles above a certain threshold adsorb at the interface (Figures 2.5 and 2.6) – in our experimental system results in a similar trend varying the salts content. Further experiments are required to see whether a difference between NaCl and TMAB is actually present also in our system, but in a narrower concentration range.

When MgCl_2 is added to a mixture of negatively charged particles, notable adsorption of particles to the air/water interface is observed at $[\text{MgCl}_2] = 0.01 \text{ mM}$ (Figure 3.5(c), left); that is, at a concentration one order of magnitude less than using monovalent salts. Similar trend in MgCl_2 concentration compared to monovalent salts is maintained for the formation of polycrystalline structures, that are observed at $[\text{MgCl}_2] = 0.05 \text{ mM}$ (Figure 3.5(c) and Figure 3.6(c), centre). Finally, particles aggregation into gel-like structures is achieved at $[\text{MgCl}_2] = 10 \text{ mM}$ (Figure 3.5(c) and Figure 3.6(c), right).

As already mentioned, particles adsorption is dependent on the height of the adsorption barrier, which is related to the repulsion between negatively charged particles and the negative charge of the water surface. The presence of divalent cations has a dramatic effect on the counterion distribution at a negatively charged surface, accumulating close to the surface and lowering the magnitude of the surface potential.^[12] As a consequence, the adsorption barrier is overcome at a lower salt concentration. Aggregation at a lower salt content using a divalent salt compared to a monovalent one is a result in agreement with the DLVO theory of particles aggregation in bulk solution.^[148] On the basis of DLVO theory, the transition from a stable charged particle suspension to an unstable one due to higher salt concentration scales as the inverse of the counterion valence. Nevertheless, an increased number of experiments at salts (NaCl and MgCl_2) concentrations close to the ones reported in Figures 3.5 and 3.6 are required in order to assess precisely at which NaCl or MgCl_2 concentration irreversible 2D aggregation of the adsorbed particles occurs.

In conclusion, we showed that salts soluble in water can be efficiently used to promote the adsorption of dispersed particles at the air/water interface, and, furthermore, control the 2D organization of the adsorbed particles into amorphous aggregates of repulsive particles at low salt content, polycrystalline structures at slightly higher salt concentration, irreversibly trapped gel structures upon further increase of the salt content. No effect has been detected employing counterions of different size and hydration properties, contrarily to what happens for mixtures of particles in bulk solution. Instead, as expected, cations of different valence shift the salt concentration required to adsorb, crystallize or aggregate particles at the water surface in a similar way as what is predicted for particles in bulk water solution.

3.3.4 Positively charged particles

As proposed in the previous chapter, and further studied in the previous sections, cationic surfactant had to be added in negatively charged particles mixtures in order to adsorb particles to the air/water interface. We suggested that it was due to the fact that surfactants

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adsorbed to the water surface and caused a decrease of the energy barrier between anionic particles and the liquid surface itself. It is of great interest, then, to study the behaviour of positively charged particles, instead of negative ones; such barrier, being dependent on electrostatic and van der Waals interactions, would be of less extent for cationic particles dispersed in water solution.

To test whether cationic particles would adsorb at the air/water interface in the absence of added molecules in the water phase, I prepared positively charged particles by modifying the surface of silica beads ($4.6\ \mu\text{m}$ in diameter) by means of controlled adsorption of positively charged polymers on the, negative, silica surface (see Annex, section A.1.1, for a description of the procedure). I chose to modify these anionic particles because they were shown to form 2D long-range ordered structures in the presence of minute amounts of surfactant (Figure 2.12). By this approach we could really focus on the effect of particle surface charge. Two polymers were tested, namely poly-L-lysine (PLL) and poly(diallyldimethylammonium chloride) (PDADMAC), which gave modified particles having a ζ -potential value of $44.0 \pm 0.1\ \text{mV}$ and $53.7 \pm 1.4\ \text{mV}$, respectively for PLL- and PDADMAC-modified particles. The obtained positive particles were stable and easy to disperse in water, and used within two days from their preparation. A mixture of $0.05\ \text{mg/mL}$ particles in pure MQ water was prepared, and the usual “flipping” procedure (depicted in Figure 2.2) was used to study whether particles adsorbed at the air/water interface, and compare the obtained results with those obtained with the bare negatively charged particles in the presence of surfactants.

Transmission microscopy images of the interface (Figure 3.7A and B) reveal that the particles indeed adsorbed in great quantity, similarly to mixtures of the same unmodified particles and DTAB at $C_s = 10\ \mu\text{M}$ (Figure 2.12). Specifically, the aggregates presented a number of adsorbed particles (N_{ads}) equal to 10^5 for PLL-modified particles and to $9.5 \cdot 10^4$ for PDADMAC-modified particles, comparable to the value for the same particles without surface modification that was $N_{ads} = 9.8 \cdot 10^4$. These results emphasize once more that the electrostatic interaction between particles and the interface is a key factor determining the adsorption properties of particles at an air/water surface. Cationic particles readily adsorbed in the absence of any added molecules or electrolytes.

The actual particle charge value plays a key role in their organization within the aggregate at the interface. In Figure 3.7C and D are reported high magnification images of the centre of the structures in A and B; from such images RDFs can be extracted, in order to quantitatively compare the particles positional order (Figure 3.7E). PLL-modified particles bear a charge, in absolute value, similar to the one that the same bare particles (or the previously used anionic polystyrene particles) have when mixed with minute amount of oppositely charged surfactant (DTAB at $C_s = 5 - 10\ \mu\text{M}$). The resulting organization at the air/water interface is comparable: long-range hexagonal packing with particles in close contact. As for the same silica particles (unmodified) plus $10\ \mu\text{M}$ of DTAB, showed in Figure 2.12, the whole structure is fully ordered. Conversely, PDADMAC-modified particles bear a higher absolute

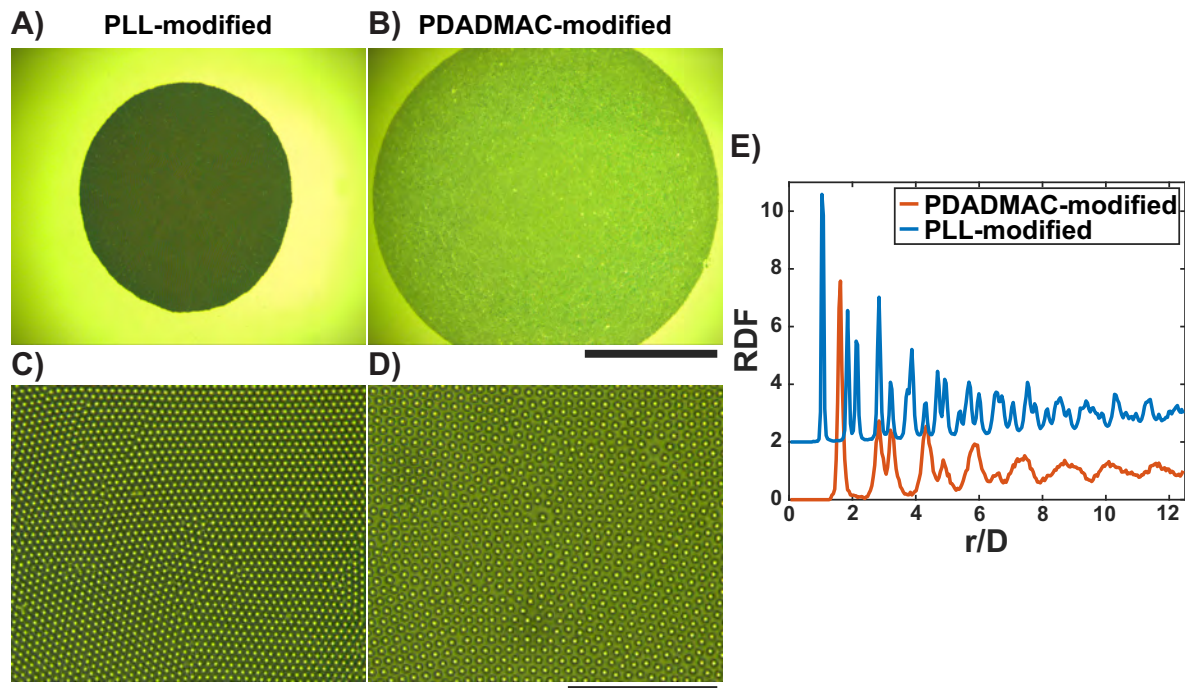


Figure 3.7: Transmission microscopy images of 2D crystals of positively charged particles with different surface modification, adsorbed at the air/water interface using the “flipping method”. A) 0.05 mg/mL PLL-modified particles in MQ water. B) 0.05 mg/mL PDADMAC-modified particles in MQ water. Scale bar for A-B: 1 cm. C-D) High magnification images of the centre of the aggregates respectively in A and B. Scale bar for C-D: 100 μm . E) RDFs obtained from the images in C (blue curve) and D (red curve). The RDFs are vertically offset for the ease of comparison.

surface charge value. As a consequence, the interparticle separation increases, with nearest neighbours at $r/D \approx 1.6$, even in the centre of the aggregate where the pressure of the surrounding particles is the highest. The particles are organized in hexagonal packing, even though with a decreased long-range ordering, as revealed by less resolved peaks at long separation distance. As predicted theoretically,^[31] a larger aggregate containing the same number of particles, but more charged and consequently more separated, would exert a lower long-range attraction, in addition to an increased particle-particle coulombic repulsion. The both effect play a crucial role in particles organization causing self-assembly into a less ordered structure compared to the PLL-modified particles case.

3.4 Conclusions

In this chapter I explored the wide-range applicability that our method for adsorbing and organizing particles at the air/water interface previously described in Chapter 2 can have in terms of system parameters (particle size, charge, surfactant-free approaches). The results demonstrated that this method to directly adsorb negatively charged particles from bulk in a controlled manner can be efficiently applied to mixture of nanoparticles of various bulk or surface composition. Minute amounts of cationic surfactant were shown to tune the 2D

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organization of adsorbed silica nanoparticles, ranging from extended polycrystalline structures (capable of intense structural colouration) to amorphous gels. Metal nanoparticles were also efficiently adsorbed, opening interesting perspectives for potential applications in optics, sensor and catalysis.

In addition, two surfactant-free approaches were tested. Although the use of salts to induce anionic particles adsorption to a liquid interface, and to control the aggregation of already formed monolayers was already reported, our results represent a starting point to expand the current scientific knowledge. For this purpose, different salts (in terms of counterions valence and size) were compared for their effect both on the adsorption properties of negative particles to the water surface, and on their consequent 2D organization. As already reported for bulk solution of similar particles, cations of increased valence were found to shift adsorption, crystallization and aggregation of particles at a lower salt content. Instead, counterion of different size and hydration properties did not modified the properties of the particles used, presumably because the other interaction at play (long-range attraction potential) was more relevant to dictate the final particles arrangement at the interface.

Finally, in the last section I presented how the particles surface charge affected their adsorption properties and subsequent collective arrangement. In particular, we showed that positively charged particles dispersed in pure water solutions readily adsorbed at the air/water interface, forming large 2D polycrystalline structures in the absence of any additive. Interestingly, the inter-particle distance could be tuned by changing the value of the surface charge.

Taken together, the results examined in Chapters 2 and 3 highlight our one-step method as a valuable platform for studying particle-liquid surface interactions, as well as particle-particle interactions in the adsorbed monolayers, in an additive-free manner, for possible applications in the fabrication of novel 2D colloidal structures. In this regard, mm-sized polycrystalline structures of nanoparticles showing intense structural colouration were reported, together with promising results using metal nanoparticles for controlled surface reflectance.

Part II

Dynamic photocontrol of particles organization at the air/water interface

Part two of the thesis is mainly devoted to the implementation of light-dependent responses on particles assemblies at the air/water interface. Stimulus-responsive colloidal systems are sought after for the development of novel devices, but are also interesting as model systems of natural self-assembled structures that are controlled by external stimulations. While light-controlled assemblies and organization of solid particles in bulk liquid phases have been subject of great interest in the scientific community, similar approaches at liquid interfaces, surprisingly, have not been explored yet. Our objective is to gain control over the collective assembly of adsorbed particles in order to switch, with a fast response-time (ms to s) between ordered and disordered structures in a fully dynamic and reversible fashion. Interestingly, the system described in Chapter 6 will demonstrate that the obtained two-dimensional crystals can be dissipative out-of-equilibrium structures that exist only throughout the external supply of energy, and quickly fall apart after stimulus removal.

Chapter 4 introduces some concepts of self-assembly, playfully described by Grzybowski as «the ultimate dream of a lazy scientist: just mix the components, and the forces of nature will assemble them into a desired structure», and the use of particles as building blocks. Dynamic dissipative self-assembly will be discussed in particular giving examples both from nature and man-made systems. Successively, the focus will be on light stimulation as the main source to drive static or dynamic self-assembly of particles, both in bulk solutions and at the liquid interface, and different operating principles will be summarized.

Chapters 5 and 6 report our two conceptually different systems where the structures of particles at the air/water interface is controlled in time and space by light patterns created using LED sources. In particular, in **Chapter 5** light absorbing particles, made of polystyrene with iron oxide inclusions, are used to convert the light stimulation into a structural response. Starting from two-dimensional crystals, several operations can be performed exploiting various light irradiation conditions and conversion of light energy into localized heat at the particle level. A low irradiation intensity allows us to control the particle-particle spacing in ordered structures (with nm precision); employing an higher intensity of the radiation causes controlled melting both in time (transitions with different kinetics) and space (using focused spots), resulting in unprecedented spatio-temporal control of particles organized at the air/water interface.

In **Chapter 6** a different method is used to gain control over the organization of inherently passive particles, this time exploiting the light response of a photosensitive surfactant. Photosensitive surfactants are molecules both photochromic and surface-active, whose properties (such as polarity) can be switched by light. In our system, the particles structure in dark condition is disordered due to the interplay of interactions among particles in the particles/surfactant mixture. The light-induced photochromic reaction, by modifying the particles potential, causes a rapid transition to an ordered state in the particles organization. Interestingly, such two-dimensional order is maintained under light stimulation, but quickly (in a

time-scale much faster than the thermal back conversion) disappears after stimulus removal, thus constituting a remarkable demonstration of a dissipative crystalline state.

To conclude, proof of principles of novel light-responsive two-dimensional colloidal systems will be described, opening the way to further studies where specific properties arising from the collective organization of particles at the interface (such as reflectance or structural colouration) could be efficiently switched on-demand by means of light stimulation.

Photocontrol of particles assemblies

4.1 Abstract

External control over particles assemblies is sought after for the purpose of constructing adaptive materials, but also for the understanding of how self-assembly is performed in stimuli-responsive natural systems. In this bibliographic chapter, the use of light stimulation as a way to gain fast and precise control over particles organization will be introduced and the main reasons why light is of much practical value, especially for the study of dynamic self-assembly, will be explained. The first section will briefly describe what is self-assembly (from static to dynamic), and how it is developed in nature and man-made systems. Successively, the main motives why colloidal particles are used as building blocks for developing self-organized structures will be discussed. Finally, in the remaining part of this chapter, various operating principles for light-responsive systems based on solid particles will be outlined, both for static and dynamic assemblies. In particular, I will introduce the use of light for optical trapping, to induce diffusiophoresis and electrophoresis, to exploit the optothermal effect, and, finally, how to implement photochromic molecules for the control on particles assemblies. Both assemblies in bulk liquid and at liquid interfaces, where much less work has been done, will be considered.

4.2 Self-assembly

To describe particles assembly, or self-assembly in general, we can start by quoting Whitesides' definition:^[155]

self-assembly is the autonomous organization of components into patterns or structures without human intervention.

The key concept is the autonomous* organization of building blocks, giving rise to more or less complex structures having properties that are not additive, but arise from the collective interactions of the components. Autonomy, the property of a system to define by itself the interactions that constitute it, is exploited in many different ways to produce a plethora of structures and functions both in living and man-made systems. Our cells are based on the self-assembly of their constituent parts: the formation of the intra- and inter-cellular membranes, or the protein folding and organization into complexes responsible for various processes are two general examples. One of such examples is reported in Figure 4.1A: the impressively organized structure of the protein complex responsible of the photosynthetic process in a bacterium, composed of spatially arranged proteins and cofactors. In molecular science, self-assembly includes the crystallization of molecular and supra-molecular structures;^[156] from the growth of single crystals of organic molecules to the construction of molecular devices and machines.^[157] In micro- and nanotechnology various entities are based on monomers that autonomously organize: self-assembled monolayers,^[158] liposomes and vesicles^[9] (Figure 4.1B), colloidal crystals^[159;160] (Figure 4.1C), and so on and so forth.

Although an infinity of products fall in the category of self-assembled systems, each with its specificity and singularity, some common characteristics can be extracted and summarized. As mentioned before, in a self-assembled process the components of the whole structure organize spontaneously; this is possible by carefully choosing the specific interactions among each other and with the environment in which the components are initially dispersed. Ultimately, it is the selection of such interactions that dictates the formation of a self-assembled system and its characteristics. All the information needed to obtain a desired motif, and not another, even similar one, are encoded in it, in the components and in their surrounding medium – for this reason the structures are formed “without human intervention”. Error repairing is ensured by the coexistence of both attractive and repulsive forces among the units, and the system can normally explore many different configurations before “falling” in the selected one. Nonetheless, the result is not always straightforward, and predictions can be hard: if a system is governed by multiple weak interactions, several different combinations can be obtained with very similar experimental conditions, as in the case of polymorphism in molecular crystals.^[162]

*Interestingly, the word comes from the ancient Greek terms *αὐτός* and *νέμω*, meaning “that govern itself”.

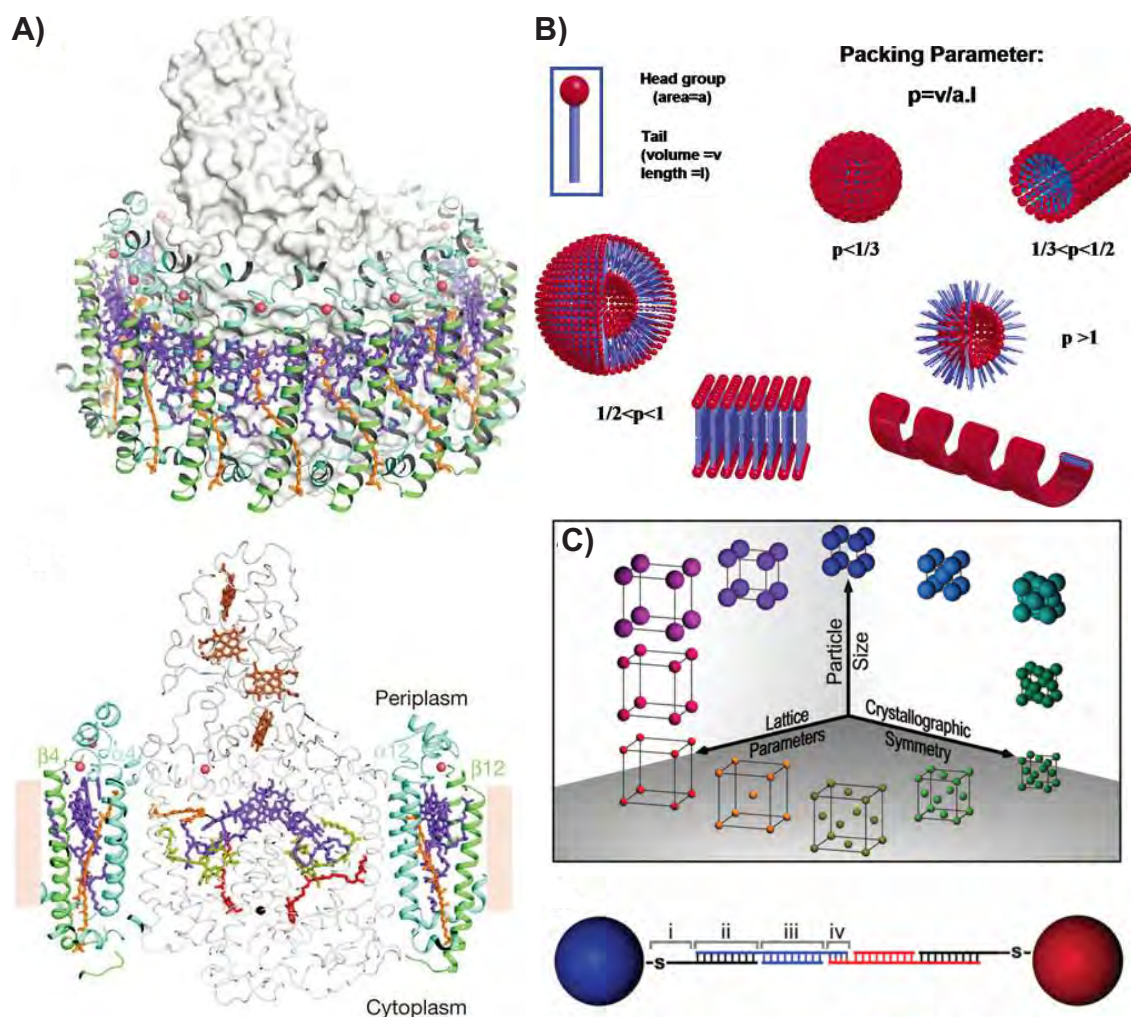


Figure 4.1: Living and man-made examples of static self-assembled systems. A) Architecture of the light-harvesting core antenna and the reaction centre supramolecular complex for light-collection, energy transfer and photosynthesis of the bacterium *Thermochromatium tepidum*. Experimental electron density map showing the various proteins and cofactors spatial organization in the lipid bilayer.^[161] B) Self-assembly of amphiphilic molecules into various structures (spherical, tubular or inverted micelles, vesicles, membranes and ribbons) depending on the monomer characteristics, as well as their concentration and properties of the solvent.^[9] C) Top: 3D nanoparticles structures engineered with DNA strands in order to control crystallographic symmetries and lattice parameters.^[160] Bottom: sketch of the building blocks, two nanoparticles coated with complementary DNA strands.

4.2.1 From static to dynamic self-assembly

Typically, there exist two main kind of self-assembly.^[163;164] The first one is static assembly, or thermodynamically driven assembly, in which the system has the potentiality to explore all the possible states and choose the one downhill in free energy: the equilibrium structure (state #1 in Figure 4.2). Belong to this category the self-assembly of lipids giving rise to a cell membrane, or the formation of a stable host-guest complex, as well as the examples in Figure 4.1. However, the term static does not mean that once equilibrium is reached the components cannot move, rearrange and exchange with the solution any more. Reversibility is crucial for the stability of the obtained structure, often capable of self-healing, that will

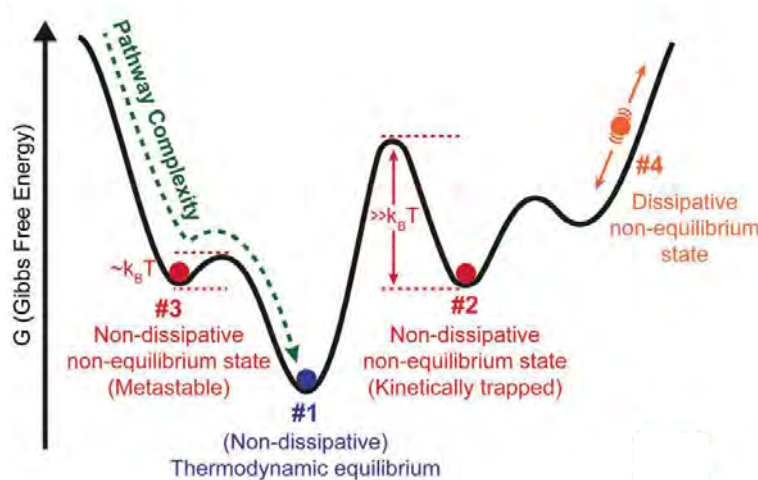


Figure 4.2: Schematic Gibbs free energy landscape of a self-assembling process along a reaction coordinate.^[165] State #1 is the thermodynamic equilibrium, global minimum of the free energy landscape. States #2 and #3 are non-dissipative, non-equilibrium states, local minima in the energy landscape; #2 is a kinetically trapped state because the energy barrier that has to be overcome to reach the global minimum is $\gg k_B T$; #3 is a metastable state because the barrier is $\sim k_B T$. State #4 is a dissipative, non-equilibrium state, constant influx of energy is required to maintain the system in this state, otherwise it will relax to a minimum of the energy landscape. Several other schematic energy landscapes have been proposed in literature, for example in refs.^[164;166;167]

seek and remain in its most stable state. The second kind is dynamic assembly, in which structures with well-defined properties or functions emerge only when the system is kept far from equilibrium by giving energy that is continuously dissipated (state #4 in Figure 4.2). The interactions responsible of the formation of such structures only occur when the system is in specific, out of equilibrium, states. Belong to this category some of the more advanced biological devices, such as motor proteins or transmembrane ion pumping complexes. Nowadays various synthetic systems are conceived in order to study, and eventually exploit, dynamic self-assembly. Apart from systems based on colloidal particles, that will be discussed later in this chapter, several examples are based on molecular building blocks that are tailored to control various micro- or macroscopic properties, such as pH gradients,^[168] gelation,^[169] or unidirectional molecular motion.^[166] Dynamic self-assembly doesn't have to be confused with kinetically trapped assembly (state #2 in Figure 4.2), where the system is not at its thermodynamic equilibrium, but in a local minima due to strong interactions among components; a local minima contained by an energy barrier much higher than $k_B T$.^[165] Such local minima are often due to experimental procedures and preparation protocols. For example, following the scheme in Figure 4.2, if the system comes from the outmost left of the energy landscape and has enough energy to overcome the small energy barrier $\sim k_B T$, it will reach the equilibrium state #1; instead, if the system comes from the right – this could be experimentally obtained, for instance, changing the sequence in which reagents are added – it will remain trapped in #2 due to the too high energy barrier $\gg k_B T$ that separates this state from #1.

In order to rationalize the synthesis of a dynamically responsive system, three general heuristic rules have been extracted by Grzybowski and co-workers.^[163;170] As in static self-assembled systems, an interplay of attractive and repulsive forces should be present otherwise the components will either clump together or simply separate. To prevent it, such interactions need to have similar strength in the length scale of the system. Finally, at least one of the interactions governing the components final organization have to be controlled by an external stimulus, *i.e.* by externally delivered energy. If this last rule is not observed, the system will end up irreparably in its equilibrium state. One of the most famous systems

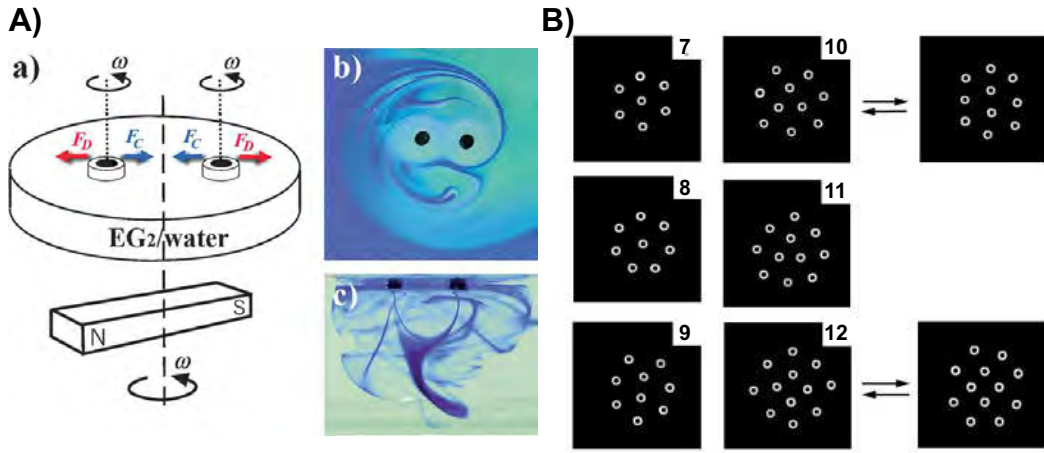


Figure 4.3: Archetypical dynamic self-assembled system based on magnetic and hydrodynamic interactions.^[171;172] A) Principle of the system: a rotating magnet drives the rotation of 2 mm-sized magnetic discs placed at the air/liquid interface. The magnetic force F_C attracts the disks towards the centre of the dish, while a hydrodynamic force F_D pushes them apart from each other. The repulsive force originates by vortex flows created by the interacting spinning disks, as evidenced by the addition of a blue dye. B) Dynamic structures formed by various numbers of interacting disks (at the same spinning velocity of the magnet). In some cases (here with 10 and 12 disks) polymorphic structures are observed, interconverting irregularly with time.

designed by Grzybowski *et al.*, for which the term dynamic self-assembly was actually coined, is represented in Figure 4.3, and nicely shows the heuristic rules previously enunciated. It is composed of mm-sized magnetic discs placed at the air/liquid interface. External energy is supplied by a rotating magnet below the dish that will attract each object toward its axis of rotation (attractive force, F_C). When two or more disks are in the same dish, as soon as the magnet, and therefore the disks, start rotating, a fluid motion is generated resulting in a repulsive hydrodynamic interaction between the disks (repulsive force, F_D). The competition between the attractive and repulsive forces having similar magnitude leads to the formation of ordered aggregates of disks whose structure depends on their number. The structures are maintained by the magnet rotation, and fall apart when the spinning magnet is stopped.

4.3 Colloidal particles as building blocks

Several non-living systems have been devised to study self-assembled processes and materials, and in some cases novel properties and functions have been discovered. Among the most common building blocks used, colloidal particles play a major role thanks to the variety of properties and interactions that can easily be included and modified with such units (for a more detailed description of their bulk and surface characteristics see Chapter 1), opening the way to explore experimental configurations both with static and dynamic self-assembly approaches.^[173]

Materials based on self-assembled colloids can require the formation of stable structures, which are in their thermodynamic minimum. Representative of this category are colloidal crystals^[159;174] (examples in Figure 4.4A and Figure 4.1C), important for technological applications^[66] as well as a model system for fundamental studies of crystallization and melting.^[92] In this case the proper environment and interactions are chosen for the correct self-assembly either in solution or at liquid/liquid or liquid/solid interfaces, and successively the formed structures can be permanently fixed if it is required for the final application. On the other end, both for fundamental understanding and for the development of novel materials where stimuli dependent responses are sought, research points towards the study of dynamic colloidal assembly, either able to switch between different equilibrium states, or in order to reach out-of-equilibrium states with emerging properties. Dynamic assembly is promising for the synthesis of reconfigurable, adaptive and “intelligent” materials, able to perform different functions, such as time- or stimulus-dependent optical, electrical, structural or mechanical responses.

Precise control over size, shape and chemical composition, for both bulk and surface, of the colloidal particles causes the addition of numerous properties combined within one object. This, in turn, results in a complex variety of consequent interactions responsible for their assembly, which allows implementing manifold stimuli to govern their organization. Therefore, depending on the specific properties of the particles used, several methods have been devised to gain control over their final structures, possibly being able to switch among various configurations having distinct functions.^[173] One possibility is given by changing the solvent, or mixture, composition: *i.e.* pH, electrolyte concentration, presence of small particles or polymers for controlling depletion interactions. While the interaction potential between particles can be precisely controlled in this manner (an example being the “plasmonic ruler” at the liquid interface showed in Figure 1.6B), reversibility is normally difficult to achieve.

Reversibility between various states is typically obtained when at least one of the interactions can be tuned by an external stimulation. For example, temperature variation offer a precise control over particles organization; in particular, it can affect the system properties by modifying its entropy or its energy. Certain polymers, such as poly-N-isopropylacrylamide

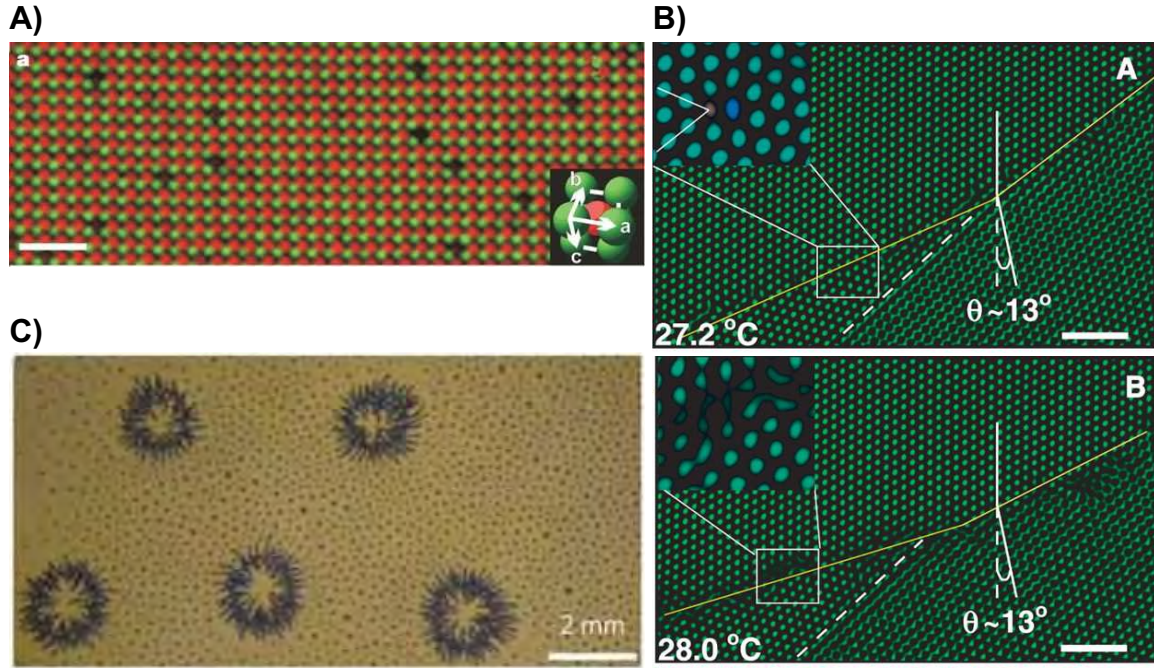


Figure 4.4: 3D and 2D assemblies of colloidal particles. A) Ionic 3D colloidal crystal of oppositely charged particles (red, positive, radius $1.08 \mu\text{m}$; and green, negative, $0.99 \mu\text{m}$. PMMA-sphere).^[174] Scale bar: $10 \mu\text{m}$. B) Images at different temperatures following the melting of a 3D colloidal crystal composed of PNIPAM particles.^[175] Scale bars, $5 \mu\text{m}$. C) 2D Self-assembled dynamic asters composed of magnetic particles at a liquid/liquid interface.^[176] The asters form in a rotating magnetic field, and disassemble upon stimulus removal.

(PNIPAM), have strongly temperature-dependent structure and size;^[177] consequently, colloidal building blocks containing PNIPAM are able to reversibly swell/deswell as a function of temperature of the solution. Therefore, they have been used to externally control their organization and study, for example, melting within bulk colloidal crystals^[175] (Figure 4.4B). Bonds between particles can be produced by the hybridization of complementary DNA strands grafted to each colloidal surface^[178] (as described by the example in Figure 4.1C); reconfigurability is ensured by the temperature dependent nature of the DNA hybridization and strand displacement – no hybridization at high temperature, bonding at a lower temperature dependent on the sequence and length of each strand – allowing, for example, to program reversible colloidal phase transitions.^[179] While temperature ensures reversibility between different states, out-of-equilibrium particles assemblies and emergent properties arising from the energy input dissipation have not been discovered yet using those systems.

On the contrary, magnetic, electric or optical stimulation have been used to control both the organization of colloidal particles, and their dissipative assembly; in some cases obtaining novel, emergent, properties. For example, the dynamic assembly of magnetic particles at a liquid interface has been reported by Snezhko *et al.*^[176;180] (Figure 4.4C). Their system is composed of ferromagnetic colloids trapped at the interface between two liquids; the energy source that drives the system out of equilibrium is provided by an alternating magnetic field applied perpendicular to the interface. The particles respond to the externally delivered

energy by collectively assembling in “asters” composed of ordered chains of particles: dipole-dipole magnetic interactions promotes the formation of chains; interface deformation and generated interfacial waves lead to the formation of asters. Depending on the concentration of the particles and the amplitude of the magnetic field, asters can further organize into periodic 2D arrays. Both the opening of the asters and their motion can be externally controlled, allowing further manipulation of nonmagnetic particles at the interface.

Although the stimuli mentioned allow controlling a large variety of particles organizations, the following part of the chapter will be dedicated to what is probably the most used stimulation to control dynamic self-assembly of colloidal building blocks, which is light. Techniques for directing static self-assembly will be mentioned as well.

4.4 Light control on particle organization

Among the various external stimuli that can be implemented to control the assembly of colloidal structures in a dynamic way, light is a very powerful and versatile input, with several major advantages. Photons can be delivered to the system from an external source in a contactless manner; the only requirement being a transparent window for the wavelength used. Precise spatial and temporal resolution, as well as in intensity and wavelength of irradiation, can be achieved. With focused irradiation only given parts of the system under consideration can be excited, and, using various wavelengths, different components can be activated on-demand in different moments. Finally, light irradiation allows also to read the system state and follow its evolution.^[181] Light is involved in many processes in natural systems, including out-of-equilibrium ones: photons can be used as an energy source (*e.g.* in photosynthesis^[182]) and/or as a signal (*e.g.* in vision related processes^[183]); and it is one of the most used stimulation in dynamic synthetic systems.^[184]

The energy added to the system by the incoming radiation can be used either directly as a novel force governing particles assembly, as in the following section 4.4.1, or it can be converted by the components of the system changing the interparticles interactions in a light-responsive manner, as described in the last section of this chapter. As we will see, several strategies, exploiting a broad spectrum physical phenomena, exist to implement a response to light stimulation.

4.4.1 Optical forces

The momentum of the photons sent to the system can be used to precisely trap particles dispersed in a liquid, by the method, often called “laser tweezers”, depicted in Figure 4.5A. This method was first described by Ashkin in 1970;^[185] it is based on direct momentum transfer from the photons to the particles using a focused, continuous, laser beam. The conversion of optical power into work is very inefficient, therefore the need of strongly-focused lasers. Nonetheless, particles can be durably trapped in the focal plane of the laser. Moving

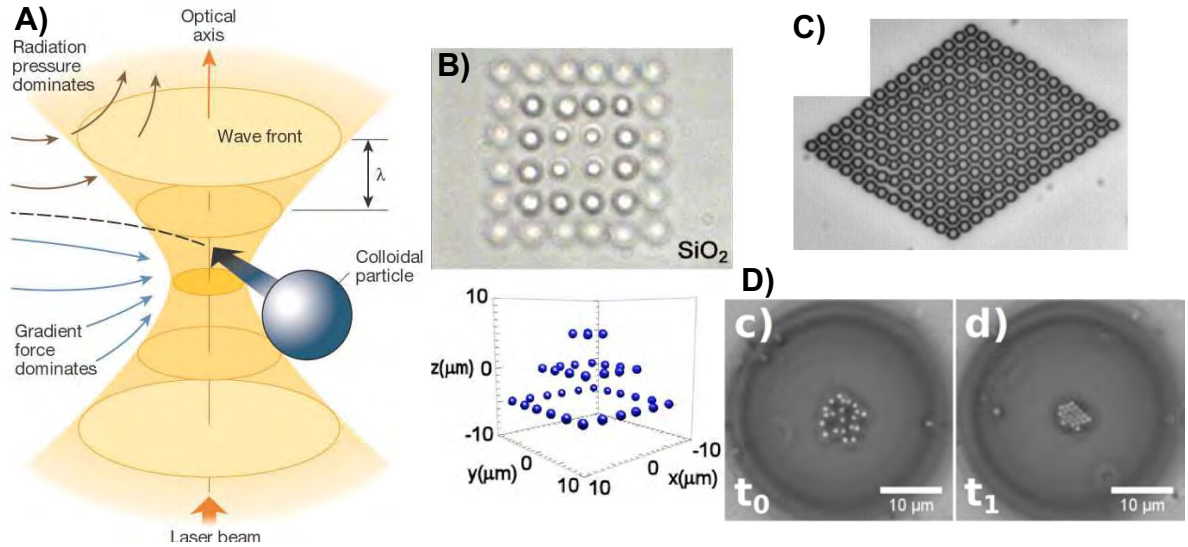


Figure 4.5: Assembly of particles by means of optical forces. A) Sketch of an optical tweezer (from ref^[186]). A focused laser beam is used to trap a particle in the focal point. B) Trapping of colloidal particles in three dimensions: microscopy images of the obtained organization (top) and 3D view of the spheres relative positions (bottom).^[187] 3D positioning is achieved using the generalized phase contrast method, building an optical set-up where two lasers are focused to obtain multiple counterpropagating-beam traps. C) 2D colloidal crystal of particles positioned in a spatially confined nematic liquid crystal film. The nematic phase keeps the particles in place due to quadrupolar interactions among them.^[188] D) Assembly of multiple particles attached to an oil drop surface by DNA hybridization of complementary single-strands, in the centre of an optical trap created switching on a laser (at t_1).^[189]

the focal plane allows to control the flotation of a particle and its precise coordinates in three dimensions.^[186;190] Various methods have been developed to arrange several particles each in the desired position^[187;191;192] (as in Figure 4.5B) for the construction of ordered materials. For example, laser tweezers are used to assist the positioning of colloids dispersed in a confined liquid crystal phase in order to self-assemble them into stable two dimensional structures^[188] (Figure 4.5C). A single laser can be used to dynamically assemble numerous particles into ordered structures in the centre of the optical trap.^[189;193] To this extent, recently, a strategy based on attaching DNA-coated particles to DNA-coated oil drops through the hybridization of complementary single-strands, has been used to collect the particles trapped at the liquid interface in the centre of an optical trap (Figure 4.5D). While DNA hybridization anchor the particles to the drop surface, the fluidity of the liquid interface allows for a precise reorganization of particles attracted by the laser beam.^[189]

As already mentioned, focused lasers beams with high power are required for precise particles trapping; in addition the positioning of multiple particles, an obvious requirement for the construction of ordered structures, can be cumbersome, with complex optical set-ups and, often, the impossibility to move more than one particle at a time.

4.4.2 Light-induced diffusiophoresis and electrophoresis

In response to a concentration gradient of a solute in a liquid, colloidal particles dispersed in it experience a force that propels them.^[194] This effect is called diffusiophoresis. Details on the chemical reactions behind the formation of concentration gradients responsible for phoretic motions can be found in ref.^[195] Light can be used to trigger photochemical reactions of photocatalytic materials, producing ions or molecules in solution. Therefore light stimulation can be engineered to control particles motion, and eventually assembly, through the diffusiophoretic effect. In some cases, the photocatalytic material can be the particle itself (self-diffusiophoresis). If the photocatalytic surface covers all the particle, direct motion can arise from surface heterogeneities or non-uniform exposure of the particle. An example are AgCl particles that autonomously move in water upon UV irradiation that causes light-induced asymmetric photodecomposition of their surface.^[196] Since those particles are not only moved by the arising electrolyte gradient, but are also the source of it, they create a gradient that draw toward them inert particles eventually present in solution (Figure 4.6A). Light induced clustering of passive particles is therefore achieved with this method.

A more efficient chemical gradient of solute molecules around a colloid, with subsequent intensified linear motion, is achieved employing asymmetric, Janus, particles. Such particles are synthesized in order to have a photoreactive side and an inert side. Self-diffusiophoresis can be based, for example, on the chemical decomposition of H_2O_2 contained in solution into H_2O and O_2 by particles surfaces covered with platinum.^[199;200] The same decomposition reaction is triggered by light stimulation in the presence of different photocatalytic materials, such as TiO_2 anatase and hematite. In the particular case of Janus particles with hematite inclusions interacting with a silica substrate, complex self-assembly patterns have been observed,^[197] as reported in Figure 4.6B. The hematite particles are attracted toward the silica surface by phoretic migration. Successively, phoretic attraction between the particles give rise to the formation of dissipative colloidal crystals, held together only by the reaction triggered by light irradiation. Light removal results in the rapid melting by thermal diffusion of the crystals. As a step further, mixtures of silica Janus particles having TiO_2 sides and passive silica particles were used to promote mixed crystallization of active and passive colloids.^[201] Dynamic crystallization under light irradiation was possible by phoretic attraction of the passive particles towards the active ones, at precise pH conditions.

Electrophoresis, the motion of charged particles dispersed in a liquid following an applied electric field, in turn, can be regulated through light irradiation. This is normally achieved using light responsive substrates. Photochemical processes at the interface of an indium tin oxide (ITO) electrode and an aqueous solution modulates the current on the interface. Therefore, varying the illumination pattern during deposition of particles on the electrode allows for precise deposition, and ordering of the particles on the electrode surface. Applying this method, both two-dimensional^[198] (Figure 4.6C) and three-dimensional^[202;203] ordered

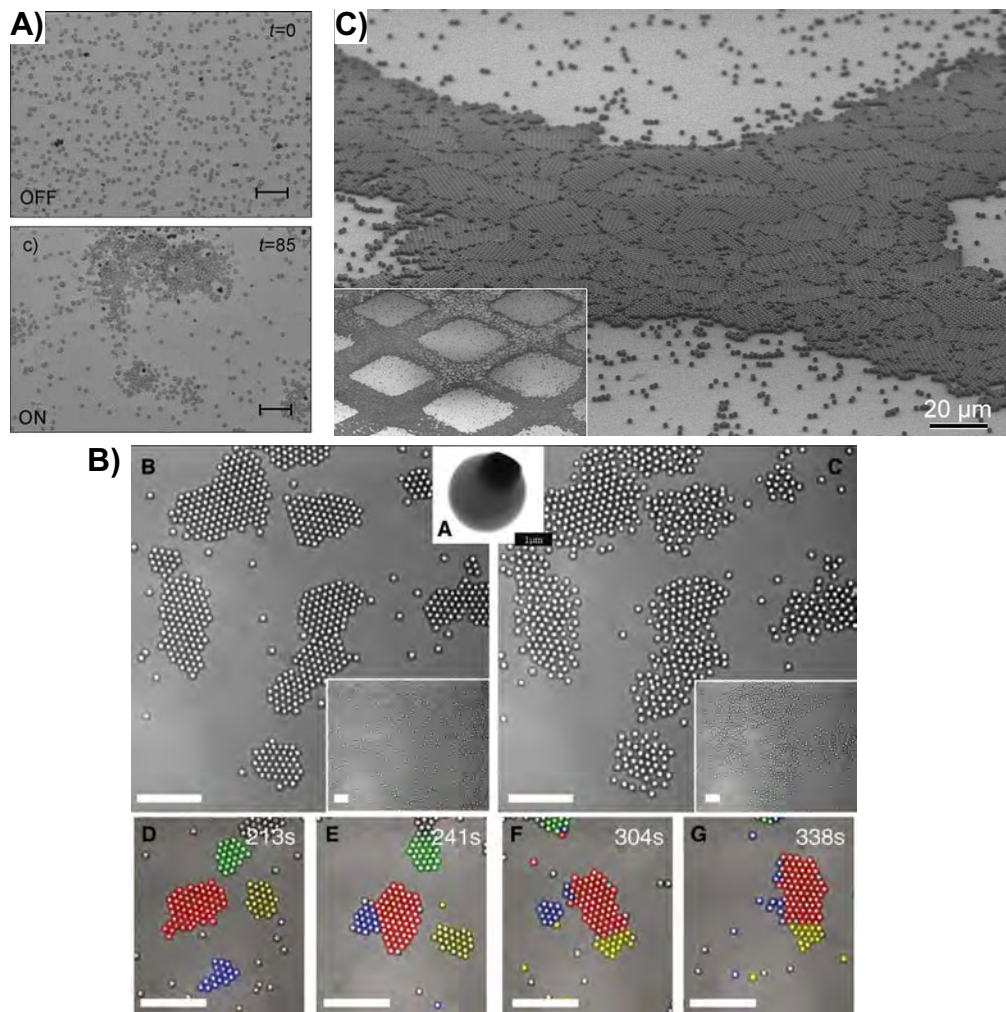


Figure 4.6: Particles organization induced by diffusiophoresis and electrophoresis. A) AgCl particles (darker objects) mixed with silica spheres in deionized water (top). Upon UV irradiation, the silica spheres actively seek out the AgCl particles and surround them (bottom).^[196] Scale bars: 20 μm . B) Living crystals of colloidal spheres with protruding hematite cube (A) assembled under blue light irradiation (B). Melting is achieved by thermal diffusion following light removal (C). (D-G) The colours show the time evolution of particles belonging to different clusters: clusters are not static but dynamically rearrange, by particles exchange, merging, breaking apart, or dissolving.^[197] Scale bars B-G: 10 μm . C) Selective particles assembly on a ITO surface by patterned UV irradiation resulting in the formation of densely packed crystalline domains.^[198]

assemblies can be directly deposited on the solid surface following the light pattern used, in specific and predesignated regions.

4.4.3 Opto-thermal effect

Light stimulation is directly converted into thermal energy by light-absorbing particles through the opto-thermal effect: photon absorption and heat generation. This method does not presume, in principle, the presence of any molecule in solution, as required, instead, to fuel diffusiophoresis and drive phoretic attraction. In many configurations, light responsive substrates are not required as well: the particles can be either directly light-absorbing, or conveniently

4.4 Light control on particle organization

covered with a light-absorbing coating.

The opto-thermal effect is normally used to induce self-thermophoresis to actuate particles in solution due to the local heating of a side of a particle to induce thermophoresis, which is the motion along a temperature gradient. Local heating is a consequence of employing asymmetric, Janus, particles. An example are half-metal coated silica particles as the one showed in Figure 4.7A, that exhibit active motion under light irradiation.^[204] Upon light absorption, the temperature of the metal coated side increases, driving the particle, in pure water, toward the colder side in the local temperature gradient. Interestingly, the thermophoretic direction can be reversed adding surfactant in solution that adsorb on the particle surface.

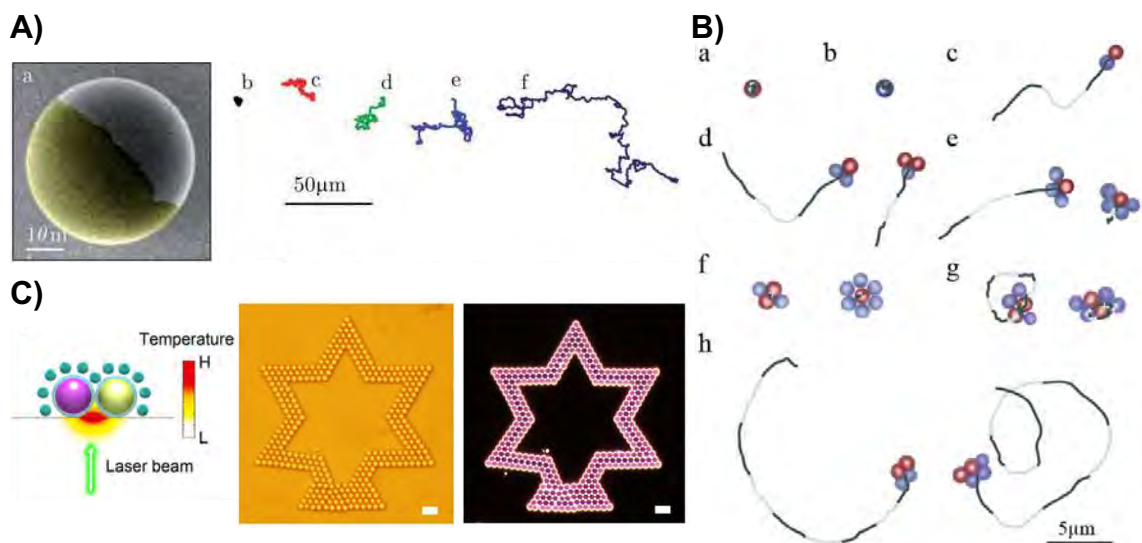


Figure 4.7: Particles actuation and assembly using the opto-thermal effect. A) Scanning electron microscopy (SEM) image of a colloidal silica particle with a 20 nm thick gold cap (highlighted).^[205] b-f: 2D trajectories (1000s) of particles as in (a), dispersed in a water/2,6-lutidine mixture slightly below the demixing temperature, for increasing illumination intensities of $I = 0, 69, 92, 115, 161 \text{ nW}/\mu\text{m}^2$ respectively. B) Building blocks, (a) light-absorbing and (b) non-absorbing particles, forming various active "molecules" upon light irradiation, when immersed in a mixture of water and 2,6-lutidine slightly below the critical demixing temperature. Lines represent particle trajectories; grey and black segments correspond to 1-s stretches.^[206] C) Schematic illustration of the optical manipulation and binding achieved using an absorbing substrate (gold film) locally heated by a laser beam. Depletion interactions between particles (here in purple and yellow) and excluded surfactant micelles (light-blue) allow precise particles positioning. Bright-field and dark-field optical images of a 2D particles assembly; the structure was built layer by layer from top to bottom.^[207] Scale bar: 5 μm .

Another actuation mechanism is based on the interfacial tension variation as a function of temperature that is a characteristic of liquid solutions. For most liquids, including water, the interfacial tension decreases increasing temperature (due to less cohesion between solvent molecules); this effect generates Marangoni flows* at the liquid surface by the so-called thermocapillary effect. Such flows are directed from the lower surface tension region, in this case

*The Marangoni effect^[208] denotes a mass transfer on a liquid interface from a lower to a higher surface tension region.

the illuminated zone, toward the higher surface tension region. If light absorbing particles are adsorbed at a liquid interface, the localized heating upon light exposure can modify the surface tension of the surrounding fluid, generating Marangoni flows. This has been demonstrated focusing light on the rear of an absorbing object, thus propelling it forward by the resulting Marangoni flow.^[209] Interestingly, the thermocapillary effect can also be exploited to activate spinning of asymmetric objects, as in the case of microgears half-covered with a light-absorbing coating.^[210]

Furthermore, local heating induced by light absorption can be exploited dispersing Janus particles in binary liquid mixtures. One example is the water and 2,6-lutidine mixture, which, at a lutidine mass fraction of $c_c = 0.286$ has a lower critical point at temperature $T_c \approx 34^\circ\text{C}$. Below such temperature the solvent is homogeneously mixed, above it demixing of the binary solvent occurs.^[211] Self-propelled particles are obtained coating half surface of a silica particle with gold, and covering it with hydrophilic COOH-terminated thiols.^[205;212] When the particles are suspended in a water/2,6-lutidine mixture, slightly below the critical temperature, no motion except Brownian one is detected. Homogeneous irradiation brings about an active motion due to self-diffusiophoresis – concentration gradient along the particle – generated by local demixing of the solvent mixture, with water accumulation around the hotter, and more hydrophilic, gold side. Figure 4.7A reports the particle used, and the 2D trajectories achieved for increasing illumination intensities. The main advantage of this method is the lower light intensity needed compared to the thermophoresis effect, especially when the sample temperature is close to the critical temperature of the mixture. The same binary liquid mixture near the critical point has been used very recently to control by light the assembly of active colloidal molecules.^[206] The system is composed of light absorbing and non-absorbing particles; light irradiation induces heating of the absorbing particles and temperature increase above the demixing point. When a hot and a non-absorbing particle come close, a Janus dimer is formed – bonding between particles is due to critical Casimir attractions by local heating of the fluid. Now the cluster is anisotropic and starts moving directionally; if it encounters another passive particle, a trimer is formed, and so on toward more complex active “colloidal molecules” (reported in Figure 4.7B).

Multiple particles assemblies have also been obtained by means of photoresponsive substrates. A gold film can locally increase the solvent temperature converting the light energy of an incoming laser into heat. The optically generated hot-spots allow, for example, precise positioning of particles in particles/surfactant mixture by depleting micelles between close particles, therefore binding them. Two-dimensional assemblies of multiple particles with specific geometries are constructed in this way,^[207] as showed in Figure 4.7C.

The opto-thermal effect has been used mainly to ratchet up particles motion, either in bulk or at the interface. Except using photoresponsive substrates, it has never been applied for controlling particles assemblies and organizations – an exception being the newly reported formation of small active colloidal molecules.^[206] Instead, one of the most efficient approaches

employed for this purpose consists in combining particles with the very well-known photochemistry of photochromic molecules. By this method, outstanding light-triggered control on particles organization has been demonstrated.

4.4.4 Photochromic molecules

Photochromes* are so called molecular switches responsive to light stimulation. A molecular switch is a molecule, or supramolecular compound, able to convert between two or more states characterized by different properties (*e.g.* mechanical, electrical, optical, magnetic, etc.). For functional applications, such conversion following an external input has to be rapid and reversible. Of much practical value, especially for the control of particles self-assembly, are switches responsive to light; and in particular, among the various families of photochromic compounds, spiropyran^[214] and azobenzene^[215] based molecules are probably the most used. Their general chemical formula and reactions are reported in Figure 4.8. Both types of

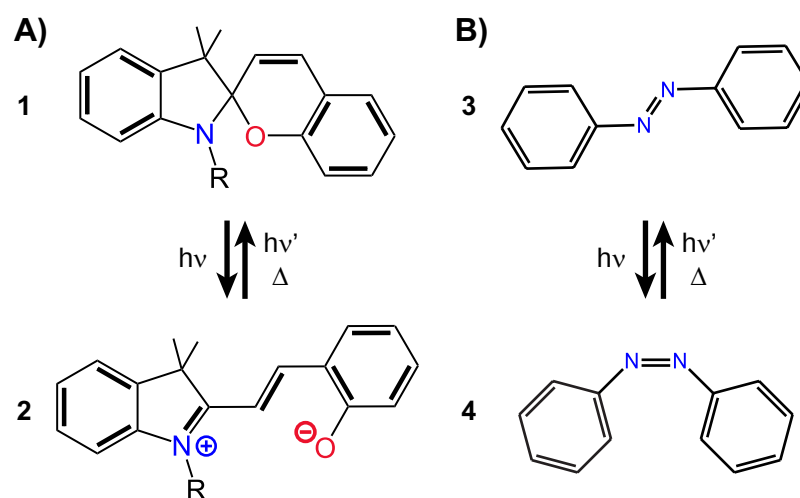


Figure 4.8: Chemical formula and reactions of two photochromic compounds commonly used for the control of particles assemblies. A) Spiropyran chemistry. Conversion between the spiropyran form (1) and the merocyanine form (2) possible using UV irradiation; visible irradiation or thermal energy allows for back 2-to-1 conversion. B) Azobenzene chemistry. Isomerization between the *trans* isomer (3) to the *cis* isomer (4) possible using UV irradiation; visible irradiation or thermal energy allows for back 4-to-3 isomerization.

molecules are sought-after for their fast reaction, the vastly different properties between the two photoswitchable states, and, especially in the case of azobenzene, for the ease of synthetic modification (for example via condensation, diazotization or cross-coupling reactions^[216]).

The spiropyrane molecule (Figure 4.8A) comprises an indoline and a chromene moiety bound together *via* a spiro junction and oriented perpendicular with respect to one another. UV irradiation gives rise to an open-ring reaction and conversion to the merocyanine isomer, a planar molecule with charge separation that causes a much larger dipole moment. The

*The term “photochromism” (from the Greek words: $\phi\omega\tau\acute{o}\varsigma$ (light) and $\chi\rho\acute{o}\mu\alpha$ (color)) is related, following the IUPAC definition,^[213] to molecules that exhibit «light-induced reversible change of colour».

absorbance of the two isomers changes dramatically, with conversion from a transparent (for the spiropyrane) to a deep-blue solution (for the merocyanine). In addition, a third isomer, protonated merocyanine, can be obtained titrating with an acid solution the merocyanine isomer, and thus protonating it. The protonated merocyanine is positively charged, and with a yellowish colour. Back conversion to the merocyanine isomer is possible adding a base solution, while the ring-closing reaction is promoted by visible or thermal back conversion. Interestingly, varying the solvent properties, such as its polarity, pH or the presence of metal ions, can stabilise the zwitterionic merocyanine to the extent that the spiropyranemerocyanine transition occurs spontaneously in the dark, making the merocyanine the stable state in solution.

The second photochrome showed in Figure 4.8 is the azobenzene. An azobenzene molecule converts between two states through the *trans-cis* (or E-Z) isomerization of the central N = N double bond activated by the absorption of a photon; although the precise wavelength strongly depends on the modification on the aromatic moieties, usually UV irradiation is required. Isomerization from the thermodynamically stable *trans* to the less stable *cis* isomer brings about changes in several properties. The most visible one is spectroscopic, a change in colour from pale yellow to orange (for an unmodified azobenzene). The shape of the molecule is modified by the reaction: from planar, to a bent conformation with the two aromatic rings at a dihedral angle of around 90°. As a consequence the dipole moment changes too, from ≈ 0 to 3.1 D. Several other properties can be switched, depending on the substitutions presents (*e.g.* ion coordination and transport,^[217] the spin state of metal complexes,^[218] etc.); some of which will be outlined in the remaining part of this section, namely particles surface charge and liquid surface tension. The back *cis-trans* isomerization takes place either directly at ambient temperature or, in a more controlled fashion, by visible light irradiation. Interestingly, suitable substitutions can stabilize the *cis* form and even reverse the thermodynamic stability.^[219]

4.4.4.1 Light-responsive particles

Colloidal particles can be decorated with covalently attached modified azobenzenes. This strategy has been applied by the group of Grzybowski to drive dynamic self-assembly of metastable crystals, or of permanent supra-particles aggregates, made of nanoparticles building blocks.^[220] Covalent modification has been obtained by covering gold particles with mixed self-assembled monolayers (SAMs) containing a fraction of azobenzene-alkane thiols (the ADT molecule showed in Figure 4.9A). Irradiation with UV light of such molecule induces a strong dipole moment, and dipole-dipole interaction among molecules attached to neighbouring particles (possible solvophobic effects were not excluded by the authors as well as cross-linking of the nanoparticles by dithiol ligands). Varying the fraction of azobenzene-modified thiols tunes the strength of this attractive interaction. Therefore, UV irradiation causes dipole-dipole interactions among particles, resulting in the formation of various structures depending on the

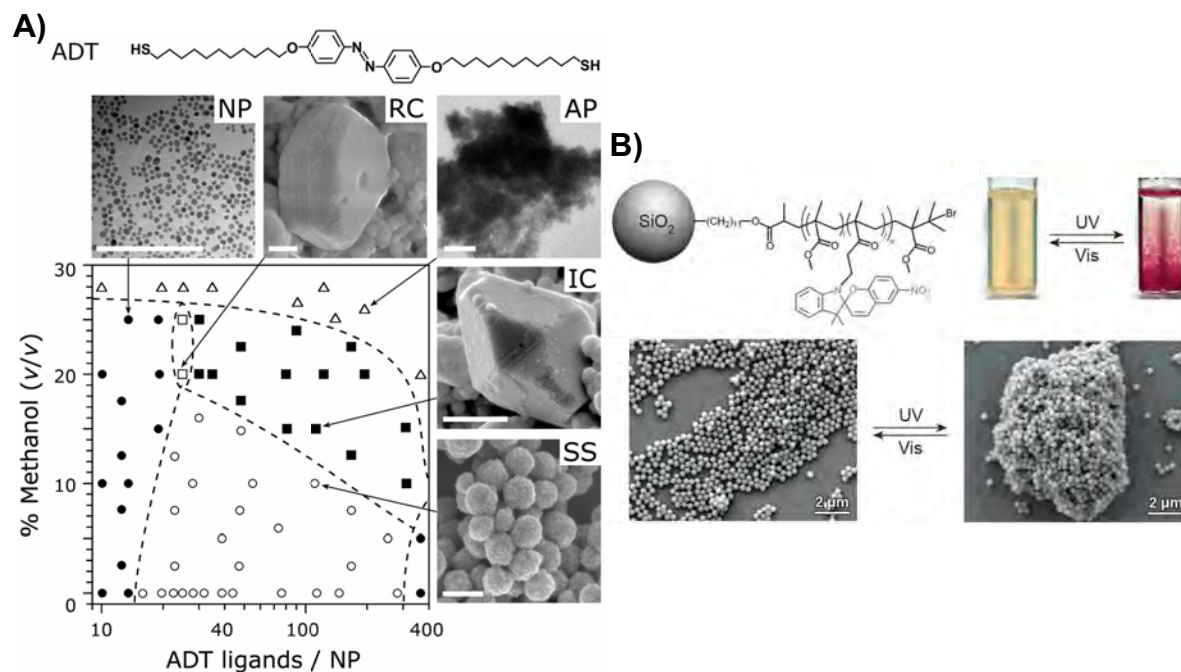


Figure 4.9: *Dynamic organization of light-responsive particles. A) Phase diagram of the self-assembly induced under UV irradiation, varying the percentage of methanol in toluene/methanol mixture, and the amount of azobenzene dithiol ligands (ADT) on the nanoparticle (NP) surface.^[220] After light illumination, several structures are obtained: unaggregated NPs (NP), reversible crystals (RC), amorphous precipitate (AP), irreversible crystals (IC) and supraspheres (SS). Scale bars: 100 nm. B) Silica particles functionalized with a spiropyran derivative.^[221] UV irradiation cause destabilization of the particles dispersed in toluene, as shown by pictures and SEM images before and after UV. Visible light redisperse the particles in solution. Image adapted from ref.^[214]*

percentage of azobenzene thiols and the amount of methanol in toluene/methanol mixture, as reported in Figure 4.9A. The most interesting structures being reversible crystals (RC), obtained when the attractive interactions were slightly stronger than the disruptive thermal agitation. These crystals fell apart as soon as UV light was removed due to back conversion and decrease of the attractive forces. It is worth noting here the need of a careful selection of the experimental conditions required to balance between attractive interactions (in this case mediated by the percentage of azobenzene thiols and methanol) and repulsive ones (thermal agitation), in order to drive the system into surprisingly different configurations (irreversible aggregates (AP), irreversible crystals (IC), supra-particles (SS) or reversible crystals (RC)).

The same methodology, with analogous azobenzene thiols, was used to control through light stimulation the reversible aggregation, or crystallization, of metal nanoparticles for various applications.^[222–224] For example, the non-equilibrium particles aggregation upon light exposure causes a red shift of the surface plasmon resonance (SPR) band of the particles, resulting in a different colouration in solution. If such particles are embedded into a gel matrix, self-erasing images can be drawn on a flexible sheet applying the desired photo-mask or focused irradiation, where the image is a consequence of the different colouration of irradiated and non-irradiate zones. In the absence of irradiation, or with the help of visible

light, the images written into the films gradually self-erase.^[225] Moreover, light controlled crystallization of similar particles can be engineered to induce reversible trapping, and consequent confinement, of target molecules dissolved in solution within the particle aggregate. The trapped molecules undergo chemical reactions with increased rates and with different stereoselectivities under confinement compared to the same reactions in bulk solution.^[224]

Similarly, control over nanoparticles aggregation can be achieved modifying their surface with SAMs containing spiropyrane derivatives^[221;226;227] (see Figure 4.9B). In this case, when the molecules are in the spiropyrane form (non-polar), the particles are normally dispersed in apolar solvents. Upon UV-triggered conversion in the charged merocyanine isomer, the suspension can be destabilized, leading to particles aggregation. Both dispersion and flocculation are strongly dependent on the solvent used. For this reason, in a biphasic system composed of a polar and an apolar solvent, the particles are able to undergo reversible phase transfer.^[228] At first the particles are dispersed in the apolar solvent; then UV irradiation induces their aggregation, but shaking of the sample causes transfer of the aggregates in the polar solvent where the particles are stabilized, therefore able to redisperse. Cycling is possible by light-induced back isomerization of the merocyanine form.

4.4.4.2 Light-responsive medium

The examples outlined before required covalent modification of the particles used. Instead, other techniques have been developed to control light stimulation through the efficient switch of photochromic compounds, for dynamic assembly of unmodified particles in solution. One possibility consists in using nanoparticles functionalized with ligands terminated with COOH groups, dispersed in a solution containing light-switchable molecules (a spiropyrane) able to modulate the pH of the solution.^[229] A sketch of the concept is shown in Figure 4.10A. The titration of an acidic solution in methanol of the dispersed particles with the spiropyrane derivative leads to the uptake of protons from the spiropyrane (SP), which converts in the protonated merocyanine (MCH⁺), and consequent destabilization of the particles, inducing their aggregation and precipitation. Irradiation of the solution with blue light activates the conversion of the merocyanine in the starting spiropyrane with consequent proton release. The H⁺ now available in solution can protonate the nanoparticles, triggering their re-solubilisation in solution. Light-source removal initiates again the aggregation of the particles.

Another class of photoresponsive molecules able to modify particles surface characteristics, and therefore their mutual interactions as well as interactions with the environment, are light-responsive surfactants. These are surfactants with a light-switchable moiety, whose properties can be controlled with light.^[232;233] The molecules absorb photons of a precise wavelength, and consequently undergo a conformational change toward a different isomeric state; this results mainly in electrostatic and/or surface tension variations in the system that can be conveniently used to drive particles assembly. A well-known photoresponsive surfactant is AzoTAB^[234] (azobenzene trimethylammonium bromide), a molecule with an

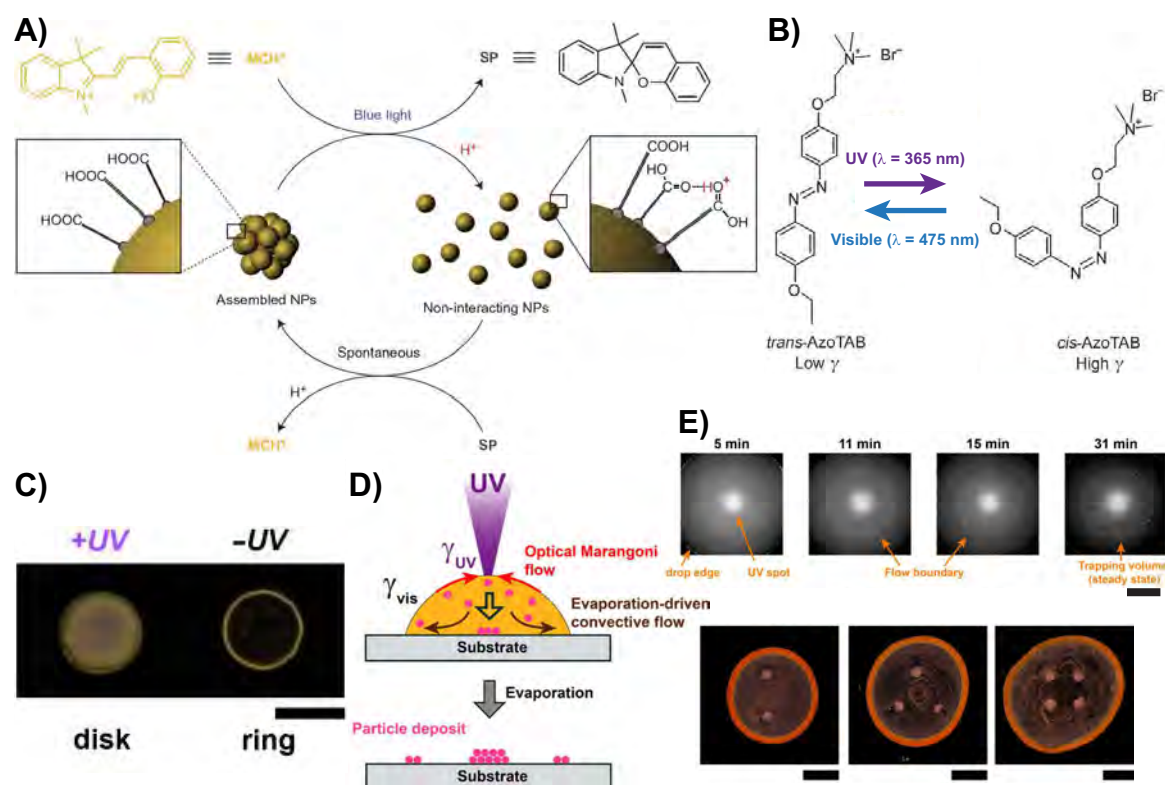


Figure 4.10: Switching particles properties using a light-responsive medium. A) The principle of light-triggered particles aggregation – the mechanism is described in the text – using pH sensitive particles and a solution containing a spiropyran photochrome.^[229] B) Molecular structure of the photosensitive surfactant AzoTAB.^[230] C) Light control of the coffee-ring effect in oppositely charged particles/surfactant mixture.^[135] Without UV light the particles are charged, fully dispersed in water, and accumulate at the periphery of the drop during drying due to the evaporation-driven flow. Light irradiation cause charge decrease of the particles, which gets trapped by the air/water interface during drying, up to homogeneous disk formation upon water evaporation. Scale bar 2 mm. D) Focused UV spot on a drying drop generates a Marangoni flow interacting with the evaporation-driven flow, resulting in particles deposition under the spot.^[231] E) Top: time lapse microscopy images of a suspension drop under UV illumination (as in D) during drying, showing particles accumulation in the spot region. Bottom: complex particle patterning on the solid substrate after drop drying, obtained applying various light spots. Scale bars: 1 mm (top), 2 mm (bottom).

azobenzene moiety in the hydrophobic tail that, as a typical azobenzene compound, converts from *trans* to the *cis* state upon UV irradiation. Its molecular structure and isomerization reaction are shown in Figure 4.10B. Back conversion occurs at ambient temperature, usually with a slow kinetic, or can be readily obtained with visible light irradiation. When the azobenzene is in the *trans* conformation, the tail of the surfactant is linear: apolar and hydrophobic. Instead, in the *cis* state the geometry of the molecule changes, the tail is bent and with a dipole moment: polar and less hydrophobic. Similar azobenzene surfactants have been reported, with various substitutions in the para-position of the azobenzene moiety and, consequently, possessing diverse critical micellar concentrations, surface activity and surface tension difference between the UV- and the blue-adapted solution.^[235;236]

At first I consider mixtures of AzoTAB (or a similar azo-surfactant) in water solution.

When the AzoTAB is in dark condition – majority of *trans* isomers – the molecules tend to accumulate at the air/water or oil/water interface like common surfactants, decreasing the interfacial tension. Upon light-induced isomerization, the more hydrophilic *cis* form will be obtained and, due to its reduced affinity to the water surface, will quickly desorb from it inducing an increase in interfacial tension within the irradiated zone. It is interesting to note, as reported by the group of Monteux, that the presence of *trans* and *cis* isomers at the water interface depends not only on the bulk isomeric composition, but also on their dynamic of adsorption/desorption from the water surface in dark/light conditions.^[235;237;238] In fact, the *trans* isomer is predominant at the water surface irrespective of the bulk isomeric composition. As a consequence, a solution adapted to light of a given wavelength, if irradiated with the same wavelength, will experience dynamic processes even though the bulk composition will not change. Upon light stimulation, the *trans* excess previously obtained at the interface will isomerize and desorb, thus generating surface tension variations. Finally, light removal causes repopulation of the water surface with *trans* azo-surfactant from bulk solution in a time much faster than the thermal back-conversion, allowing to control dynamic processes in a much faster time-scale. Light induced interfacial tension changes have been used in a variety of experiments to trigger Marangoni flows for drops,^[230;239] liquid marbles^[240] and particles^[235;236] actuation and manipulation. Alternatively, the light-induced desorption from the water surface has been used to remotely control foam stability, triggering bubbles destabilization upon UV irradiation,^[237] and to study the induced fluid flows in thin-films and 3D foams.^[241;242]

When positively charged photosurfactant are mixed with oppositely charged particles, other effects have to be considered. In the mixture, the photosurfactant will electrostatically adsorb to the particles surface, varying their surface charge as a function of particles and surfactant concentration. The adsorption ability is dependent on the surfactant polarity: it has been shown that a surfactant with higher polarity, such as the *cis*-AzoTAB compared to the *trans* isomer, leads to less cooperative adsorption on the particle surface. Therefore, this mechanism can be exploited, at precise surface coverage and fixed particles and surfactant concentration, to modify by light stimulation the binding ability of the molecule to the particle, allowing in this way to control the particle surface charge in a fast and contactless manner.^[135] This, in turn, has been applied to tune on-demand particles affinity to the air/water interface, ultimately for applications such as the suppression of the coffee-ring effect^[135] (see Figure 4.10C). In another experimental configuration, light controlled Marangoni flows at the water surface of drying drops containing particles have been used to dynamically accumulate particles in precise locations on the underlying solid substrate^[231;243] (Figure 4.10D, E). This has been achieved combining Marangoni flows with the evaporation-driven convective flows present inside pinned drying drops.^[244] The recirculating Marangoni flow points toward the light spot, where surfactants are depleted, while the evaporation-driven flow is directed toward the drop edge – a sketch of the concurring flows are drawn in Figure 4.10D – their sum

results in a flow pattern that efficiently deposits particles under the light spots. The final particles deposits are determined by the size and position of the light spots.

4.5 Conclusions

In this bibliographic chapter I reviewed the available experimental techniques, and the underlying physico-chemical principles, to direct colloidal particles motion and organization through external light stimulation. Prior to that, an introduction to self-assembly (static and dynamic) and the use of particles as valuable building blocks to construct self-assembled structures was provided. Successively, the various configurations to move and organize particles under optical control were presented. This included the use of optical forces, light-induced phoretic or thermal effects, and the combination of particles with photochromic compounds. Throughout the chapter, the goal was to describe systems where particle self-assembly was tuned by means of light patterns.

Systems both in bulk liquid phase and at the liquid interface have been taken into account. As we demonstrated, very few work has been performed with particles at liquid interfaces, especially regarding controlling their light-induced two-dimensional collective organization (assembly/disassembly). It is therefore a very exciting and attracting subject, that will be extensively studied in the following chapters. Based on the results with particles/surfactant mixtures reported in the previous part, two different approaches to control the organization of particles adsorbed at the air/water interface by light stimulation will be reported in the following chapters. Ranging from reconfigurable 2D crystals composed of light-absorbing particles, to dissipative crystals formed mixing passive particles with photosensitive surfactants, they represent conceptually new systems that open the way to novel actuation techniques for interfacial systems.

Photothermally reconfigurable colloidal crystals at the air/water interface

5.1 Abstract

On-demand switching of colloidal particles arrangement in ordered structures is sought after for a variety of applications in stimulus-responsive devices. To tackle this objective, by self-assembling two-dimensional crystals of light-absorbing particles at the air/water interface, we demonstrated a fast, reliable and reversible control over their organization state. Taking advantage from the heat dissipation by the absorbing particles, in our system visible light irradiation allows both tuning with nanometre-precision the particle-particle distance in ordered structures, and to control melting of the crystals in a spatio-temporal manner. Since those dynamic structures relax to their initial state after stimulus removal, they open the way to the formation of highly controlled two-dimensional colloidal crystals with tunable structural properties.

5.2 Introduction

Colloidal particles are commonly employed as building blocks for the fabrication of functional materials and devices.^[40;65] Fine control over their structural organization is of remarkable importance to tune the functionalities of the assembled structures, where usually long-range ordered architectures are required for the final application. In particular, modification of the relative position between particles inside the formed structures is sought after for the increased stimulus-responses offered. When two-dimensional (2D) materials are required, the liquid interface is often used as a template to direct and control colloidal self-assemblies.^[64;122] This is nowadays investigated both with a material science perspective,^[130] but also for a more fundamental point of view.^[89] As a consequence, there is a broad interest in understanding and influencing the collective behaviour of particles at liquid interfaces.

Both the structural organization and the inter-particles spacing in ordered structures can be successfully tuned varying ionic strength and pH of the aqueous subphase,^[38;86;245;246] by adding surface-active molecules,^[38;247] or by changing the surface pressure by means of moving barriers.^[22;73;131] However, those methods cannot be employed for external dynamic control over particles arrangement: a concept of importance for the construction of stimuli-responsive devices. For this purpose, light is an attractive stimulus offering the possibility to switch on-demand the interactions among colloids in self-assembled structures.^[220;229;231;243] For example, light-induced 2D particles organization on a solid substrate has been reported for photocatalytic Janus particles with well-defined surface chemistry,^[197;201] or using light-absorbing particles in a water/lutidine mixture.^[206] At liquid/liquid interfaces light stimulation has been employed to induce the motion^[236;248] and spinning^[210] of single particles, or to move particles aggregates.^[235] To our knowledge, there are only two recent examples oriented to dynamically control the organization of interfacial colloidal monolayers. One is the colloidal crystallization achieved at an oil/water interface using optical trapping.^[189] This approach however requires complex optical setup and the effectiveness of the light irradiation was limited to only a few particles at once, leading to very small assemblies. The other example will be described in the following Chapter of this thesis and offer the advantage of addressing extended assemblies of thousands of particles using a LED source. This was achieved by mixing anionic particles with cationic photosensitive surfactant. Based on the out-of-equilibrium adsorption/desorption dynamics of the surfactant isomers at/from the water surface, cycles between disordered (without stimulus) and highly crystalline (under light) colloidal structures were achieved. This approach has however several limitations. First, the ordered structures required constant irradiation. Second, only switching between ordered and disordered structures were achieved, meaning that it was impossible to optically tune properties within an ordered structure (*e.g.* inter-particle distance). Third, it required the use of specific photosensitive surfactant.

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To achieve such dynamic spatio-temporal control on the 2D particle organization at the air/water interface, we show here that low-power, defocused, visible light irradiation from a LED source can be efficiently used to tune the organization of non-transparent particles exploiting the opto-thermal effect. The opto-thermal effect, without the requirement of specific chemicals in solution, is applicable to any particle that is light absorbing, or after surface treatment with a light absorbing coating. This energy conversion allowed us to control in a dynamic fashion, with millisecond response time, the interparticle spacing in 2D crystal structures; and to precisely tune the kinetic of melting and subsequent re-crystallization of 2D colloidal systems. Furthermore, focused light irradiation coupled with geometrical constraints of the curved air/water interface around a particles patch, (*cf.* Chapter 2), allowed for the formation of “living” colloidal crystals where particles continuously escape from and successively re-enter the ordered assembly.

5.3 Experimental results and discussion

The experimental system is shown schematically in Figure 5.1. It is composed of anionic polystyrene particles (Figure 5.1B, diameter 4.5 μm) with homogeneous incorporation of nanometer-sized iron oxide crystallites inside the outer polystyrene layer. The iron oxide insertion allows such particles to strongly absorb visible light contrarily to pure polystyrene particles, which are transparent. In a typical experiment (Figure 5.1A), the light-absorbing colloids were mixed with an aqueous solution of cationic surfactant dodecyltrimethylammonium bromide (DTAB, $C_s = 1 \mu\text{M}$) in a cylindrical cell (diameter 7 mm). DTAB was added in minute quantity with the scope to screen the adsorption barrier and allowed adsorption of particles to the air/water interface (see Chapters 2 and 3). The aqueous mixture partially wetted the walls of the cell (contact angle $\approx 80^\circ$), resulting in a slightly concave air/water interface. As previously described (Chapter 2), the particles were brought to the liquid interface by gravity, flipping a first time the cell containing the sample upside down. Successively, the cell was turned with the air/water interface up and, due to the slightly concave liquid surface, the adsorbed particles collected in the centre of the cell. The concentration of particles (C_p , 0.05 mg/mL) was chosen in order to obtain a stable crystalline structure in equilibrium under dark (by which we mean ambient light condition required for microscope imaging). Figure 5.1C (I) shows a magnified view of the centre of the obtained monolayer, using brightfield transmission microscopy, revealing a close-packed hexagonal array of ordered particles. Such ordered array expanded overall the interfacial aggregate, having a typical diameter of $0.57 \pm 0.05 \text{ mm}$ for this C_p .

Light irradiation, with a wavelength of 440 nm, was achieved through the microscope objective by means of a LED source, ensuring a homogeneous light spot at the air/water surface of $\approx 4 \text{ mm}$ in diameter. When light was switched on, the absorbing particles heated by thermal diffusion the surrounding liquid surface due to dissipation of the incoming irradiation

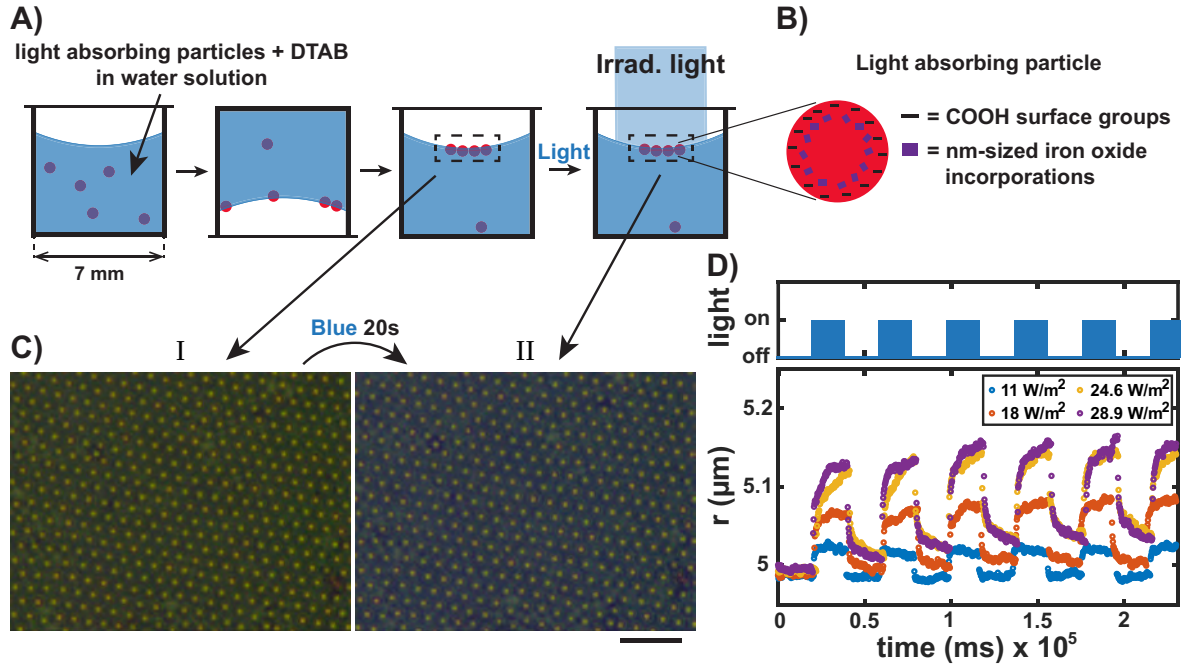


Figure 5.1: *Light-controlled reconfigurable two-dimensional (2D) colloidal crystals.* A) Set-up for particles adsorption at the air/water interface and successive light irradiation. The surfactant (dodecyltrimethylammonium bromide, DTAB, $C_s = 1 \mu\text{M}$) particle mixture is placed in the cell prior to flipping it upside down so that gravity brings the particles to the air/water interface. After 2 h, the sample cell is turned back to its original position. Adsorbed particles accumulate at the centre of the concave interface to form a 2D colloidal crystal. B) Sketch of the light-absorbing particles containing iron oxide inclusions, depicted in violet, inside an outer polystyrene layer functionalized with carboxyl surface groups. C) Brightfield transmission microscopy images of the centre of the colloidal crystal at the air/water interface, with a particle concentration of $C_p = 0.05 \text{ mg/mL}$, before (I, left) and after (II, right) 20 s of visible light irradiation ($\lambda = 440 \text{ nm}$, intensity = 24.6 W/m^2). Scale bar: $20 \mu\text{m}$. D) Scheme of light stimulation (top) and crystal response in terms of particle-particle distance (bottom). Cycles of 20 s light Off and 20 s light On at various intensities were performed. The first nearest neighbours distance (r), averaged from images as in C, was monitored as a function of time for each light intensity used.

into heat. In the following section we studied how the 2D particle crystals responded to such light-induced increase of thermal energy.

As a first step, I performed experiments using a low intensity of light irradiation (Figure 5.1D) and I looked at the structural response in the centre of the particle assembly. Specifically, I programmed cycles of 20 seconds light Off and 20 seconds light On, and measured the corresponding response of the nearest neighbours distance (r) in the particle assembly, averaged over whole images as in 5.1C, containing around 410 particles, as a function of time. While the hexagonal arrangement of the particles under such conditions was not perturbed (Figure 5.1C, II) I observed an increase of the particle-particle distance (r) in the ordered structure under light irradiation, with a response upon switching the stimulus within milliseconds timescale. Fine tuning over tens of nanometers of the averaged particle-particle distance was possible at precise light irradiation conditions and fixed particle concentration.

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Irradiation with 11 W/m^2 resulted in an increase of r by approximately 40 nm (blue points in Figure 5.1D); such value was kept constant, on average, for a long period of irradiation (I experimentally tested up to 4 minutes). The original r value was successively retained as soon as light stimulation was removed; the particles structure reached a similar equilibrium under ambient light condition as the initial one. The structural response upon various light On/Off cycles at this light intensity remained qualitatively similar. Varying the light intensity used permitted to increase the particle-particle distance under light irradiation up to a maximum of around 120 nm (Figure 5.1D). Note that, after irradiation with higher light intensities, 20 seconds without stimulation were not enough to allow relaxation of the crystal structure to the initial condition. Instead, the r value remained slightly higher and a successive irradiation increased the particles distance even more. Experimentally I observed a maximum value of $r = 5.15 \text{ }\mu\text{m}$, after which the particles had more and more translational freedom resulting in a decrease of the crystalline order in the aggregate. In summary, irradiation with an intensity $I \leq 28.9 \text{ W/m}^2$, for the C_p and C_s used, allowed us to control the particle-particle spacing inside 2D crystal structures without disrupting the long-range particle ordering.

I then explored increased intensities of irradiation of the 2D colloidal crystal structures (Figure 5.2). An increase of the externally delivered energy resulted in a dramatic change in the structural response. By video recording I followed the evolution of the assembly at the air/water interface under light irradiation: from the initial ordered structure (Figure 5.2A, I), to complete melting of the crystal in 4 minutes of light irradiation (for an intensity $I = 39.5 \text{ W/m}^2$, Figure 5.2A, II), up to re-crystallization following 6 minutes without light stimulation (Figure 5.2A, III). The radial distribution functions (RDFs) obtained from the images were used to gain quantitative information from the order-to-disorder and disorder-to-order transitions. The RDF of the initial ordered state presents well defined peaks, typical of the hexagonal packing, up to distances (r) normalized with respect to the particle diameter (D) of $r/D = 10$. In the disordered structure (II), the RDF shows only the first peak indicating that the particles were still in close proximity, but not ordered any more. The novel ordered state obtained after 6 minutes following light stimulation (III) was characterised by having a higher number of crystal domains in comparison with (I); the corresponding RDF was similar to the one in (I), indicating an overall ordered assembly, but with less defined peaks for $r/D < 8$ due to the smaller dimension of the domains.

Differences observed between the crystalline order in (I) and (III) can be explained considering the history of the sample. State (I) was obtained after turning for the second time the cell containing the sample (Figure 5.1A). Before turning, the particles adsorbed at the air/water interface accumulated mainly at the meniscus due to gravity. After turning the cell, the particles collected one by one in the centre of the slightly concave meniscus, where they could organize in an ordered state in around 20 minutes. Successively single particles arriving in the centre of the cell increased the size of the crystal structure. The final state was reached in around 70 minutes. Conversely the crystal in (III) was reached starting from

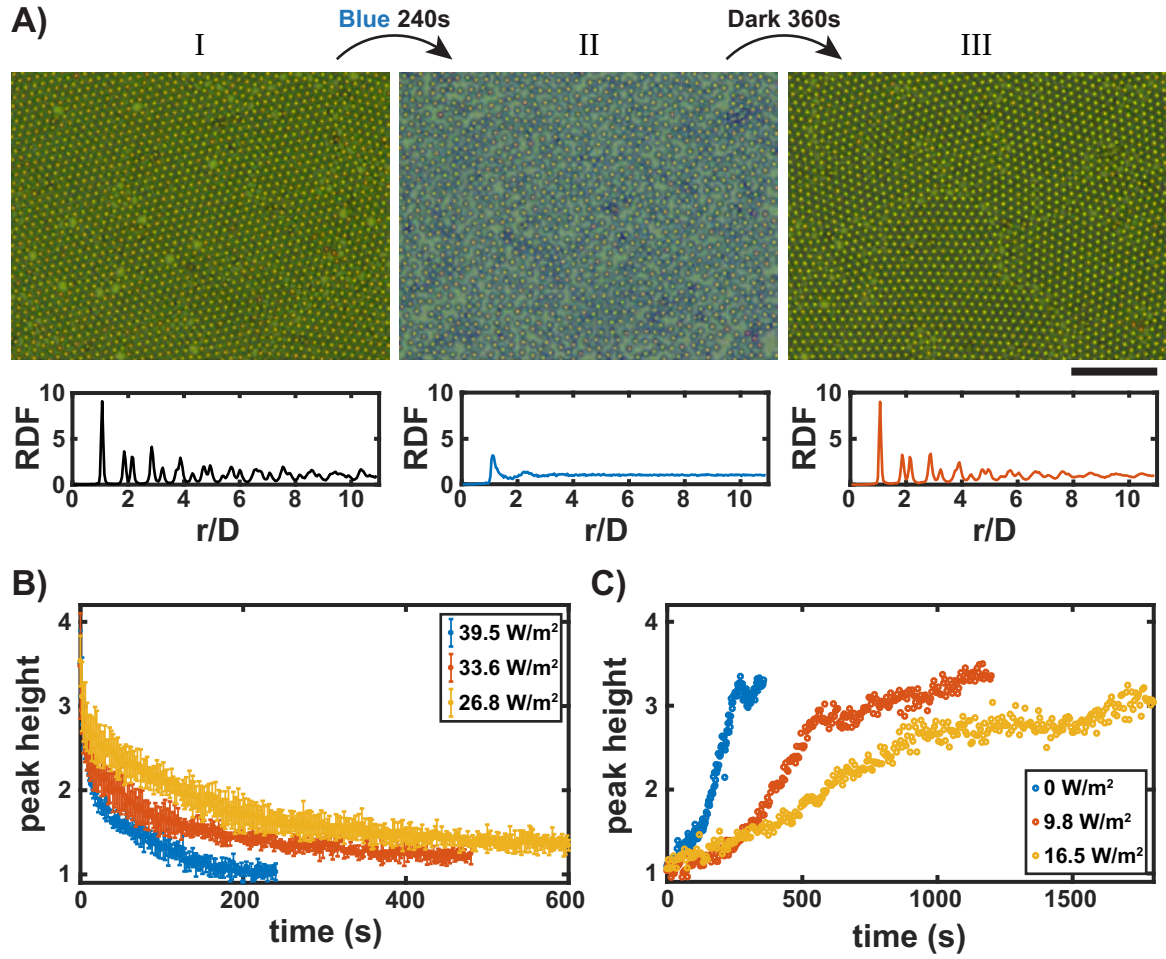


Figure 5.2: Light-controlled melting and re-crystallization of 2D colloidal aggregates. A) Brightfield transmission microscopy images of the centre of the colloidal crystal at the air/water interface ($C_p = 0.05$ mg/mL) in the initial state (I, left), after 240 s of visible light irradiation (II, $\lambda = 440$ nm, intensity = 39.5 W/m²), and after 360 s under dark (ambient light condition, III). Scale bar: 50 μ m. Bottom: radial distribution functions (RDFs) corresponding to each image. B) Kinetic of 2D melting, quantified following the height of the second peak in the RDFs as a function of time for constant light irradiation at different intensities. Symbols and error bars show mean values $\pm$ sd from three individual experiments. Representative images of the final states are showed in A, II and Figure 5.3. C) Kinetic of 2D re-crystallization after photothermal melting under dark (blue curve) and under different light intensities. Representative images of the final states reached are showed in Figure 5.5.

a disordered aggregate already containing all the particles in close proximity. It was thus obtained only in few minutes, making it difficult for the particles to rearrange within the structure to repair eventual errors during crystal formation.

The kinetic of the order-to-disorder transition, or two-dimensional melting, could be controlled either by applying different power of light irradiation (Figure 5.2B and 5.3), or by tuning the number of particles adsorbed at the air/water interface (Figure 5.4). For a quantitative study of the transition kinetics we plotted the height of the second peak in the RDFs as a function of time, peak corresponding to the second nearest neighbours in the particles arrangement. The higher the peak, the more ordered the crystal structure, while a value of

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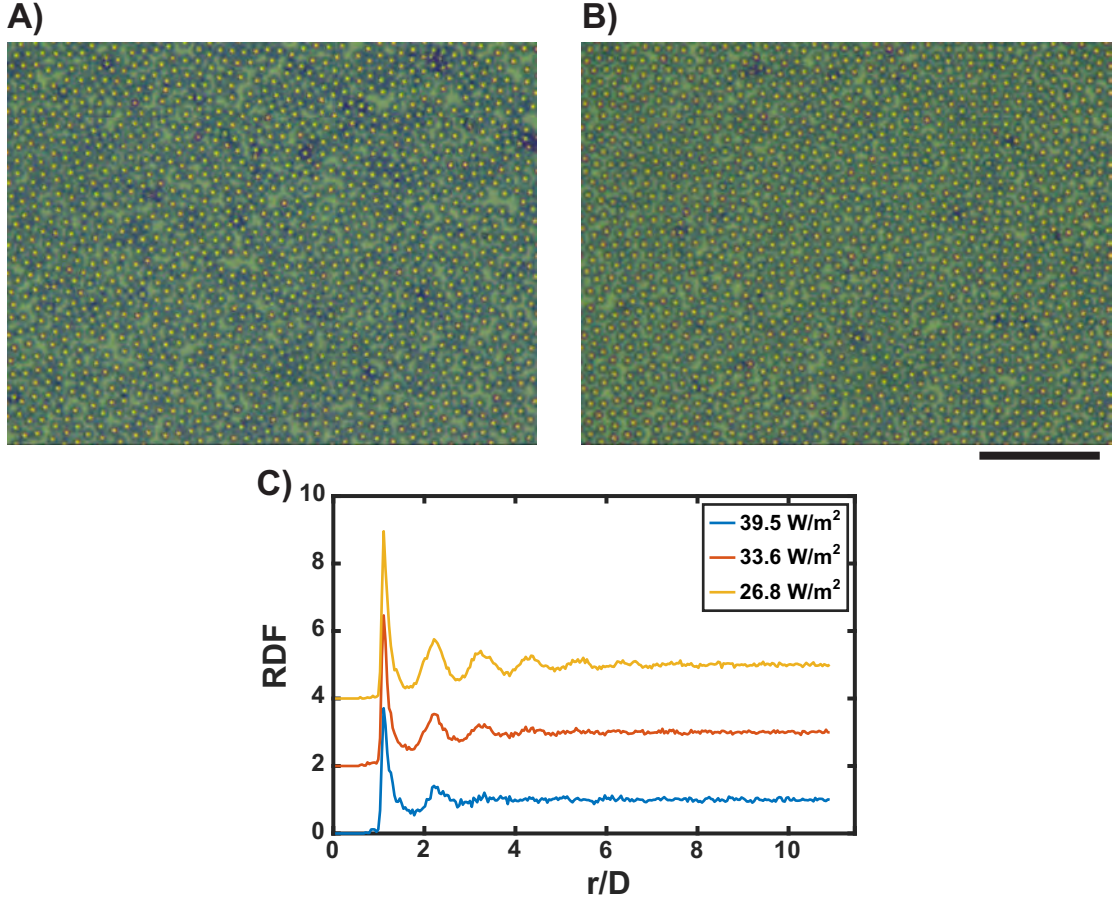


Figure 5.3: Brightfield transmission microscopy images of the centre of particle aggregates ($C_p = 0.05 \text{ mg/mL}$) obtained after irradiating the samples with different light intensities (and for different times). A) $I = 33.6 \text{ W/m}^2$ for 8 min; B) $I = 26.8 \text{ W/m}^2$ for 10 min. Scale bar: $50 \mu\text{m}$. C) RDFs corresponding to the images showed in Figure 5.2, II (blue curve, $I = 39.5 \text{ W/m}^2$), and images in A (red curve) and B (yellow curve).

1 indicates an amorphous structure.

Applying decreasing light intensities on samples having the same bulk particle concentration ($C_p = 0.05 \text{ mg/mL}$), resulted both in a slower kinetic of melting and in a slightly more ordered final state (Figure 5.2B and Figure 5.3). While a light intensity of 39.5 W/m^2 allowed complete melting of the aggregate (Figure 5.2A, II) in around 200 seconds, a light intensity of 33.6 W/m^2 and 26.8 W/m^2 brought the systems to a final state, respectively in around 400 and 500 seconds. In that case the state reached was overall amorphous but presented small clusters of ordered particles (Figure 5.3). Especially, under 26.8 W/m^2 , ordered clusters containing up to roughly 30 particles could be located, and the RDF showed unresolved peaks until $r/D = 5$. Decreasing the concentration of particles in bulk (C_p) resulted in a lower number of adsorbed particles at the air/water interface (*cf.* Chapter 2) that assembled in a 2D crystal of smaller size. Irradiating samples having $C_p = 0.01 \text{ mg/mL}$ with $I = 39.5 \text{ W/m}^2$ caused complete melting of the structure in a faster timescale (around 70 seconds, see Figure 5.4), presumably due to the decreased long-range attraction potential governing the

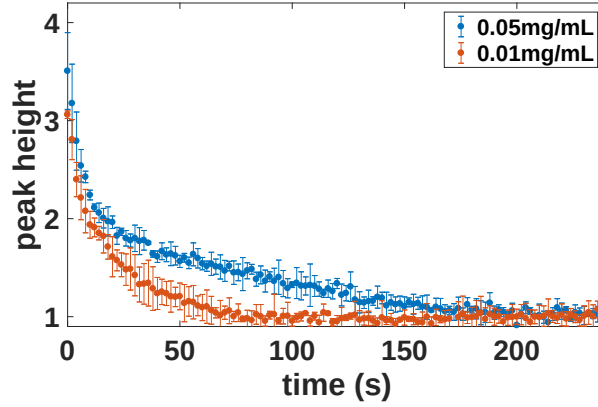


Figure 5.4: Kinetic of the melting transition under light irradiation intensity $I = 39.5 \text{ W/m}^2$ of samples having different bulk particle concentration ($C_p = 0.05 \text{ mg/mL}$, blue points; $C_p = 0.01 \text{ mg/mL}$, red points) followed plotting the height of the second peak in the RDFs as a function of irradiation time. Symbols and error bars show mean values $\pm \text{sd}$ from three individual experiments.

particles organization.

Control over the successive disorder-to-order transition, or two-dimensional crystallization, could be achieved by using different light patterns (Figure 5.2C, 5.5 and 5.6). In order to compare the results, all samples were first melted in the same conditions (light at 39.5 W/m^2 for 4 minutes). In Figure 5.2C the disorder-to-order transition for the same sample under various constant light intensities, is reported. To deal with the same number of adsorbed particles (therefore of long-range attraction potential) and to avoid effects due to sample-to-sample variation, those experiments were done on one sample. The blue curve in Figure 5.2C is the kinetic of re-crystallization under dark (the final state is showed in Figure 5.2A, III, and was reached in around 300 seconds). Successively the sample was melted a second time, and the re-crystallization was followed under constant light irradiation at 9.8 W/m^2 (red curve in Figure 5.2C). Although the kinetic was slower, with the final ordered state obtained in around 1100 seconds, such state was similar to the previous one in terms of number of defects and grain boundaries (Figure 5.5). Finally the sample was melted a third time and re-crystallized under 16.5 W/m^2 of light intensity. A crystal structure qualitatively similar to the two previous ones but with a slightly lower value of the second peak was obtained in around 1700 seconds. In Figure 5.6 I report another experiment performed to tune the kinetic of re-crystallization of the particles aggregate, in which, after melting the samples at $I = 39.5 \text{ W/m}^2$ for four minutes, I progressively decreased in a continuous manner the light intensity up to switching off the stimulus. The re-crystallization kinetic was in phase with the decrease of light intensity; instead, the final state was similar irrespective of the time required by the sample to reach it.

To summarize, independently of the light conditions applied during re-crystallization of the melted particle assembly, the final organized states showed qualitatively similar characteristics. Roughly a similar number of grain boundaries and defects could be identified,

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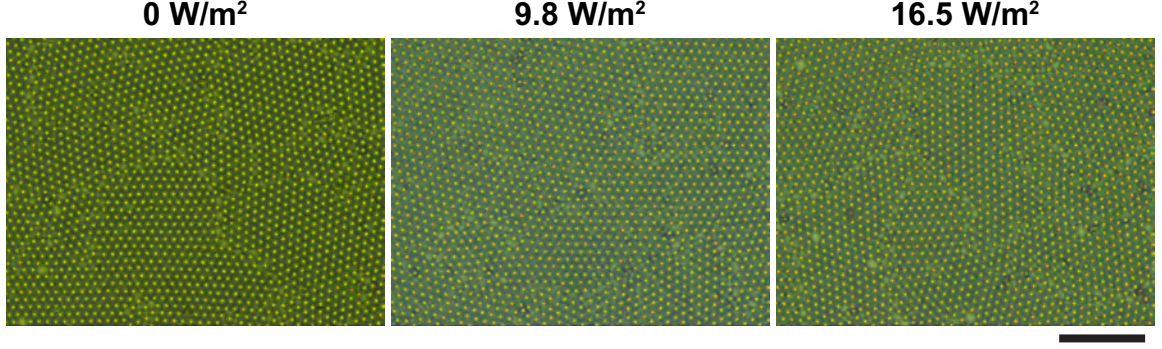


Figure 5.5: Images of the final state of a sample irradiated with $I = 39.5 \text{ W/m}^2$ for four minutes, followed by crystallization under various constant light intensities. Scale bar: $50 \mu\text{m}$.

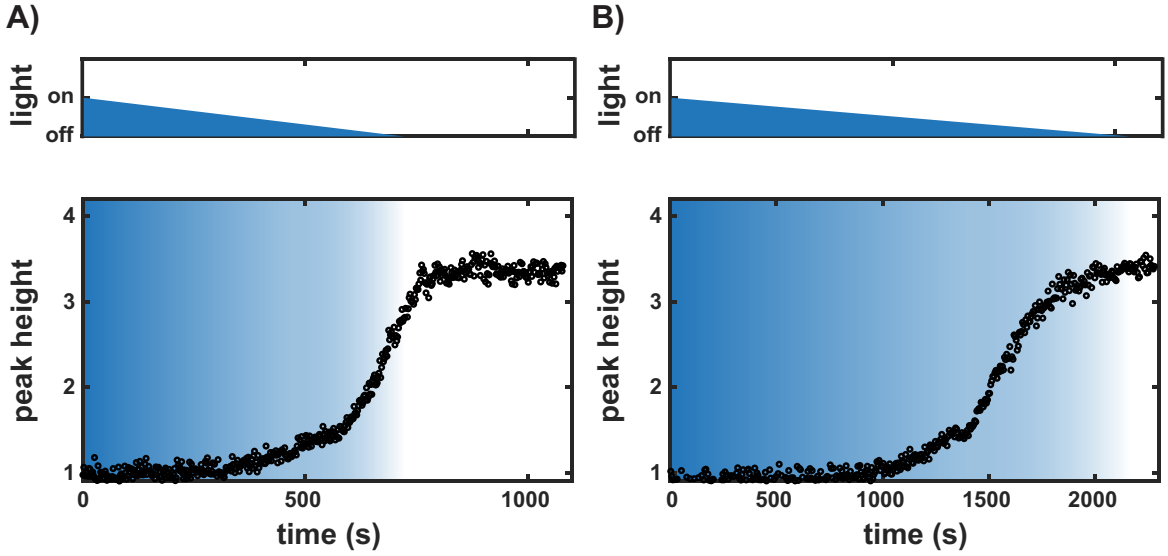


Figure 5.6: Crystallization kinetics under a progressive decrease of light irradiation. The two samples were previously melted irradiating with $I = 39.5 \text{ W/m}^2$ for four minutes, and successively the recrystallization kinetic was followed under progressive decrease of the light intensity used (top) from $I = 39.5 \text{ W/m}^2$ up to zero in 12 min (A) or 36 min (B) by plotting the height of the second peak in the RDFs curves (bottom).

regardless of the conditions to recrystallize the sample (under dark, Figure 5.2A; fixed light irradiation, Figure 5.5; or continuous decrease of the light intensity, Figure 5.6). We can therefore conclude that such final state was independent on the light stimulation used. We hypothesize that ultimately it was the quality of the particles batch used, in terms of polydispersity in size and surface chemistry, that dictated the number of defects in the crystal structure; defects that could not be decreased by applying various light patterns. We note that, in any case, the final crystal state showed a long range positional order, which extended over tens of particles diameters ($r/D \approx 10$).

Overall, the experiments here presented demonstrated that the photothermal effect exploited in our system could be efficiently used to control externally the melting of 2D colloidal crystal structures adsorbed at the air/water interface. It was possible to regulate both the

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kinetic of melting and the kinetic of the subsequent re-crystallization of the adsorbed particles patch.

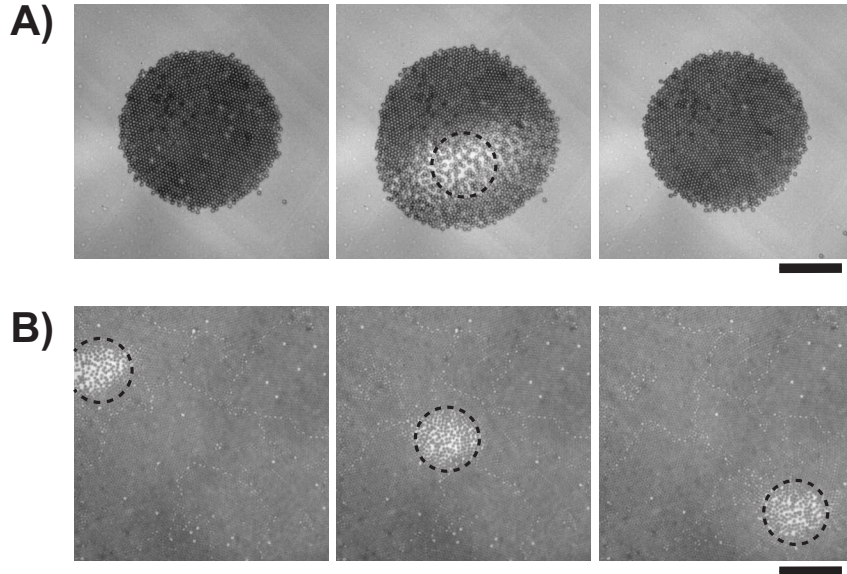


Figure 5.7: Focused light irradiation for spatio-temporal control over melting of 2D colloidal aggregates. A) Brightfield reflection microscopy images of a colloidal crystal at the air/water interface, with a particle concentration of $C_p = 0.05$ mg/mL, before (left), after (middle) 120 s of visible light irradiation ($\lambda = 440$ nm, intensity: $1.4 \cdot 10^3$ W/m²) focused in the dotted circle, and after 390 s at ambient light condition. B) Brightfield reflection microscopy images of a colloidal crystal at the air/water interface, with a particle concentration of $C_p = 0.1$ mg/mL, subjected to focused light irradiation at different positions as showed with a dotted circle. Time between the images: 20 s. Scale bars: 100 μ m.

I then investigated the response of colloidal assemblies to spatially resolved light irradiation patterns. To investigate whether our 2D colloidal crystals could resolve the spatial resolution of a focused light beam, I optimized a custom-built setup for focused light irradiation (having a diameter of the beam ≈ 100 μ m, see Annex A.2.2), coupled with an inverted microscope to track the particle positions. Figure 5.7 shows the spatio-temporal control over melting of 2D colloidal aggregates of different dimensions. In Figure 5.7A I show the irradiation, for 120 seconds, of a small crystal prepared at the air/water interface having a diameter of 0.26 mm. Note that I used the same C_p as in Figure 5.2, but a much lower total sample volume (in order to have the particle assembly at the air/water interface at the focal distance of the inverted microscope used for imaging and coupled with the setup for focused light irradiation), therefore lower number of particles in solution. Although only a part of the structure was affected by the light irradiation, the melted zone was larger than the spot size. Complete recovery of the ordered structure was possible after light removal (Figure 5.7A, right). Instead, light irradiation on a much larger crystal structure (diameter of 0.8 mm, Figure 5.7B) ensured precise spatial control over melting inside the structure. The size of the aggregate allowed for rapid “error repair” of the melted zone within the crystal in few seconds after light removal.

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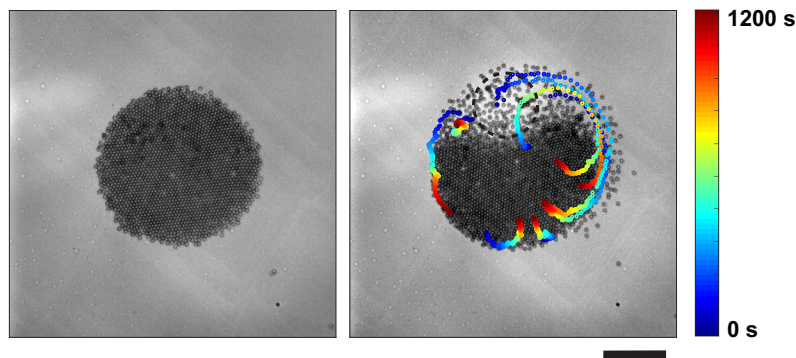


Figure 5.8: “Living” colloidal crystal under continuous focused light irradiation. Brightfield reflection microscopy images of a colloidal crystal at the air/water interface, with a particle concentration of $C_p = 0.05$ mg/mL. Left: initial state at ambient light condition. Right: superimposition of the image of the colloidal crystal after 20 min of light irradiation focused in the dotted circle, and of the tracking of eight particles trajectories from the beginning until the end of the light irradiation. Scale bar: 100 μ m.

Interestingly, continuous focused light irradiation at the edge of a small crystal patch caused melting of the irradiated zone and displacement of the heated particles presents inside. Those particles did not leave their initial position in a random fashion; instead, due to the geometrical constraints of the curved air/water interface around their positions, they circumnavigated the crystal structure and accumulated in the non-irradiated zones in an ordered manner (Figure 5.8). This “living” crystal reached a dynamic steady-state of triggered dissolution and collective re-organization; with a flow of particles from outside the irradiated spot toward the crystallized region, and from the centre of the crystal structure toward the light spot (as showed in the image by the tracking of few particles). We note that such “living” crystals are conceptually different from the works already published, where Janus colloids displays self-phoretic motion upon illumination, triggering the formation of dynamic crystallites at the solid/liquid interface.^[197]

Possible effects governing particles organization under light irradiation. We identify two possible components that can influence the structural organization of light-absorbing particles trapped at the air/water interface and subjected to light stimulation. Dissipation of the light energy into heat by particles results in an increase in temperature expected to be of the order of a few degrees.^[206] This temperature rise is accompanied by an increase in thermal energy, and therefore of 2D Brownian motion of the particles. This evolution is in phase with what we have observed: applying increasing light intensity resulted in higher disordered state, from larger inter-particle distance in ordered assemblies (Figures 5.1) to total melting of the crystal structure (Figures 5.2). However, due to the relatively moderate change of temperature, the contribution of the increased Brownian mobility is probably not enough to explain the light induced melting. This was confirmed by a control experiment

where the water solution was kept at a constant temperature of 35°C and did not result in a perturbation of the polycrystalline structure formed by the adsorbed particle assembly.

The second component we envision to affect particle organization is a localized variation of the temperature of the water surface. The particles heated up by the incoming light irradiation dissipate part of the thermal energy to the liquid surface through heat diffusion, resulting in: i) a decrease of temperature of the particles, and ii) a heat transfer to the air/water interface. Since the particle assembly is of mm size, we can expect that, at the timescale of the experiment, the water surface inside the assembly reaches a temperature upon irradiation slightly higher than the surrounding bare liquid surface. This, in turn, causes a surface tension difference between inside the particle assembly and the outside water surface caused by the dependence of the water surface tension on temperature (typically a variation of $\Delta\gamma = -0.1 \text{ mN} \cdot \text{m}^{-1} \text{K}^{-1}$). The obtained surface tension variation after light irradiation can thus create Marangoni stresses from the lower (inside the particle assembly) to the higher surface tension region (surrounding liquid), resulting in an expansion of the particle patch. With an expected difference of roughly 5 K between the liquid inside and outside the particle patch, a $\Delta\gamma \approx -0.5 \text{ mN} \cdot \text{m}^{-1}$ can be reasonably anticipated, which is sufficient to generate significant surface flows. The long-range attraction potential caused by the local deformation of the interface by the adsorbed particles counteracts the Marangoni flow by pushing the particles toward the centre of the assembly (*cf.* Chapter 2). At low irradiation power, a balance between deformation of the interface and Marangoni stresses results in a variation of the inter-particle distance in crystalline structures; at higher irradiation power, such long-range attraction potential is not enough to prevent melting of the particle assembly.

To conclude, the two effects here mentioned go in the same direction in describing, qualitatively, the experiments reported in this Chapter. They probably both coexist, and to quantify the contributions of each component, a quantitative modelling is required, together with a measure of the temperature in the system at the air/water interface as a function of light irradiation power, a not straightforward experiment of much practical value in describing the interactions at play in the system.

5.4 Conclusions

Exploiting the method described in Chapter 2, we engineered 2D polycrystalline structures of light-absorbing particles trapped at the air/water interface, which were stable in the absence of any light stimulation. Energy dissipation into heat of the particles following visible light irradiation from a LED source allowed multiple controls over their structural organization. Fine tuning of the inter-particles distances in 2D crystals was demonstrated employing a low power light source (intensity $\leq 28.9 \text{ W/m}^2$), while precise spatio-temporal control over 2D melting was achieved at higher irradiation intensities and with focused light spots. Interestingly, localized melting of slightly curved crystals resulted in reaching a dynamic

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steady-state of triggered dissolution under the light spot and collective re-organization in the non-irradiated periphery of the crystal, therefore obtaining “living crystals”.

These results open the way to a novel, simple yet powerful, way to precisely arrange monolayers of light-absorbing particles, where fine tuning or melting transitions are achieved in a fast and reliable manner, with no fatigue. We envision that our method/effect could be applicable to any particle that is light-absorbing (such as metal particles), offering an additional control over properties arising from highly ordered particles arrangements. On the contrary, a different method to control by light the organization of non-absorbing particles at the air/water interface will be presented in the following chapter.

Photoswitchable dissipative 2D colloidal crystals

6.1 Abstract

Control over particle interactions and organization at liquid interfaces is of great importance both for fundamental studies and practical applications. Rendering these systems stimulus-responsive is thus a desired challenge both for investigating dynamic phenomena and realizing reconfigurable materials. Here we describe the first reversible photocontrol of two-dimensional colloidal crystallization at the air/water interface. This is achieved through the out-of-equilibrium behaviour of photosensitive surfactant added to the suspension, allowing us to dynamically switch the particle organization between a highly crystalline (under light) and a disordered (in dark) phase, with no fatigue and a fast response time (crystallization in ~ 10 s, disassembly in ~ 1 min). These results also show a new kind of dissipative system where the ordered state can be maintained only upon energy supply.

6.2 Introduction

Precise regulation over the interaction governing the assembly of colloidal particles at liquid interfaces is the subject of a vivid interest in the scientific community either for the design of novel materials^[65;131] or for studies of more fundamental phenomena.^[92;122] Specifically, while reconfigurable structures are sought for the development of innovative devices,^[173] dissipative systems are studied also to understand how matter organizes itself.^[170] Devising a system that can dynamically respond in a dissipative fashion to an external stimulation is a desired and demanding task,^[164] giving rise to reconfigurable, emergent, functions.^[155] Such a major challenge has been addressed only by few studies so far.^[166;220;249]

Assembling particles at liquid interfaces has the advantage of creating “soft” 2D structures, where the colloids can move and re-organize and their interactions tuned on-demand.^[130] Conventionally, the structural properties of these colloidal assemblies are controlled using either mechanical constraints^[22;73] or modification of the bulk phase(s),^[38;86;245] making dynamic actuation rather difficult. Stimulus-responsive systems, including dissipative ones, offer an interesting alternative to both generate switchable colloidal structures and study fundamental features of dynamic self-assembly. Several examples of dissipative particle organizations at liquid interfaces have been reported using various stimuli,^[250;251] and in particular magnetic fields.^[171;176;180] Beside magnetic or chemical stimulation, light appears as a valuable alternative for the study of dynamic assembly,^[170] thanks to its tunability (wavelength, power), high spatio-temporal resolution and non-invasive character. However, light stimulation has never been used to dynamically trigger the formation of extended 2D ordered colloidal structures at liquid interfaces.

Optical regulation of particle organization has been reported in several cases but mainly in bulk (*i.e.* in suspension) or on solid substrates. For instance, aggregation in bulk was triggered both with photoresponsive^[252] and non-photoresponsive particles.^[229;231] Light was also shown to control the crystallization of colloids, either with active particles,^[197;201] photoresponsive particles,^[220] light-sensitive substrates^[198;203] or not responsive colloids.^[202;253] To our knowledge, the only report^[189] on photocontrol of colloidal crystallization at a liquid interface was recently achieved using optical trapping at the interface of an oil-in-water drop and led to ordered, yet very small, assemblies.

Here we describe the first system where extended, macroscopic 2D colloidal crystallization is induced on-demand using a light input. The system is composed of inherently passive anionic microparticles mixed with minute amounts of a cationic photosensitive surfactant. The light-induced dynamic adsorption/desorption behaviour^[235] of the surfactant from the air/water interface allows us to tune the particle interaction under light command. As a result, mm-sized colloidal assemblies are photoreversibly switched between a disordered and a highly crystalline state. We analyse both structural and dynamic features of the colloidal assemblies in response to different irradiation profiles, and perform cycles of assembly/disassembly

to assess the reversibility of the process. Ultimately, our experiments demonstrate the dissipative, out-of-equilibrium nature of the ordered colloidal assemblies since the crystals are formed only throughout continuous energy supply provided by light irradiation, while energy removal leads to a rapid disassembly of the colloidal structure.

6.3 Experimental results and discussion

The system studied consists in a mixture of 0.01 mg/mL anionic polystyrene particles (diameter 5.1 μm) and the cationic surfactant AzoTAB. AzoTAB is a photosensitive surfactant, with an azobenzene moiety in the hydrophobic tail, that can isomerize from *trans* (thermodynamically stable isomer) to the *cis* isomer upon suitable light irradiation (Figures 6.1A, 6.1B). Particles were adsorbed at the air/water interface of a cylindrical cell by flipping up and down the cell (Figure 6.1C top). I previously showed that micromolar amount of conventional, non-photosensitive cationic surfactants (*e.g.*, DTAB, CTAB) induced the adsorption of anionic particles by decreasing the adsorption barrier at the air/water interface. This decrease was attributed to the local accumulation of cationic surfactants at the liquid interface. At such low surfactant concentrations ($\sim \text{CMC}/1000 - \text{CMC}/100$), particles adsorbed with a low contact angle and remained highly charged (small amount of adsorbed surfactant on particles), thus forming disordered assemblies or polycrystalline patches in a surfactant concentration-dependent manner (*cf.* Chapter 2). We demonstrated in particular that the final structure was mainly dictated by the long-range attraction potential between particles caused by the collective deformation of the interface and the short-range electrostatic repulsion between like-charged particles. In this work, to explore the possibilities to dynamically switch particle assemblies at the air/water interface at a constant surfactant concentration, I used AzoTAB photosensitive surfactant at a fixed concentration of 10 μM , which is about three orders of magnitude lower than its CMC (12.6 mM and 14.6 mM for *trans* and *cis* isomers, respectively^[231]). I found that, similarly to the case of non-photosensitive surfactants (Chapter 2), almost all particles adsorbed at the air/water interface and accumulated at the centre of the cylindrical well containing the sample due to the slightly concave shape of the meniscus. AzoTAB thus accumulated at the air/water interface to promote particle adsorption. In the absence of light irradiation, particles formed a disordered structure with particles in close proximity and voids distributed within the particle assembly (Figure 6.1Ci).

Irradiation with UV light ($\lambda_{exc} = 365 \text{ nm}$, intensity = $8.1 \text{ W} \cdot \text{m}^{-2}$) of the sample promoted fast *trans* to *cis* isomerization of the AzoTAB molecules in solution. By coupling absorption and NMR spectroscopies, we measured the isomeric composition in the bulk, in the dark and under UV irradiation. We found that the system was initially composed of 100% *trans* molecules and reached, after about one minute of irradiation, a photostationary state composed of 5% *trans* and 95% *cis* (Figures 6.1B, 6.2, 6.3A).

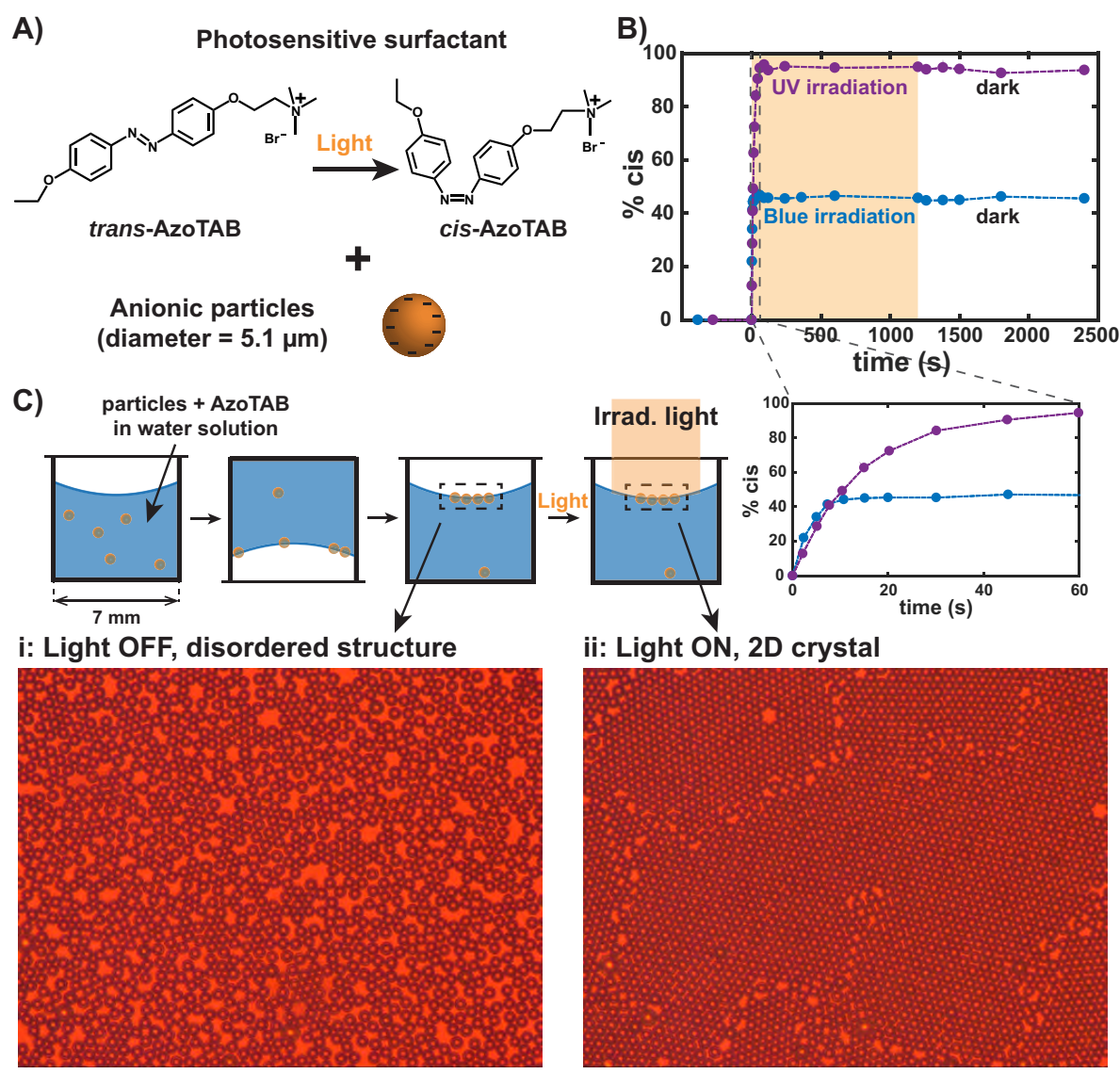


Figure 6.1: Light-induced two-dimensional (2D) colloidal crystallization at air/water interface. A) Components of the system: the cationic photosensitive surfactant AzoTAB (10 μM) which, upon suitable light irradiation converts from the *trans* (less polar) to the *cis* (more polar) isomer; and anionic polystyrene microparticles (5.1 μm diameter, 0.01 mg/mL) in water. B) Top: percentage of the *cis*-AzoTAB isomer in solution before, during and after either UV (violet points) or blue (blue points) light irradiation. Bottom: zoomed graph of the first 60 s of light irradiation. C) Top: setup for particles adsorption at the air/water interface and light irradiation. A mixture of particles and AzoTAB in water is turned upside down for 2 h to bring the particles at the interface via sedimentation prior to bringing it back to its initial position and let it overnight for adsorbed particles to accumulate at the cell center. Bottom: Transmission microscopy images under red light (no AzoTAB isomerization) before (left) and after (right) UV irradiation for 30 s. UV and blue irradiation was done at 365 nm ($8.1 \text{ W} \cdot \text{m}^{-2}$) and 440 nm ($63 \text{ W} \cdot \text{m}^{-2}$), respectively. Scale bar 100 μm.

I optimized the setup for light irradiation in order to have a homogeneous light spot at the air/water interface in the centre of the well with a diameter larger than the adsorbed particle patch (Figure 6.1C). Strikingly, the irradiation resulted in a fast and dramatic change in particle organization: in a few seconds the whole amorphous patch evolved into a mm-

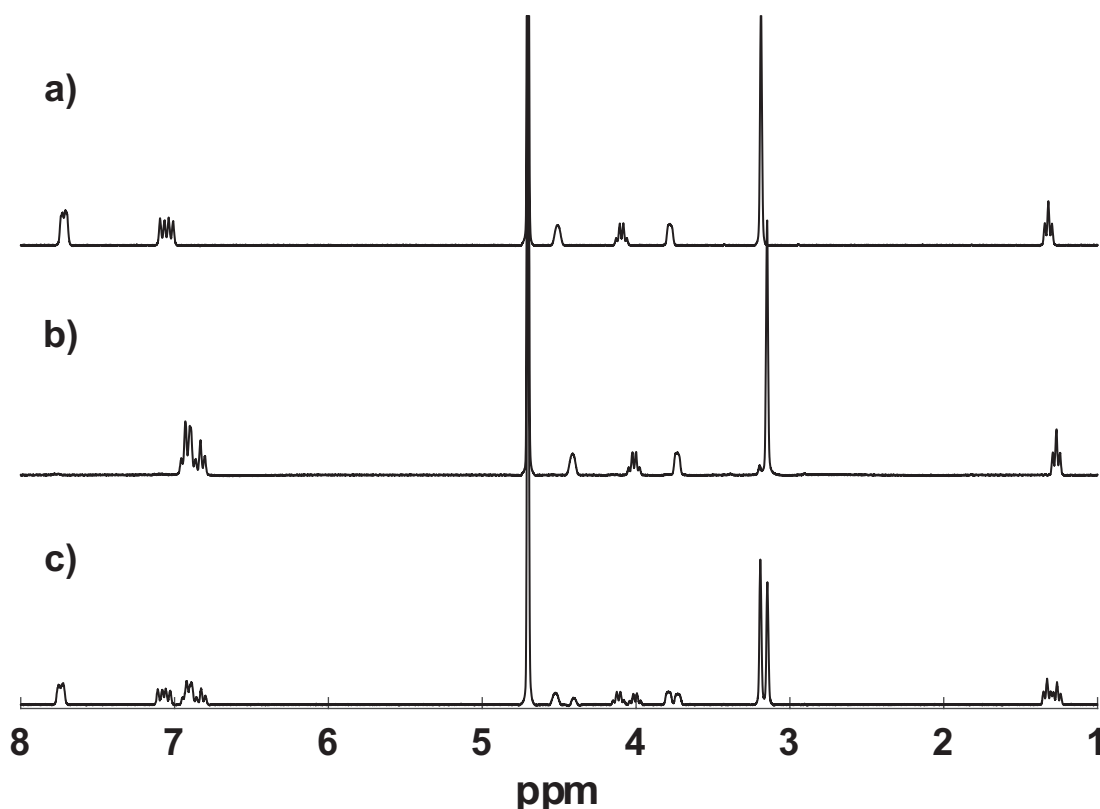


Figure 6.2: ^1H NMR (300 MHz, D_2O , 298 K) spectra of (a) a solution of AzoTAB (10 μM), (b) the same solution after exhaustive irradiation at $\lambda = 365$ nm and (c) the same solution in (a) after exhaustive irradiation at $\lambda = 440$ nm.

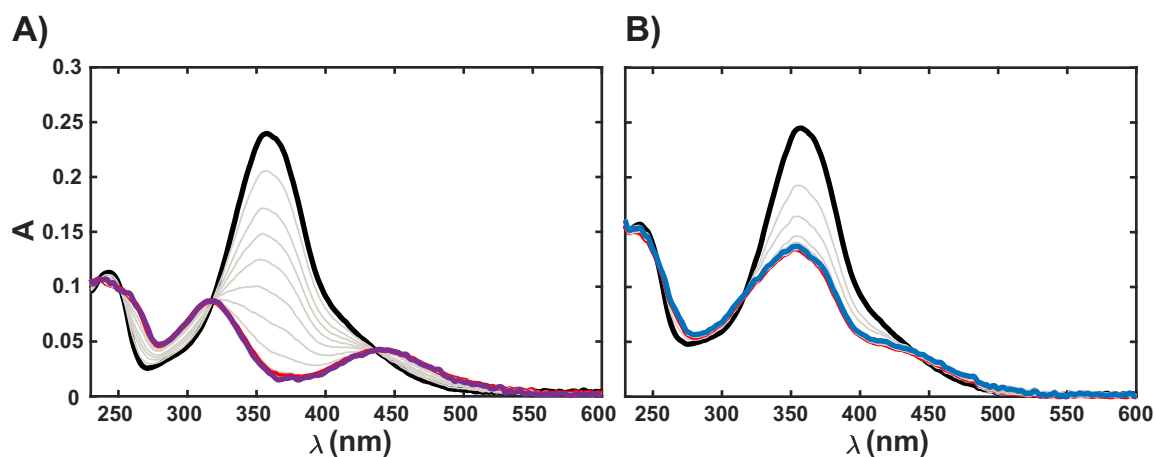


Figure 6.3: Absorption spectrum of an aqueous solution of AzoTAB (10 μM) (black line), and spectral changes observed after irradiation of the water solution (room temperature) A) at 365 nm and B) at 440 nm, showing the *trans-cis* photoisomerization. The red line shows the absorption spectrum after 1 min, the purple/blue line after 20 min of irradiation.

sized 2D crystal that remained crystalline upon irradiation (Figure 6.1Cii). The crystalline state was composed of monocrystalline domains made of thousands of hexagonally packed particles (including occasionally a few vacancies) separated by grain boundaries. To our knowledge, this is the first time that such a dynamic photoresponse of a large colloidal

6.3 Experimental results and discussion

assembly at the air/water interface is reported. A control experiment was performed with the non-photosensitive cationic surfactant Dodecyltrimethylammonium bromide (DTAB) having a CMC ($13.4 \text{ mM}^{[231]}$) close to that of AzoTAB. In that case, the structure of the adsorbed particles did not change upon extensive irradiation with UV light (Figure 6.4), showing that AzoTAB photoisomerization was instrumental in controlling the colloidal organization.

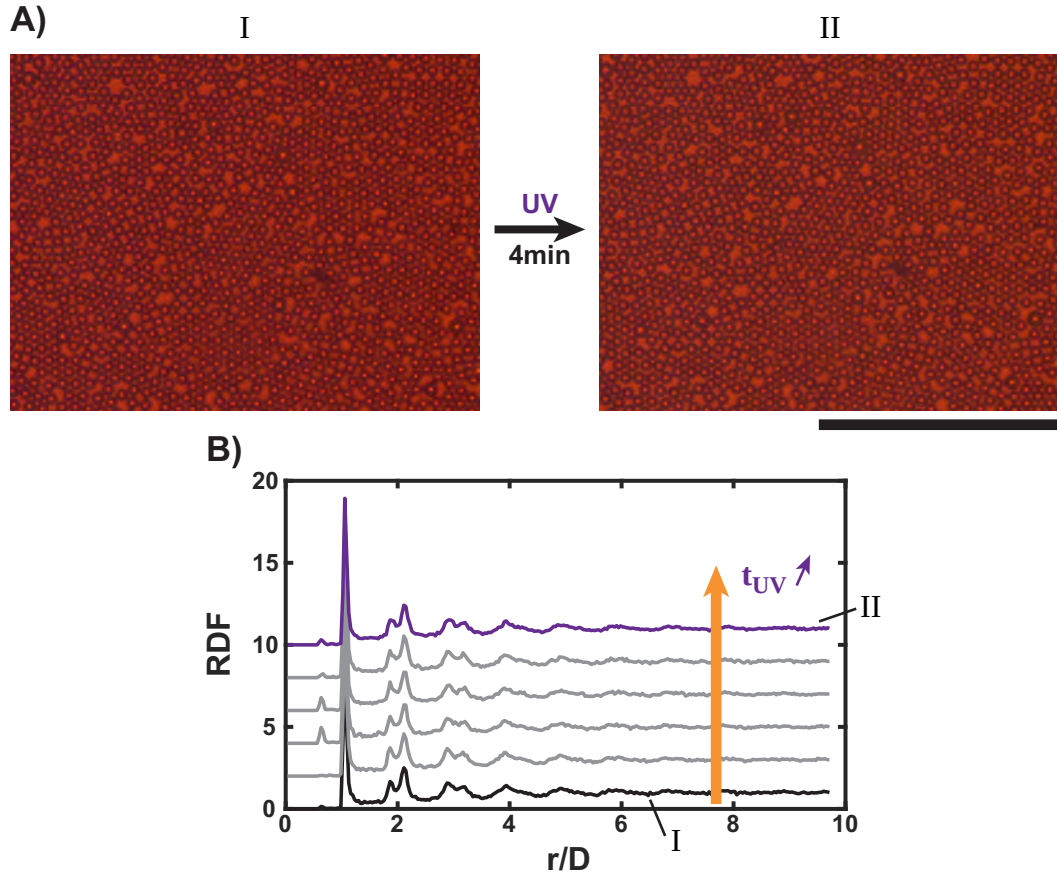


Figure 6.4: UV irradiation of a mixture of the cationic surfactant DTAB ($10 \text{ } \mu\text{M}$) and anionic polystyrene particles (0.01 mg/mL) trapped at the air/water interface. A) Typical transmission image of the centre of the particle assembly at the air/water interface before light irradiation (I) and after 4 min of UV irradiation (II). Scale bar $100 \text{ } \mu\text{m}$. B) Radial distribution functions (RDFs) curves before (black curve, corresponding to image I) and every 48 s up to 4 min (violet curve corresponding to image II) of UV irradiation. The image analysis was done in a box of $218 \times 165 \text{ } \mu\text{m}^2$; r is the distance with a reference particle, D the diameter of a particle. The curves are offset in the y-axis for clarity.

I then characterized the UV-induced disorder-to-order transition dynamics by computing the radial distribution function (RDF) from images of the colloidal patch as a function of UV irradiation time (Figure 6.5). Several peaks appeared in the RDF in the first seconds of irradiation and, after about 10 s the structure reached a stable state composed of well-defined peaks up to $r/D = 9$ (where r and D were the distance to particle centre and the particle diameter, respectively) showing long-range hexagonal packing (Figure 6.5B). Interestingly, while this structure was maintained upon prolonged UV exposure (20 min, Figure

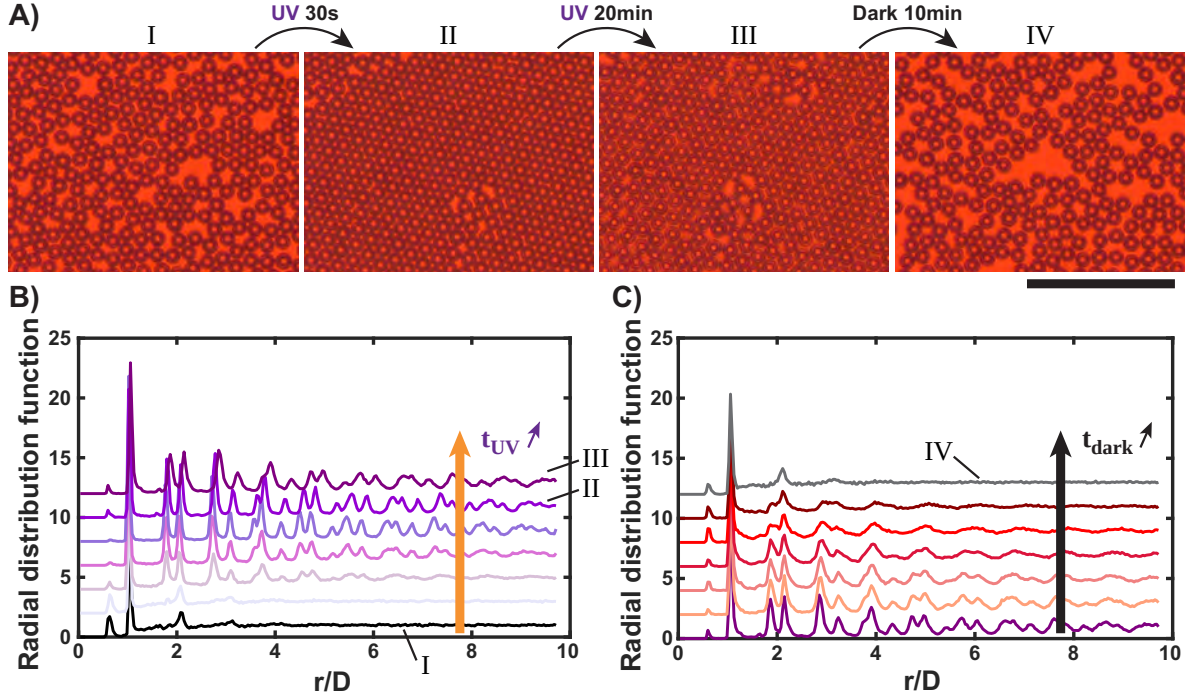


Figure 6.5: Structural evolution of colloidal assembly upon application and subsequent removal of UV irradiation. A) Typical transmission image of the center of a colloidal assembly before irradiation (I), after 30 s of UV irradiation (II), after 20 min of UV irradiation (III) and after 10 min following removal of the UV irradiation (IV). Scale bar: 50 μm . B) Radial distribution functions (RDFs) before (black curve) and after exposure to UV irradiation for 2, 4, 6, 10, 30 and 1200 s, as a function of the ratio between r the distance with a reference particle and D the particle diameter. The curves are offset on the y -axis for clarity. UV irradiation was done at 365 nm ($8.1 \text{ W} \cdot \text{m}^{-2}$). C) RDFs obtained after switching off the UV stimulus, at 0, 30, 60, 120, 180, 300 and 600 s under dark conditions.

6.5A, II-III), switching off the irradiation resulted in a transition back to the disordered state. The crystalline structure progressively lost its order, reaching a state similar to the initial amorphous state and composed of particles in close proximity but without any long range positional order (Figure 6.5A, IV). This transition took about 5 min (Figure 6.5C) as evidenced by the vanishing of most of the peaks in the RDF curves. Only the peak at $r/D \approx 1$ remained showing that particles were still in close proximity. These results demonstrate not only the photoreversible nature of the particle organization in our system but also emphasize the surprising behaviour that, after light removal, particles switch from a highly ordered to a disordered state in an isothermal manner. To have a better insight in the underlying mechanisms of these dynamic processes, it is interesting to compare the response dynamics of the particle organization to the isomerization characteristics of AzoTAB upon different irradiation conditions. UV-induced enrichment in *cis*-AzoTAB was very fast, with the bulk composition rapidly increasing from 0% to 50% within 10 s (Figure 6.1B, bottom). After 60 s, this value reached 95% and stayed approximately constant upon extended irradiation (Figure 6.1B, top). The transition time from disordered to crystalline particle assembly at the air/water interface thus followed similar kinetics, which can be interpreted as follows.

Upon *trans-cis* isomerization, AzoTAB became more polar and desorbed from the air/water interface, in a way similar to what was reported for similar photosensitive surfactants in the absence of particles.^[235] Upon surfactant desorption, the screening between like-charged particles by the cationic surfactant decreased but particles remained adsorbed because of the too high energy of detachment.^[6] The resulting increase of electrostatic repulsion added to the long-range attraction potential between particles caused by the collective deformation of the interface, resulted in the formation of a highly crystalline structure. Interestingly, when light was switched off, the transition from the ordered to the disordered phase was achieved in a few minutes while the AzoTAB *cis/trans* composition was not affected at this time scale (Figure 6.1B). We thus conclude that the colloidal structure was not controlled by the relative composition of *cis/trans* AzoTAB isomers in the bulk but was instead mediated by the adsorption/desorption dynamics of AzoTAB. In the photostationary state under UV irradiation, the bulk was composed of 5% *trans* isomer and, as soon as the irradiation was removed *trans* molecules could adsorb to repopulate the interface. This resulted in a progressive decrease of the repulsion between particles and therefore a rapid evolution back to the disordered state. The ordered structure was thus maintained only under continuous UV irradiation (Figure 6.5A) to keep AzoTAB desorbing from the interface. Note that dynamic adsorption/desorption of the few surfactants at the particle surface upon light irradiation would cause similar behaviour. Therefore the 2D crystals reported here do not correspond to a minimum in the free energy landscape of the system. On the contrary, they constituted an example of an out-of-equilibrium self-assembled structure where the structural complexity was obtained reaching a dissipative state through continuous consumption of energy by surfactant isomerization and depletion from the air/water surface. Since the particles organization was dependent on the amount of surfactants adsorbed at the interface, therefore on the adsorption dynamic of the *trans* molecules, and not on the bulk concentration of the two isomers, the system after irradiation responded in a time that was much faster than the *cis-trans* conversion in dark at ambient temperature.

To gain more information about these dissipative colloidal crystals, I investigated whether they could be obtained with a less efficient bulk photoconversion process. To this end, I irradiated the sample with blue light ($\lambda_{exc} = 440$ nm, intensity = $63 \text{ W} \cdot \text{m}^{-2}$) that induced a *trans-cis* conversion of the AzoTAB molecules up to a photostationary state that contained much less *cis* than the one at 365 nm (Figure 6.1B). The photostationary state was reached within one minute and was composed of 55% *trans* and 45% *cis* (Figures 6.2 and 6.3B). Although this photostationary state was significantly different from the one obtained after UV irradiation, the response of the colloidal assembly at the air/water interface was strikingly similar. Blue irradiation induced a fast disorder-to-order transition and the formation of extended highly crystalline colloidal assemblies (Figure 6.6A, 6.6B). Crystals were maintained upon blue irradiation and switched back to the disordered phase as soon as light was

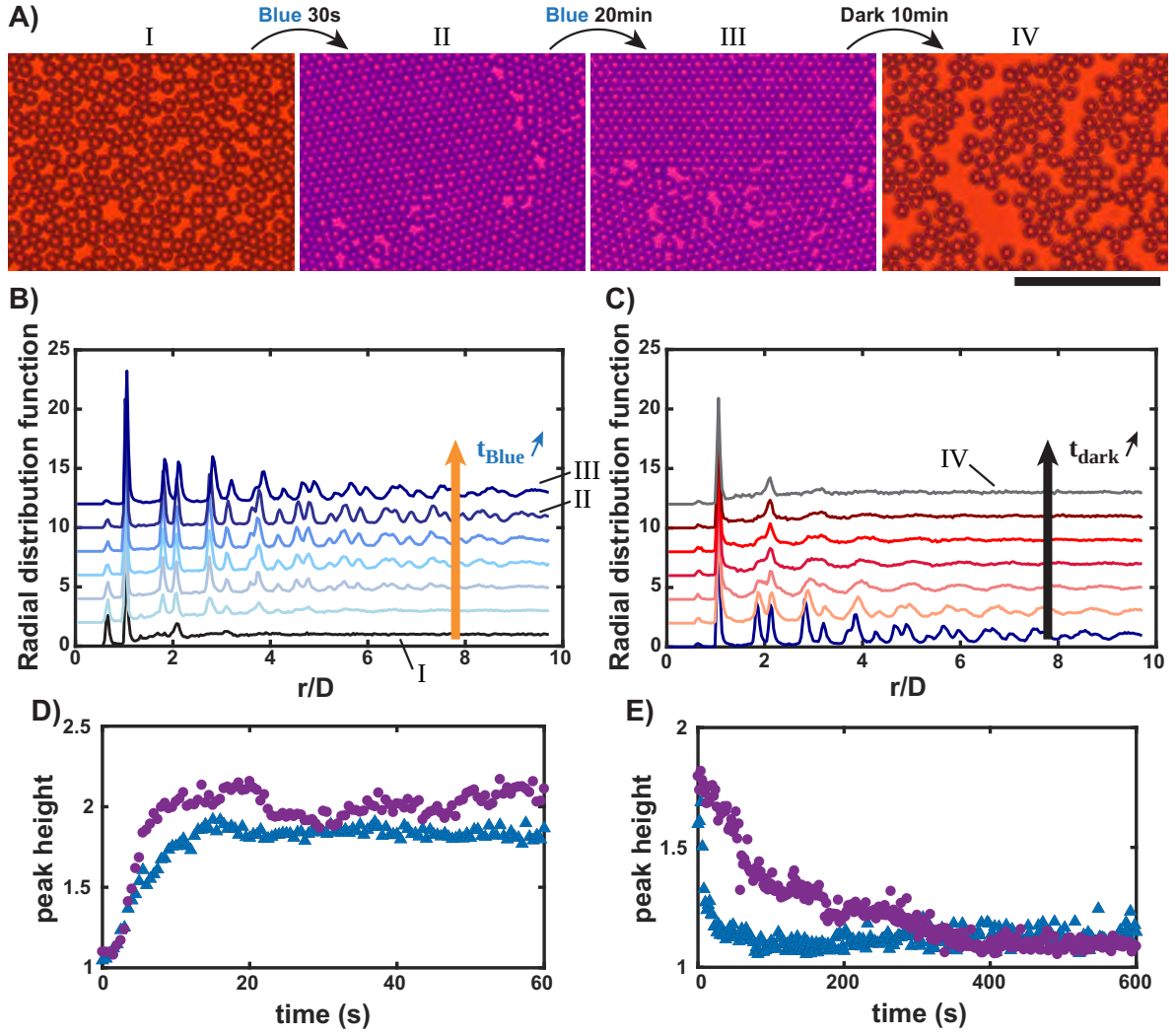


Figure 6.6: Light-induced crystallization and relaxation process in dark: comparison between blue and UV light irradiation. A) Typical transmission image of the center of the colloidal assembly before irradiation (I), after continuous blue irradiation for 30 s (II), 20 min (III), and 10 min after switching off the blue stimulus (IV). Scale bar: 50 μm . B) Radial distribution functions (RDFs) before (black curve) and after exposure to blue irradiation for 2, 4, 6, 10, 30 and 1200 s. The curves are vertically offset for clarity. C) RDFs after switching off the blue stimulus, at 0, 4, 10, 20, 30, 60 and 300 s under dark conditions. D) Height of the 12th peak in the RDFs as a function of irradiation time for samples irradiated with UV (circles) or blue (triangles). E) Height of the 12th peak in the RDFs as a function of time under dark after switching off the light stimulus for samples exposed to 20 min of UV (circles) or blue (triangles) irradiation. UV and blue irradiation was done at 365 nm ($8.1 \text{ W} \cdot \text{m}^{-2}$) and 440 nm ($63 \text{ W} \cdot \text{m}^{-2}$), respectively.

switched off (Figure 6.6A, 6.6C). The structural properties of light-induced colloidal assemblies were very similar for UV and blue irradiation but a few differences could be noticed in the transition kinetics. Taking the height of the 12th peak in the RDFs curves ($r/D \sim 5.8$, long-range crystalline order signature) as a function of the irradiation time, I compared the kinetics of light-induced crystallization and relaxation to disordered state for the two wavelength used. Light-induced crystallization was achieved in around 10 s for both irradiation wavelengths (Figure 6.6D) but relaxation in the dark was faster after blue irradiation

6.3 Experimental results and discussion

(~ 30 s) than after UV irradiation (~ 350 s) (Figure 6.6E). These results first confirmed that our system was not controlled by the bulk composition of AzoTAB under light irradiation as two different photostationary states led to very similar structures. It was thus the continuous light-induced desorption of AzoTAB from air/water interface that maintained the system out-of-equilibrium where particles electrostatically repelled and crystallized due to the long-range attraction potential. Interestingly, the system was shown to be history-dependent with two different kinetics under dark conditions as a function of the previously applied light wavelength. This can be explained by the different composition of the bulk which was richer in *trans*-AzoTAB after blue irradiation. The larger concentration of *trans*-AzoTAB made the kinetics of readsorption faster but the final state, which was mainly controlled by the interfacial composition, was similar regardless of the wavelength.

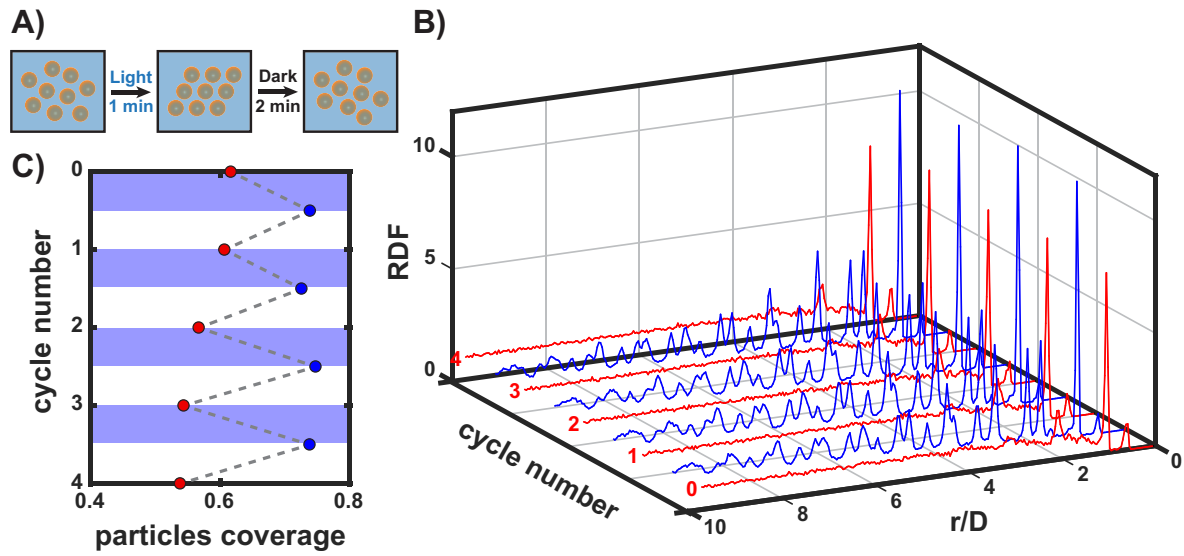


Figure 6.7: Photoreversible crystallization/disassembly upon light On/Off cycles. A) Sketch of a disorder-order-disorder transition sequence made by a cycle of blue light On and Off. B) RDFs of the same sample subjected to cycles of blue light On (blue curves) and Off (red curves). C) Fraction of the total area covered by particles in the centre of the colloidal assembly, in a box of $218 \times 165 \mu\text{m}^2$, along cycles of blue light On (blue background) and Off (white background). Each cycle consisted of irradiation with blue light (440 nm , $63 \text{ W} \cdot \text{m}^{-2}$) for 1 min and dark conditions for 2 min.

To assess the reversibility of the system, I applied successive light On/light Off cycles on the colloidal assembly (Figure 6.7A), choosing blue light as stimulus because of the faster response of the system after light removal. One minute of irradiation efficiently crystallized the whole particle assembly (Figure 6.7B, blue curves), whereas two minutes in dark were enough for the system to switch back to the disordered state (Figure 6.7B, red curves), and several cycles could be achieved without any apparent fatigue (Figure 6.7B). I also analysed the fraction of surface occupied by particles in the center of the assembly and found that it was oscillating in phase with the light cycle, with an increase/decrease of the 2D packing density upon irradiation/dark conditions that correlated with the crystallization/disassembly process (Figure 6.7C). Cycles between amorphous and crystalline structures were obtained

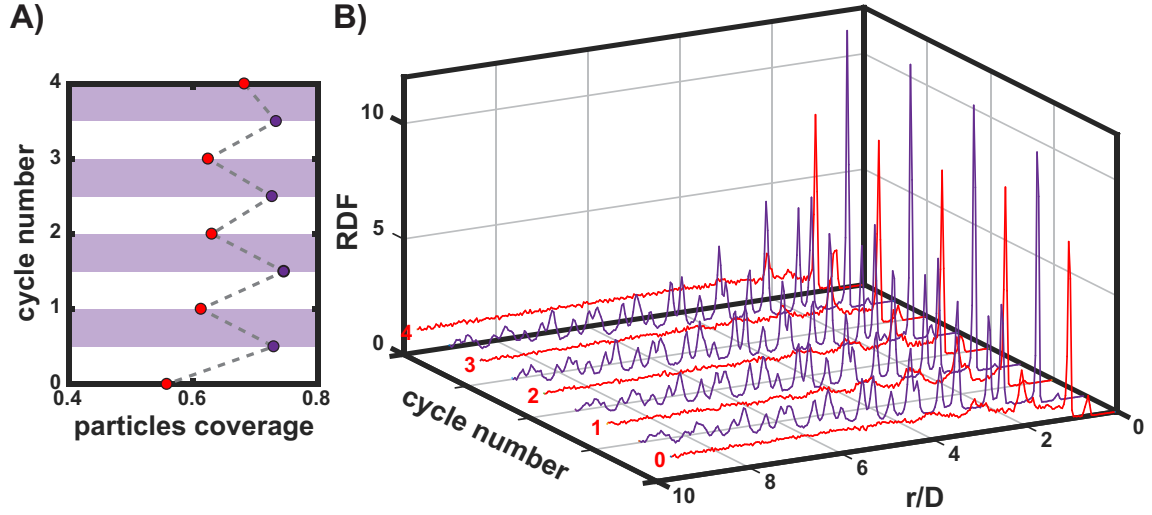


Figure 6.8: Successive light On/Off cycles using UV irradiation induce reversible transitions between 2D crystal and amorphous particle aggregates. A) Fraction of the total area covered by particles in the centre of the colloidal assembly, in a box of $218 \times 165 \mu\text{m}^2$ for a sample subjected to UV irradiation (1 min, blue areas) and light Off (5 min, white areas) cycles. B) RDFs of the same sample subjected to light On/light Off cycles after respectively 1 min of UV light irradiation (violet curves) and 5 min without light irradiation (red curves).

using UV light as well (Figure 6.8), but the order-to-disorder transition after UV irradiation was slightly slower and required 5 minutes. To our knowledge, this is the first time that fully photoreversible colloidal crystallization at the air/water interface is reported.

In Figure 6.9 I summarize our proposed description of the mechanism governing the photodependent 2D crystallization of colloidal particles at the air/water interface. The amount of surfactants adsorbed at the water surface, at a given bulk composition, is dependent on the energy supplied by light irradiation. If the system is irradiated with a wavelength suitable for *trans* to *cis* isomerization, the concentration of adsorbed surfactants will decrease due to the lower affinity of the *cis* isomer to the air/water interface (Figure 6.9A, middle). As long as energy is given to the sample, adsorbed surfactants are isomerized and depleted, and the system is kept out-of-equilibrium. Once the light stimulus is switched off, the *trans* isomers present in bulk solution can re-adsorb at the interface without being isomerized and removed (Figure 6.9A, right). The particle organization is mainly governed by the long-range attraction potential due to the collective deformation of the interface by the adsorbed particles and the short-range electrostatic repulsion between anionic particles. Since the number of adsorbed particles is fixed in this system, the first component is almost constant and can only slightly vary upon small changes of packing density. On the contrary, the second component is strongly dependent on the amount of surfactant at the air/water interface. As sketched in Figure 6.9B, the equilibrium structure in the absence of light stimulus is amorphous (left). The light input, through surfactant desorption from the interface, decreases the electrostatic screening by surfactants thus enhancing the repulsion component between negatively charged

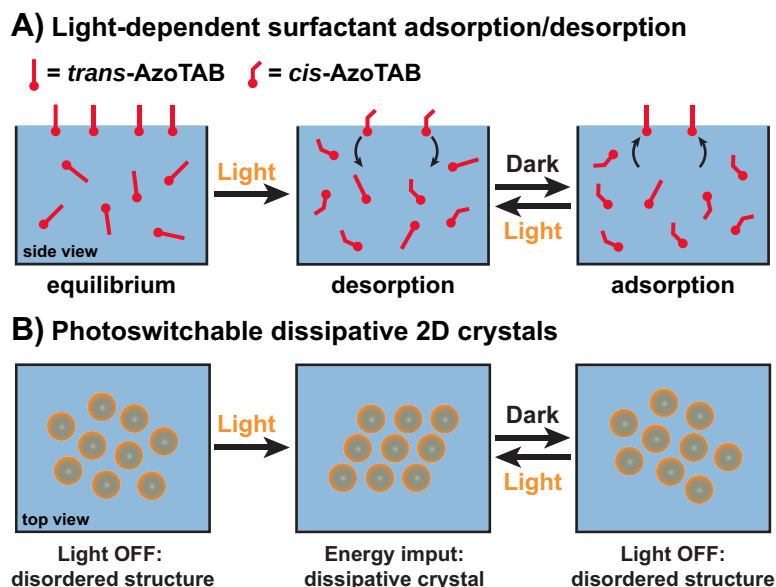


Figure 6.9: Proposed mechanism for photoswitchable crystallization of colloidal particles at the air/water interface. A) Upon continuous light irradiation, *trans*-AzoTAB surfactants at air/water interface isomerize into the *cis* and more polar form, inducing its desorption from the interface. When light is removed, the *trans* isomers in bulk solution repopulate the interface by adsorbing there, even though the bulk composition does not evolve at this time scale. This dynamic desorption/adsorption behaviour thus allows to cycle the process even if the equilibrium photostationary state has been reached in the bulk solution. B) The light-induced depletion of surfactants from the interface decreases the electrostatic screening between repulsive anionic particles and triggers the particle crystallization. These crystals are dissipative: they exist only upon continuous light energy supply that maintain the interface in an out-of-equilibrium state depleted from surfactant. As soon as the light input is switched off, surfactants repopulate the interface and particles evolve to a disordered state. The process is fully photoreversible and can be cycles several times.

particles. This in turns favours the formation of structural order, and 2D crystals at the interface can be obtained (middle). Such structures are dissipative because continuous supply of energy is needed to deplete surfactants from the air/water interface and maintain the particle-particle interactions favourable for long range ordering. Switching off the light will allow the system to reach equilibrium where the surfactant concentration at the air/water interface is increased. We hypothesize that such an increase in surfactant concentration is enough to alter the particle-particle interactions causing the maintaining of a long range ordered hexagonal structure unfavourable. As a consequence a disordered structure similar to the initial one is obtained (Figure 6.9B, right). Since particle organization in this system depends mainly on the amount of absorbed surfactant, and not on the photostationary composition of the bulk liquid phase, fast cycles between amorphous structures and 2D crystals can be performed by desorbing/adsorbing surfactant using light/dark conditions.

6.4 Conclusions

We have designed a photoresponsive dissipative self-assembling system composed of anionic microparticles and cationic photosensitive surfactant, where the structural properties of the colloidal assemblies adsorbed at the air/water interface can be controlled by light stimulation. We exploited the out-of-equilibrium adsorption/desorption dynamics of the surfactant isomers at/from the water surface to control the particle-particle potential in a fast and reversible fashion. As a consequence, cycles between disordered and highly crystalline colloidal structures were achieved with a single wavelength switch, without being hindered by the very slow thermal relaxation of the excited surfactant isomers.

This system, together with the one presented in the previous chapter, represents a proof of principle of novel light-responsive 2D colloidal systems where specific properties arising from the collective organization of particles at the interface could be efficiently switched on-demand by means of light stimulation. By evidencing the emergence of a highly organized self-assembled structure that exists only through continuous energy consumption, it expands the realm of currently known dissipative systems, opening routes to man-made devices closer to biological systems and capable of properties such as adaptiveness, reconfigurability and degradability.

Part III

Magnetic actuation using deformable liquid interfaces

The third part of the thesis collects the work done on developing a revolutionary concept to manipulate discrete liquid entities floating on a liquid surface, in a contactless and remote way by means of magnetic actuation. In the field of digital microfluidics, which concerns the controlled manipulation of discrete drops deposited on surfaces for a plethora of applications ranging from analysis and detection to carrying out (bio)chemical reactions, various actuation mechanisms for drops handling (*e.g.* merging, splitting, sorting, etc.) have been developed. The concept of digital microfluidics stems from the implementation of the electrowetting on dielectric technique (EWOD), which allows performing operations on drops on software-controlled electrode arrays (lab-on-a-chip). Different options have been studied to offer valuable alternatives to the EWOD technique, which has many advantages, but presents also some drawbacks, such as the need of patterned electrodes and electric current. Among the different actuating principles successively developed, magnetic control, which mainly rely on dispersing magnetic particles in the targeted drops, allows for enhanced reconfigurability and portability of the microfluidic chips, and practical applications (*e.g.* real-time PCR) have been proved. However, its main limitation so far lies in the necessity to integrate inside the sample magnetic particles, making the approach highly system-specific, costly, and prone to contamination and clogging. Alternatives, not requiring specific characteristics of the moving drops, are therefore a highly desirable challenge.

The **7th Chapter** presents the concept of microfluidics (the handling of small amounts of liquids in devices), successively focusing on droplet microfluidics, in which discrete drops are manipulated either in closed channels or on open surfaces (the latter technique usually referred to as digital microfluidics). Various techniques (both passive and active) to perform operations on drops are presented, comparing advantages and drawbacks. Finally, magnetic actuation methods are described, from the successful strategies based on using magnetic particles, to particles-free alternatives, such as the recently reported “magnetosensitive surfactants”.

In **Chapter 8** I describe the experiments done using a custom built setup conceived in our laboratory in order to measure precisely the surface tension of diamagnetic and paramagnetic liquids under homogeneous magnetic fields of moderate strength (~ 100 mT). An accurate measurement of the surface tension in homogeneous magnetic fields, by excluding bulk effects present when a non-homogeneous field is employed, is crucial to correctly assess the extent of the surface tension variation with such stimulation. The results presented here will help understanding the mechanism behind the magnetic actuation principle, which will be the main subject of the following chapter.

Chapter 9, adapted from *Angew. Chem. Int. Ed.* **2017**, 56, 16565–16570, reports our new way to magnetically control the motion of a broad variety of discrete liquid drops. Not relying on additives added in the drops, it is based on exploiting the magnetic-induced deformation of paramagnetic liquid substrates in order to direct, using a portable magnet, the motion of various floating liquids, ranging from naked drops to liquid marbles. Various

liquids (such as water or oil), including diamagnetic or non-magnetic ones, can be efficiently transported at a speed up to $cm \cdot s^{-1}$ using moderate magnetic fields (≈ 50 mT). The mechanism, substrate deformation directing the motion of floating liquids, has been demonstrated both experimentally and with the help of a theoretical model.

In summary, a novel concept for the manipulation of drops floating on liquid surfaces using magnetic fields will be presented, together with complementary experiments required to understand the underlying mechanism. These results could offer a starting point for developing techniques to magnetically control fluids flows and drops formation and handling, without magnetic particles, inside microfluidic channels, for example by controlling the deformation of the interface between immiscible liquids.

Actuation strategies in (digital) microfluidic systems

7.1 Abstract

Drops manipulation by means of external triggers finds several application in science and technology, allowing to transport discrete liquid entities for further analysis or (bio)chemical reactions, where screening of multiple conditions can be performed on small amounts of samples. Among the possible external stimuli, magnetic manipulation is a valuable technique, and, depending on the magnetic field source (being it permanent magnets or electromagnets), various advantages exist. In this bibliographic chapter the concept of microfluidics is introduced, as well as the sub-field so called digital microfluidics, with which we refer to the actuation of discrete drops, individually manipulated on surfaces. Successively, several techniques to perform operations on drops, such as splitting, merging, sorting, etc., both in continuous-flow droplet-based microfluidics (inside closed channels) and digital microfluidics (on flat surfaces), will be discussed. In particular, the last section summarizes the main actuation methods in digital microfluidics (electrowetting on dielectric, optofluidics and magnetic actuation), comparing the techniques and looking for advantages and drawbacks. The chapter ends reviewing the recently reported “magnetosensitive surfactants”, ideally a valuable alternative for magnetic actuation techniques that otherwise rely on magnetic particles dispersed in the drops to be manipulated.

7.2 Microfluidics

Microfluidics, citing once more a definition proposed by Whitesides:^[254]

is the science and technology of systems that process or manipulate small (10^{-9} to 10^{-18} litres) amounts of fluids, using channels with dimensions of tens to hundreds of micrometres.

Here the keywords are the precise handling of small amounts of liquids, and their incorporation in tiny channels, instrumental for their manipulation. The subject evolved, since several years now, for the various capabilities it offers to different fields (*e.g.* physics, chemistry, biology, medicine and engineering). Probably, the most important characteristic is the possibility to deal with very small quantities of samples and reagents, facilitating the study of expensive and/or rare substances. High sensitivity and resolution are ensured, especially by coupling with optical detection techniques. Therefore microfluidic devices are seek for detection purposes, being able to sense very dilute chemicals present in small sample volumes. In fact, microfluidics primarily arises as an evolution of microanalytical methods, such as gas-phase chromatography (GPC), high-pressure liquid chromatography (HPLC) and capillary electrophoresis (CE), going beyond toward the construction of miniaturized, more flexible and adaptable equipment, able to perform multiple operations in a parallel manner.

Another, fundamental, characteristic of microfluidics is that the physics governing the fluids behaviour changes rapidly as the size decreases.^[255] Viscous dissipation dominates over inertial effects causing a reduction of turbulences and instabilities, normally presents when we look, in everyday life, at liquids motion. Fluids in a microchannel will not mix convectively, instead they will flow in parallel – the so called laminar flow – and they mix only at their interface through diffusion. Surface effects become more and more important at small sizes, overcoming gravity. Those properties, different from the macro-scale physics, are interesting both from a fundamental point of view, and as a tool to develop novel, useful devices.^[256;257] To cite one example, laminar flow allows for the generation of precise concentration gradients (in space and time) that are instrumental in the study of cell migration.^[258]

A lot of research in the microfluidic field is primarily oriented to the development of “lab-on-a-chip”, or micrometer-scale total analysis systems (μ TASs), devices; which are small chips in principle able to perform by themselves all the functions required. Such a device needs methods to move, mix and sort fluids inside it; plus detectors and other components to screen the output (for example a bio(chemical) analysis or reaction). In most cases, supporting instrumentation to use the chip are required, therefore the so-called transition from lab-on-a-chip to chip-in-a-lab, which denotes the need of various complementary equipments surrounding the chip, such as microscopes, flow controllers, chromatographic columns to isolate single chemicals, etc. This transition hinders the widespread diffusion of this technology. A highly integrated chip for molecular synthesis is reported in Figure 7.1A, the inset shows the tubing surrounding the device, hence giving a hint of the complex platform required

7. ACTUATION STRATEGIES IN (DIGITAL) MICROFLUIDIC SYSTEMS

to run the reaction. It is for this reason that researchers are focusing on the development of simple, low-cost devices, with a minimum requirement of external components for their functions.^[259;260] An outstanding example is a bioassay device conceived by Whitesides and co-workers^[259] (see Figure 7.1B) composed of hydrophobic patterns on paper generating channels and detection regions for multiple analysis of biological samples. Fluid pumping is ensured by capillary action in the millimeter-sized channels produced on the paper substrate, while appropriate reagents can be loaded and stored in the test areas.

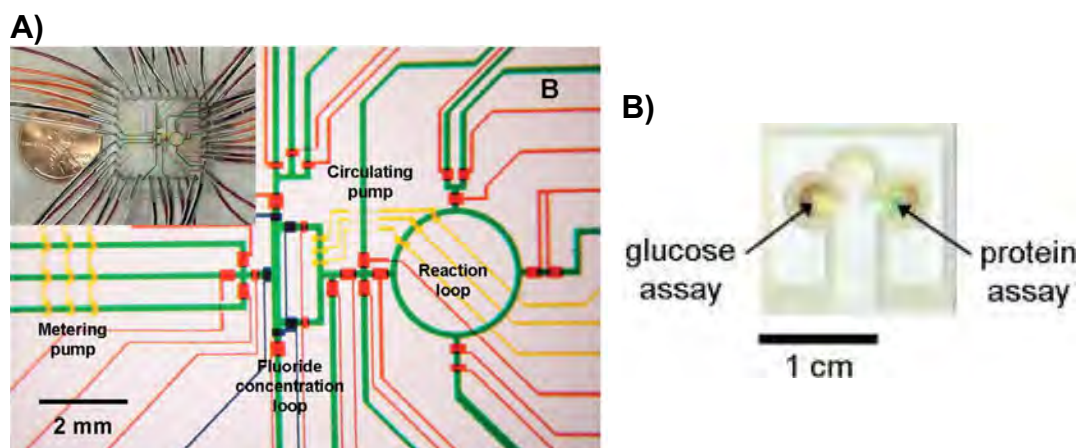


Figure 7.1: Microfluidic chips. A) Microfluidic system for the synthesis of radiolabeled molecules with included sites for: $[^{18}\text{F}]$ fluoride concentration, water evaporation, radiofluorination, solvent exchange and hydrolytic deprotection. Optical image of the central region of the device, with dyes to show the channels; in the inset the full device, close to a coin of 1.9 cm in diameter, with the loading tubes.^[261] B) Paper-based microfluidic chip for bioassays. The grey lines are cured hydrophobic photoresist, the lighter areas are unexposed paper; a glucose and a protein assay are stored in two areas of the chip.^[259]

The final “lab-on-a-chip” device should be not only exempt of – too many – laboratory instruments and low-cost for practical applications in resource-limited environments; but, depending on the application purpose, it should be also programmable, reconfigurable, and reusable on-demand for various reagents, solvents and processes.^[262]

7.3 Droplet microfluidics

A subcategory of microfluidics has been further developed, called droplet microfluidics. It consists in the generation and manipulation of pico- to microliter drops instead of handling continuous phases. Those drops can be either generated in a consecutive manner inside closed microfluidics channels, or can be individually manipulated on plain surfaces or inside open channels. The latter case has been referred to as digital microfluidics*.

*In literature the terminology is ambiguous; sometimes droplet microfluidics is referred to as digital microfluidics. Here I consider droplet microfluidics as the whole field of controlling small-volume droplets, and, following for example refs,^[262;263] I separate between continuous-flow droplet-based microfluidics, where multiple drops are handled in small channels, and digital microfluidics, where discrete drops are manipulated on surfaces or open channels.

The advantages of having discrete drops rather than continuous flows are manifold.^[264;265] The first one is their increased miniaturization; droplets up to subpicoliter volumes can be produced, simplifying the analysis of single cells or molecules. Compartmentalization is guaranteed: each drop containing a determined analyte can be handled independently, sorted and processed. Parallel analysis is carried out producing large quantities of monodisperse, identical drops for high throughput screening without increasing the device size. Thanks to high frequency drops generation, large data sets can be acquired in a short time. Droplets in a microfluidic chip can be used as microreactors for chemical, or bio-chemical, reactions: their volumes ensure the use of small quantities of reagents; their surface over volume ratio facilitates faster reaction times (both heat and mass transfer times and diffusion distances are shorter); their number allows performing parallel combinatorial chemistry, screening multiple reactions in the same chip.

7.3.1 A microfluidic chip

In continuous-flow droplet-based microfluidics, the drops are produced inside closed channels. Starting from two or more immiscible flowing liquid phases, one of them is broken with various techniques to continuously create drops, usually monodisperse in size, at a rate that can reach up to twenty thousand drops per second.^[266] The large majority of devices are nowadays made of polymers, especially poly(dimethylsiloxane) (PDMS), an optically transparent, soft elastomer. The development of soft-lithography^[158] in PDMS, for the fabrication of prototype devices with complex structures in a fast and simple way,^[267] contributed extensively to the widespread diffusion of microfluidics. Other materials, such as glass and silicon, are used as well, especially to deal with organic solvents that would otherwise swell and deform architectures built in PDMS. Furthermore, the recent improvement in 3D printing technologies is facilitating the construction of more and more sophisticated devices directly from a computer-built design, with the possibility to choose among various materials.^[268]

To begin with, immiscible fluid phases for droplet-based microfluidics are introduced into the channels via open inlets in the structure. To ensure good and stable performances of the device, the forces used to inject the fluids should be stable. Motion of fluids can be controlled either by syringe pumps imposing flow rates, or by pressurized reservoirs; alternatively, gravity can be exploited as well placing reservoirs of the liquids at different heights with respect to the channels.

Successively, inside the chip, one of the continuous fluid phases is split into drops. The capillary number (Ca) – one of the many dimensionless numbers used in microfluidics to assess the various physical parameters involved dictating the fluids behaviour^[255] – estimates whether the fluid stream in the channel will break, and can be used to predict the size of the forming drops. It relates viscous forces over surface tension in the system, and it is defined as:

$$Ca = \frac{\eta v}{\gamma} \quad (7.1)$$

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where η and v are respectively the viscosity and velocity of the continuous phase, and γ is the interfacial tension between the phases. At a certain Ca value, system-dependent, the continuous phase will break into drops. The characteristic drop size is then $R \approx h/Ca$, with h the smallest dimension of the channel. Energy has to be provided to break a continuous flow because of the increase in interfacial area, which is contrasted by the interfacial tension value. Therefore, passive and active methods exist to generate drops. Passive methods do not rely on externally delivered energy: the fluids meet at a junction, with a more or less intricate channel geometry, where one of the fluids is deformed up to droplet breakup. Several devices exist for the scope, where the incoming flows meet with different geometries (as showed in Figure 7.2A), such as: coflow, cross-flow (or T-junction) and flow-focusing devices.^[269]

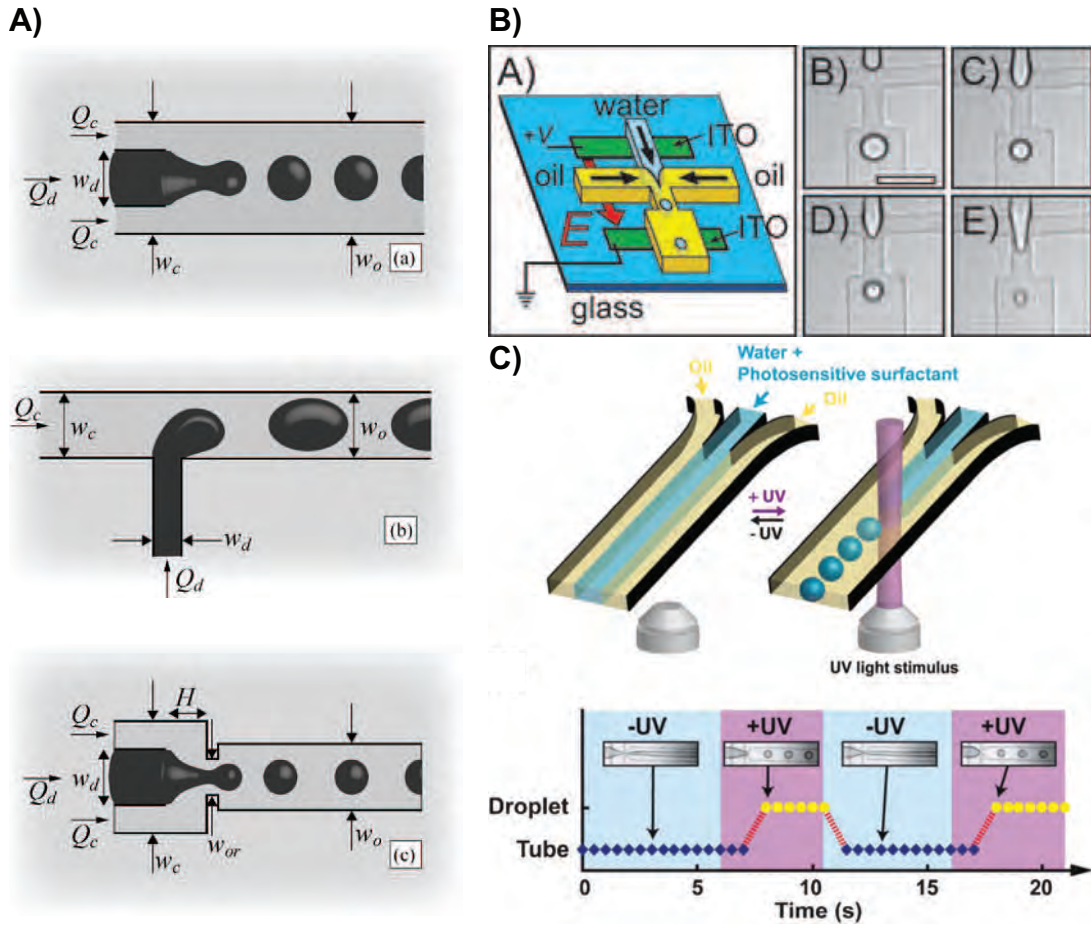


Figure 7.2: Passive and active mechanisms for drops production in a microfluidic chip. A) Sketch of the three main geometries used for drops formation:^[269] (a) co-flowing streams, (b) cross-flowing streams in a T-shaped junction, and (c) flow focusing geometry. Q_d and Q_c are respectively the flow rates of the dispersed and continuous phase with arrows indicating their directions, W the width of each channel. B) Generation of water drops by charging the oil/water interface, and control of the drop size as a function of applied voltage.^[270] C) Photoreversible drops generation by UV-induced dewetting of a water/photosensitive surfactant solution. Applying UV induce transition from continuous flow to drop formation in the irradiated region.^[271]

Alternatively, active methods to externally deliver energy can be used to continuously produce drops. Electric and magnetic fields, as well as light, thermal or mechanical energy

are employed for the scope. Electric stimulation is the most used energy source to actively brake fluid flows. It is provided by means of electrodes embedded in the chip, and various mechanisms are exploited, such as: charging an oil/water interface^[270] (as in Figure 7.2B), electrowetting on dielectric (EWOD)^[272] or dielectrophoresis. Micromotors plugged on the chip, for example miniature peristaltic pumps, are used to deliver immiscible phases in a controlled fashion, producing drops in a robust manners, with definite size and composition.^[273] Our group previously showed how light irradiation could be used to trigger drops formation in a biphasic system composed of an outer oil phase and an inner water phase with dissolved in it the photosensitive surfactant AzoTAB^[271] – whose properties and molecular structure are described in Chapter 4. A sketch of the experimental set-up is showed in Figure 7.2C. The wettability of the water phase in the channel depends on the isomeric state of the surfactant: higher for *trans* and lower for *cis*-AzoTAB isomer. In turns, the isomeric state depends on the applied light irradiation: *trans* without any stimulation, *cis* under UV irradiation. At a defined applied pressure, the continuous water flow in the wetting situation can be switched to a stable droplet generation regime by irradiating with UV light and decreasing the wetting properties. Reversible switch from drops to continuous flow is possible simply removing the light stimulation. Moreover, by applying a photomask, the drops can be produced in different positions inside the channel.^[271] Magnetic fields can be used as well for on-demand drops formation; for example approaching a permanent magnet to a ferrofluid phase allows controlling both drops release and their size.^[274] The working principle is simple: the controlled attraction of the ferrofluid solution to the incoming magnet add a new force in the system, that can be efficiently controlled to perform the operations required.

Once formed, drops can be manipulated in several ways inside a microfluidic chip, depending on the final application purpose. They can be fused, mixed, sorted, split or trapped using a plethora of different techniques, which once again can be separated between passive and active. Passive methods are based on carefully chosen channel geometries: folds and turns in the channel promotes mixing within the drops^[275] (Figure 7.3A); sorting of distinct drops populations is obtained using channels of varied sizes,^[276] or gravity; splitting is achieved with branching^[277;278] (Figure 7.3B), or obstructed,^[278] paths.

Active methods use external triggers to perform similar operations, with the goal to achieve an increased control over the droplets behaviour. For example: electrodes can be used to control the fusion of targeted drops through electrocoalescence^[279] (Figure 7.3C); electrostatically charged drops can be merged, split and sorted with opportunely patterned electrodes in the device;^[270] dielectrophoresis too can be exploited for high speed sorting of water drops^[280] (Figure 7.3D). Light actuation can be used to perform various operations inside microfluidic chips, with the advantage to avoid the rather cumbersome implementation of specific elements, such as pumps, valves or electrodes within the device; making it less system-specific. It is possible to mix continuous phases by generating drops of a third phase

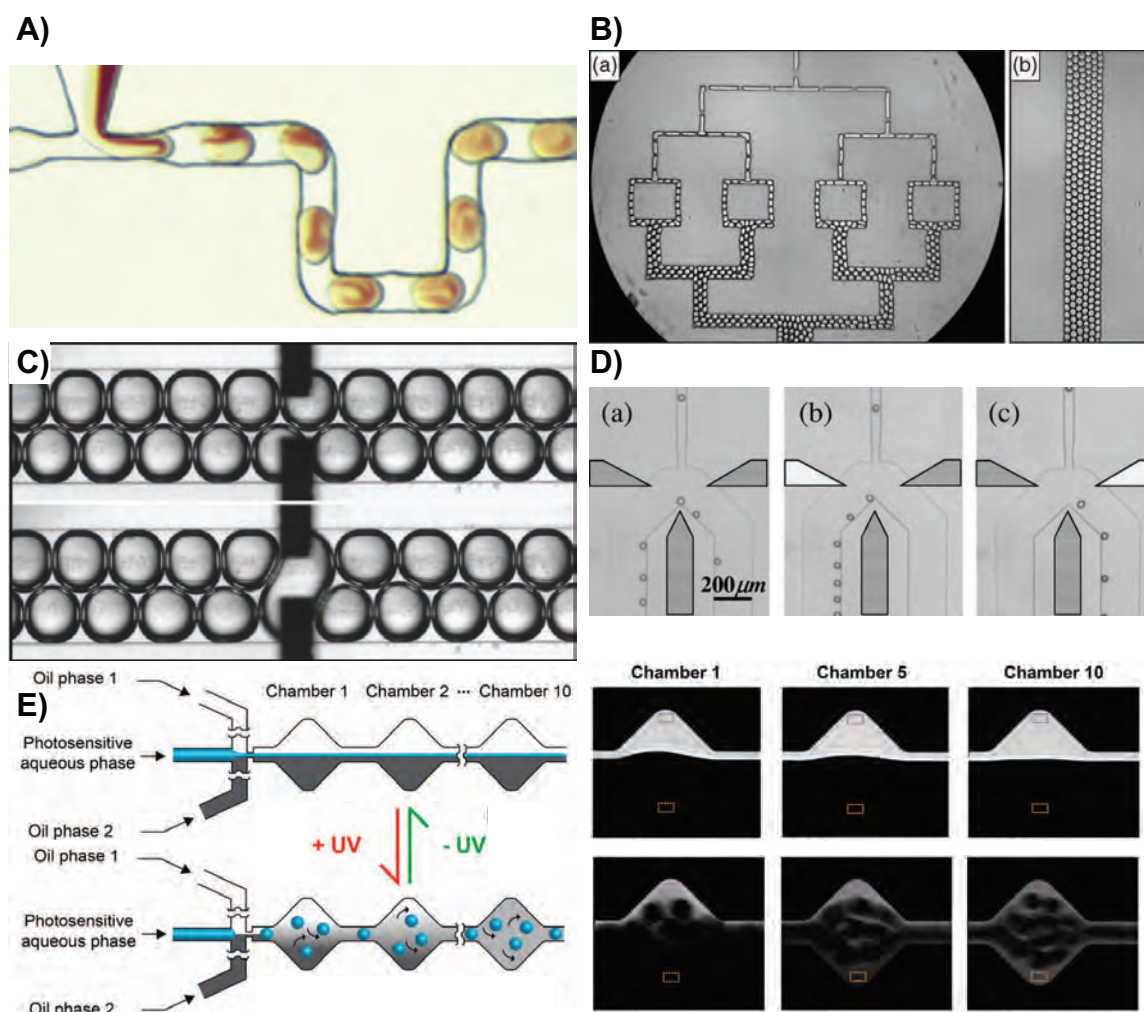


Figure 7.3: *Passive and active mechanisms for drops manipulation in a microfluidic chip. A) Passive mixer: drops are mixed by chaotic advection promoted stretching and turning them by means of turns in the channel*^[275] *B) Sequential passive breakup into smaller droplets*^[278] *C) Electrocoalescence of targeted drops when a potential pulse is applied between two electrodes (here in black)*^[279] *D) Controlled drops direction by means of dielectrophoresis:*^[280] *(a) electrodes are off and drops (coming from top) goes randomly in both bottom channels; (b-c) turning on one electrode (white in figure) cause the drops stream to flow toward the desired channel with the charged electrode.* *E) Light controlled mixing of two oil phases separated by a water stream containing photosensitive surfactants.*^[281] *The drops formed by UV irradiation stir the oil streams in the chambers of the chip, inducing their mixing. Left: sketch of the chip and the mechanism; right: images of consecutive chambers without (top) or under (bottom) UV light.*

that would stir the streams,^[281] as in Figure 7.3E; to fuse drops by means of laser beams;^[282] and to sort drops by optically-induced dielectrophoresis.^[283]

Applications of continuous-flow droplet-based microfluidics. The large amount of identical drops produced in a chip can be used to perform multiple parallel reactions. The technique is used for bio(chemical) analysis: several reaction conditions can be screened with much lower time and reagents consumption compared to traditional bench-top reac-

tions.^[284;285] Droplet microfluidics is exploited also for the synthesis of novel micro- and nanoparticles;^[286] in the remaining part of this paragraph I will give some more detailed examples on this subject (a topic related to the synthesis of particles described in Chapters 1 and 4). Each drop acts as a microreactor, protecting the reaction from contaminants and ensuring homogeneity of the product thanks to well-controlled mixing and uniform size. Particles of various materials can be produced, with high monodispersity in size and having several shapes depending on the reaction conditions. More complex suprastructures can be produced as well; for example, a capillary microfluidic device can be used to fabricate capsules containing particles showing full spectrum structural colouration depending on their size.^[287;288] Two immiscible fluids are injected through a hydrophobic capillary: the fluid with higher affinity to the wall (in this case ethoxylated trimethylolpropane triacrylate (ETPTA) as the oil phase) will flow along the capillary, enclosing the other fluid, a water solution containing particles. Emulsification of this core-sheath flow in a continuous phase made of water generates water-in-oil-in-water liquid capsules: water drops covered by a oil membrane and dispersed in the water phase. Successively, transfer of water across the membrane is controlled by the osmolarity of the continuous phase, allowing precise shrinkage of the capsules for controlled structural colouration due to assembly of the particles inside them. Uniform structural colouration, independent on the illumination angles, is ensured by the amorphous particles assembly. Alternatively, a cross-junction device has been used to emulsify an aqueous dispersion of polystyrene colloids in order to produce “photonic balls”:^[78] 3D particles assembly showing 2D order on the ball surface, and increasing disorder towards the centre. After emulsification, water is removed by heating at 45°, resulting in shrinking of the drops and ordering of the particles. The diameter of these photonic balls is controlled by the colloids concentration and size of the emulsion drops generated by the device.

7.3.2 A digital microfluidics platform

In continuous-flow droplet-based microfluidics, the focus is typically on high throughput drops formation; however, the generated drops are usually not manipulated individually, and each chip, being structurally complex to perform all the required operations, is usually application-specific. On the contrary, digital microfluidics is addressed to the handling of discrete drops, not confined in closed three dimensional channels, but deposited on surfaces. The goal is the engineering of software-driven platforms able to perform similar operations (*e.g.* drops sorting, mixing, combining, etc.) on a lower number of drops, but eliminating the need for tubes, pumps, and valves, thus creating chips that are less specific, and therefore reconfigurable.

The concept of digital microfluidics date back to the late 1990s, and is due to the development of the electrowetting on dielectric technique (EWOD).^[262] The manipulation of droplets is based on controlling their wetting behaviour upon applying an electric field; the main requirement being that the liquid has to be conductive, which normally is not a problem

when handling aqueous solutions. The drop is placed in contact with a hydrophobic insulated electrode; successively application of a voltage results in a decrease of the interfacial tension between the drop and the insulating layer. If a series of electrodes can be switched on-off individually, the interfacial tension gradients generated can be used to manipulate drops.^[289] The EWOD technique allowed constructing software-based platforms (true lab-on-a-chip devices) for multiple purposes, exempt of single-uses mechanical parts, able to perform molecular detection, complex fluids handling (mixing, filtering, incubation, etc.) and analysis. Their main application is in diagnostics, especially for point-of-care testing. Actually, in all the microfluidic field research is going toward the design of chips apt for applications where non-specialist can use them; therefore not only lab-on-a-chips, but also user-friendly. Besides, other applications are, for example: controlled microreactors for bio(chemical) reactions, proteomics, manipulation of DNA and cells. Successively, other techniques have been developed for on-chip single droplets manipulation, each with its advantages and drawbacks; examples are optical and magnetic actuation mechanisms, as well as the use of surface acoustic waves.

7.4 Digital microfluidics: actuation mechanisms

7.4.1 Electrowetting on dielectric

As already mentioned, the droplet manipulation based on the EWOD actuation mechanism started the field of digital microfluids thanks to the great number of complex operations that can be performed in a contact-less, computer-controlled manner. A typical EWOD chip is composed of two plates inside which droplets are injected, as depicted in Figure 7.4B. The bottom plate is the chip surface, with arrays of controllable electrodes coated with an insulating layer and a second hydrophobic layer to ensure smooth droplet actuation; the top plate is the ground electrode, in turn coated with an hydrophobic layer. The gap where the drop is injected is normally filled with an immiscible fluid to protect it and avoid its evaporation. Alternatively, a single layer containing both controllable electrodes and the ground electrodes is possible. Such design, called co-planar, can be conveniently realized in printed circuit board technology. Interestingly, targeted drops floating on an immiscible liquid surface can be actuated as well, by controlling electrodes patterned on the surface below,^[292] exploiting in this case the dielectrophoretic effect. In this configuration the drops float on a liquid surface; as a consequence, while contamination from air to the targeted drops is now an issue, it avoids contacts with solid surfaces, thus preventing contamination from the solid substrate, and, especially of the solid surface itself, which would preclude recycle of the chip.

A great number of operations on fluids has been performed with the EWOD technique^[262;291] (some examples are reported in Figure 7.4C). By careful application of electric potentials to neighbouring electrodes in the structure, drops can be transported, split, merged and mixed

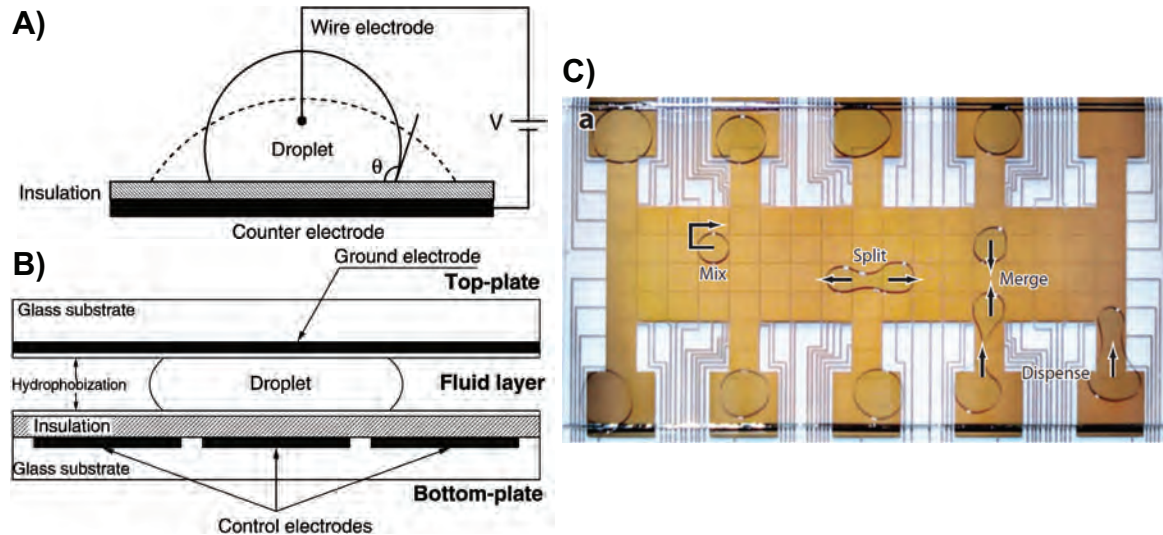


Figure 7.4: An EWOD-based chip. A) Principle of the EWOD effect: a drop of conducting liquid initially forms a contact angle θ with a hydrophobic insulator. Application of a voltage V between the drop and a counter-electrode underneath the insulator reduces the interfacial tension, leading to a decrease of θ and improved wetting of the solid by the drop (dashed contour).^[290] B) Cross-section drawing of a two-plates device depicting the various layers required for correct functioning.^[290] C) Typical operations that can be performed on an EWOD-based chip; each square is an independently controlled, wired, electrode.^[291]

with great ease. For example, splitting is possible by creating liquid fingers of a big reservoir.^[290] a liquid finger is attracted by adjacent electrodes, once it reaches the targeted electrode all the electrodes between the end of the liquid finger and the reservoir are switched off, causing the liquid to retract and break creating the small droplet. Mixing is ensured by shuttling a drop rapidly on a given path, generating in this way multiple flows inside the drop.

Although this actuation mechanism is very powerful and popular, some drawbacks and limitations exist. Despite the great improvements in microelectronics technologies, opening the way to construct very complex printed circuit boards, an EWOD chip is still a composite device, that requires cumbersome lithographic techniques, not straightforward for non-specialists, to be assembled. The absence of channels ensure the possibility for a drop to follow multiple paths inside the same chip, by charging different electrodes; nonetheless it can follow only the pre-assembled electrodes arrays, therefore, in terms of flexibility, the device still has some limitations. Finally, developing electric-power free devices would expand the applicability of low-cost microfluidics in any environment (obviously if only low-cost chemicals are required for their functioning).

7.4.2 Optical manipulation of drops

Other techniques have been demonstrated to increase the flexibility of a given chip, avoiding complex electrodes patterning and wiring. To this extent, optical stimulation has the

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great advantage that can be easily delivered in any part of the device in a well-controlled fashion, without the need of predefined electrodes paths. The group of Chiou, for example, reported an interesting alternative technique to EWOD, called optoelectrowetting.^[293] They built a device with a photoconductive layer between the dielectric layer and the electrode array, and applied an AC voltage; light illumination would cause a decrease of the resistance of the photoconductive layer under the light spot (forming a virtual electrode), resulting in a reduction of the contact angle of a deposited water drop. An uneven change of the contact angle value is then used to direct the drop, which would follow the focused light spot. Actuation of multiple drops, as well as more complex manipulations, was later reported using this principle^[294;295] (an example is showed in Figure 7.5A). The need of lasers was successfully avoided by using optical projectors or liquid crystal displays,^[296] and drops actuation was showed even on flexible substrates.^[297]

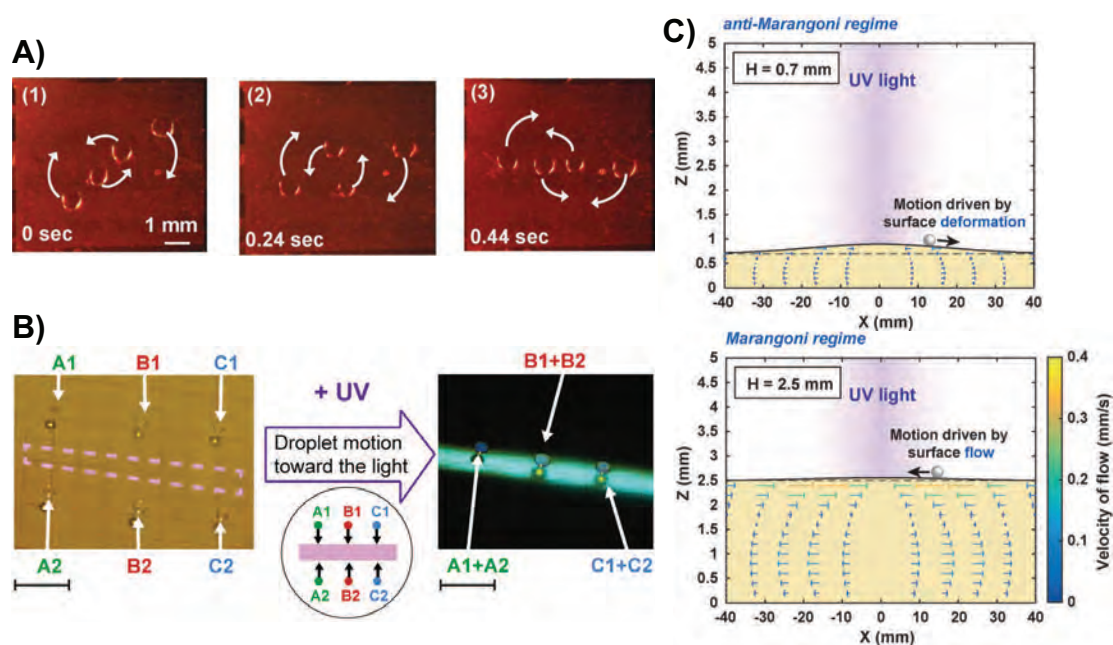


Figure 7.5: *Optofluidics*. A) Multiple transport of drops by means of optoelectrowetting: four lasers (5 mW, 532 nm) move independently four water drops sandwiched in a two-plates chip.^[295] B) Parallel fusion of six oil drops floating on a water solution containing photosensitive surfactant, obtained by shining UV light in the dashed region. Organic reactions could be initiated by fusing drops containing the reagents.^[239] Scale bar: 1 cm. C) Transport of a liquid marble floating on a solution containing photosensitive surfactant; illustration of the anti-Marangoni (top) and Marangoni (bottom) regimes. The surface deformation was measured experimentally, and the flow profile indicated by arrows was calculated by an analytical model. For $H = 0.7$ mm, light-induced surface flows induce a significant deformation that propels the marble upstream, whereas for $H = 2.5$ mm, deformation is negligible and the marble moves in the direction of the strong surface flows.^[240]

Light has already been shown to induce photochromic reactions in molecular switches – see section 4.4.4 – in turns causing various physico-chemical modifications in the system. An example is the control over the wettability of drops deposited on solid surfaces for their manipulation, that have been reported by means of substrates coated with an organic layer

containing photochromic compounds such as azobenzene modified calixarenes^[298] or rotaxanes.^[299] Only linear droplets motion could be realized, the main limitation being the too moderate change of drop contact angle, often unable to overcome the hysteresis of contact angles.

On the contrary, light has been demonstrated to be much more efficient in controlling drops motion by varying the interfacial tension of drops floating on liquid substrates. Lasers focused on a liquid interface can induce the thermocapillary effect, the variation of the surface tension due to local heating in the irradiated zone, that will create Marangoni flows able to propel floating objects. To actuate liquids in an isothermal way, our group proposed another methodology, called the chromocapillary effect:^[230;234] the light induced surface tension variation of liquids containing photosensitive surfactants. The system is composed of targeted drops floating on a water substrate containing the photosensitive surfactant AzoTAB. While immiscible drops (such as oil) are simply added on top of the water bath, miscible liquids can be actuated in the form of liquid marbles^[52] (see section 1.4.1), wrapping them inside a hydrophobic powder. Even if the actuating mechanism is simple, a decrease of the surface tension in the UV irradiated zone due to *trans-to-cis* AzoTAB isomerization creating Marangoni flows, various configurations can be used to actuate drops in different directions. If UV light is focused on the periphery of an oil drop, momentum conservation results in motion of the drop in the opposite direction of the generated Marangoni flow.^[230] If UV light is focused on the water bath close to the drop, the surface tension decrease will attract the drop toward the light spot^[239] (as in Figure 7.5B). Interestingly, if the water bath is below a certain thickness, the light-induced Marangoni flow will accumulate liquid in the irradiated area, creating a small bump that would propel a floating liquid marble downhill, against the generated flows^[240] (the mechanism is depicted in Figure 7.5C). Complex trajectories and fusion of multiple drops for light controlled chemical reactions, were demonstrated using the chromocapillary effect.

Finally, it was showed that photoinduced pH gradients can be exploited to propel drops by the so-called photo-chemopropulsion.^[300] Spatially controlled light irradiation induces dissociation of a water soluble organic acid, which in turn cause variation in the surface tension of a lipophilic droplet, resulting in its motion. 2D actuation of drops on water surfaces has been demonstrated, as well as 3D motion in bulk water, opening the way to several applications where complex 3D motion is sought-after.

7.4.3 Magnetic actuation

Magnetic actuation in digital microfluidics mainly rely on adding magnetic particles inside the targeted drops.^[263;301] The word magnetic particles includes paramagnetic and superparamagnetic particles, as well as ferrofluids, which are colloidal, stable, suspensions of coated nanoparticles. The actuation mechanism is simple: the particles are pushed toward the direction of a generated magnetic field, dragging the drops with them. A magnetic field gradient

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can be created either using permanent magnets, or with electromagnets. Electromagnets can be opportunely switched on/off using an electric impulse for time-controlled stimulation, and, eventually, they can be patterned in desired positions inside the chip (using micro coils) giving very sharp magnetic field gradients and ultimately acting as electrodes. Sharp magnetic fields are obtained also patterning magnetic pillars inside the chip structure. On the contrary, permanent magnets are sought for different purposes: they do not require any electric power source to operate, and can be easily manipulated by hand. As in the case of using light for manipulating drops, magnetic actuation offers the advantage of being totally reconfigurable inside the chip, and does not require, necessarily, any prefabricated path on the surface. In addition, magnetic-based platforms, depending on the magnetic field source, are both compatible with automated control systems, but can also be operated manually or by other means, such as mechanic motors, not necessitating external power sources, opening the way to design truly robust and low-cost microfluidic devices. For applications in diagnostics, magnetic particles offer the additional benefit of a dual functionality: besides being the drops carrier, they provide a solid substrate for molecular adsorption, separation and reaction.^[302–304]

For magnetic manipulation on solid substrates, no specific fabrication steps are, normally, required, except the deposition of a hydrophobic layer to ensure smooth water droplets actuation. As already mentioned, usually magnetic particles are added inside the drops; motion is performed by attracting the particles either by moving permanent magnets, or inducing magnetic fields through electromagnets. For example, Lehmann and co-workers^[305] reported a lab-on-a-chip device for DNA purification based on the controlled motion and splitting of drops containing magnetic particles: the drops are actuated through a multilayer set of coils on a printed circuit board (see Figure 7.6A). The printed circuit board modulates a homogeneous magnetic field in which the chip is placed. Hydrophilic patterns are added on the surface for trapping drops in desired locations and to favour drops splitting. Larson *et al.*^[306] studied the manipulation of droplets loaded with magnetic particles deposited on a surface and carried by a moving small permanent magnet. For a complete characterization of the system, they varied important parameters, such as particles type and droplet volume, and reported a phase diagram of the drops behaviour – transport or particles extraction – as a function of particles concentration and magnet velocity. A drop could follow a magnet moving at a speed up to 3 mm/s, as showed in Figure 7.6B where the light gray circle below the drop is the magnet; the particles, in black in the figure, move toward the magnet and in turn pull the drop. Instead, higher magnet speeds would lead to particles extraction into smaller droplets. Multiple operations on drops are facilitated by the use of additional substrate modifications, either physical^[308] or chemical,^[304] for more complex handling; but at the same time, resulting in a limitation of the constructed chip to more specific applications.

An example of a device performing true lab-on-a-chip operations is reported in Figure 7.6C and D, where real-time PCR (polymerase chain reaction) steps are executed.^[302;303] A water droplet containing magnetic particles is deposited on the surface of the chip and covered

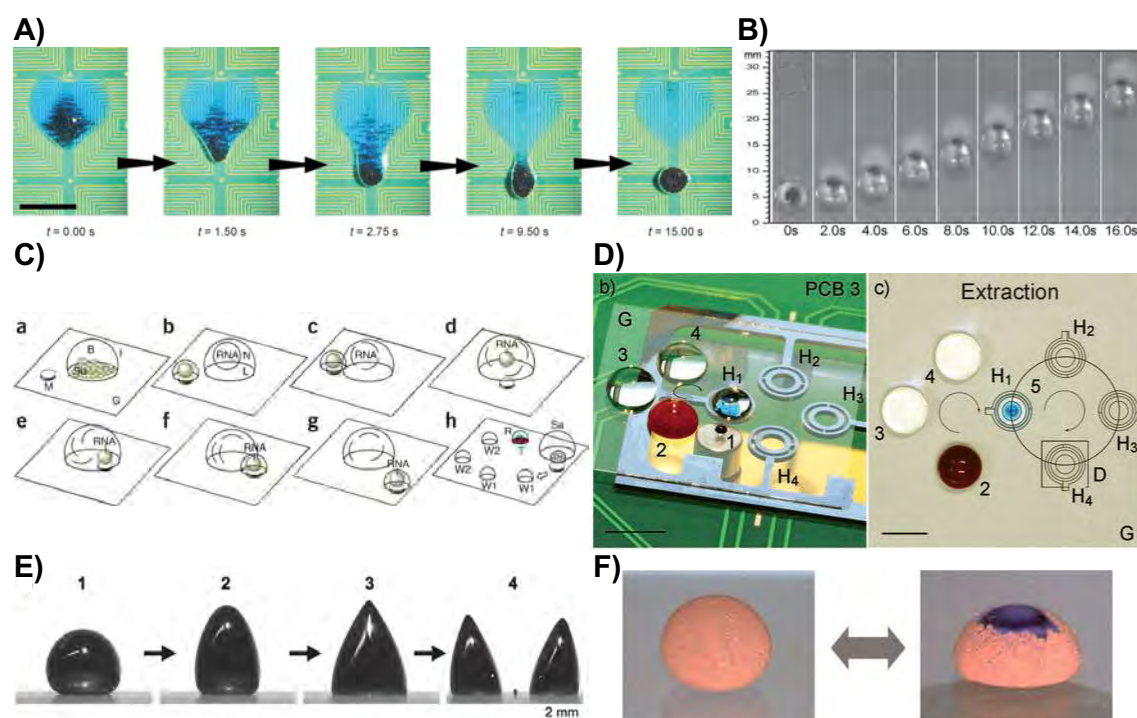


Figure 7.6: Digital microfluidics controlled by magnetic particles. A) Drop manipulation on a printed circuit board.^[305] A 12 μL water drop is initially trapped on a hydrophilic pattern, modulation of the magnetic field allows splitting the initial drop into a 2 μL drop containing the magnetic particles. B) Droplet actuation by means of a permanent magnet.^[306] The drop containing the particles follows the linear motion of a magnet placed below the surface (visible in light grey). C) Sketch of the sequential processes for sample preparation and PCR.^[302] a) Aqueous buffer (B) containing magnetic particles, surrounded by a thin layer of oil (I) deposited on the chip surface. b-g) merging, mixing and splitting for solid-phase extraction. h) Sequential mixing with four washing solutions (W) and desorption of the RNA into the PCR solution (R) on a thermocycler (T). D) Photograph of a chip for sample preparation and PCR, where four heater/temperature sensors and a fluorescence detector are added on a printed circuit board.^[303] E) Ferrofluid drop deformation and splitting caused by approaching from below the hydrophobic surface a magnet, therefore increasing the magnetic field (from step 1 to 4).^[249] F) A liquid marble coated with magnetic particles; approaching a magnet (on the right) cause stripping off the coating particles showing the inner liquid.^[307]

with a thin layer of oil (to prevent evaporation and reduce friction). The drop is manipulated moving a magnet below the surface. The various steps in Figure 7.6C include: merging with a drop containing the targeted RNA, mixing within the drops, and solid-phase extraction and separation of the RNA from the raw sample solution. Successively, the drop containing RNA attached to the particles is mixed with four washing solutions and finally desorb into a PCR solution positioned on top of a thermocycler. Figure 7.6D reports a variant of the chip, with integrated four different temperature zones and a fluorescence detector.

Ferrofluids, colloidal suspensions of stable nanoparticles, are readily actuated in magnetic fields.^[309;310] The contact angle of a sessile drop is modified with an anisotropic magnetic field – the so-called magnetowetting – causing drop motion. By varying the field strength both drop deformation and splitting is reported,^[249] as showed in Figure 7.6E. Interestingly,

multiple ferrofluid drops self-assembled in a static manner at defined magnetic fields (with an inter-drops distance depending on drops curvature and their magnetic moment); while dynamically assembled patterns were obtained with oscillating permanent magnets.^[249]

An alternative to the use of micro- or nanoparticles was proposed, based on dissolving metal ionic liquids – liquids composed of organic cations and inorganic, paramagnetic, anions – in water. Due to the high concentration of magnetic ions, the water droplets can be actuated by an external magnetic field. For example, after generation of a double emulsion with water drops containing the metal ionic liquid, different patterns of applied magnetic fields were used to cause different behaviours of the droplets, realizing: capture and release, coalescence, rotation and distortion, mixing, sorting and phase separation in continuous flow.^[311]

Magnetic actuation has been extensively used also for the manipulation of drops in the form of liquid marbles. The magnetic particles are added in two ways: hydrophilic particles can be dispersed inside the water drops,^[312;313] while hydrophobic ones can be used both to wrap the liquid marble, and to actuate it.^[307] Properly selected particles ensure coating of various solvents, including organic ones.^[314] Liquid marbles offer the great advantage that can readily float on liquid surfaces at high speeds, and to be very stable on both solid and liquid substrates. This last characteristic is useful for controlled actuation and sample storage, but a limitation when merging or sample removal is required. Sample handling inside liquid marbles has been demonstrated by careful stripping off the coating magnetic particles using an attracting magnetic force^[307] (Figure 7.6F); by this method the top of a marble could be accessed in order to inject reagents, control the reaction by means of optical probing and, eventually, release the product. Instead, merging of two liquid marbles is a more demanding task: on a liquid surface, only sample release by marble breaking has been reported so far;^[315] conversely, coalescence of two neighbouring marbles on a glass plate is possible, if both coated with magnetic particles, in the presence of a strong magnetic field.^[316]

Finally, a different strategy to control drops motion using magnetic stimulation was proposed, based on magnetically deformable flexible solid substrates.^[317;318] The solid substrate is made of an elastic polymer impregnated with a magnetic material. Approaching a magnet below the surface results in deformation of the polymer creating a small depression where the drop will roll; the position of the deformation, therefore of the drop, is directly controlled by moving the magnet. With this technique inherently non responsive drops can be actuated, but more complex surfaces are required; in addition only few fluid operations have been demonstrated.

7.4.3.1 Magnetic surfactants

So far, the large majority of magnetic actuation methods relied on the addition of magnetic particles, being it either inside the sample drops, or coating them. Although multiple operations have been demonstrated, the necessity of magnetic particles limits broad applicability

of this technique, for example due to possible side reactions with reagents inside the drops, or sample contamination.

Recently, the group of Eastoe reported a class of magnetic ionic liquid surfactants (MILSs) responding to magnetic stimulation.^[319–321] MILSs are obtained by mixing metal complex anions with cationic surfactants, in order to replace their previous counterions (an example of their molecular structure is in Figure 7.7A, bottom). Besides reducing the water surface tension due to their amphiphilic structure, a further surface tension decrease is reported, for aqueous MILSs solutions, when a permanent magnet is approached to a pendant drop of the solution (see Figure 7.7B for the experimental values reported). The authors hypothesized

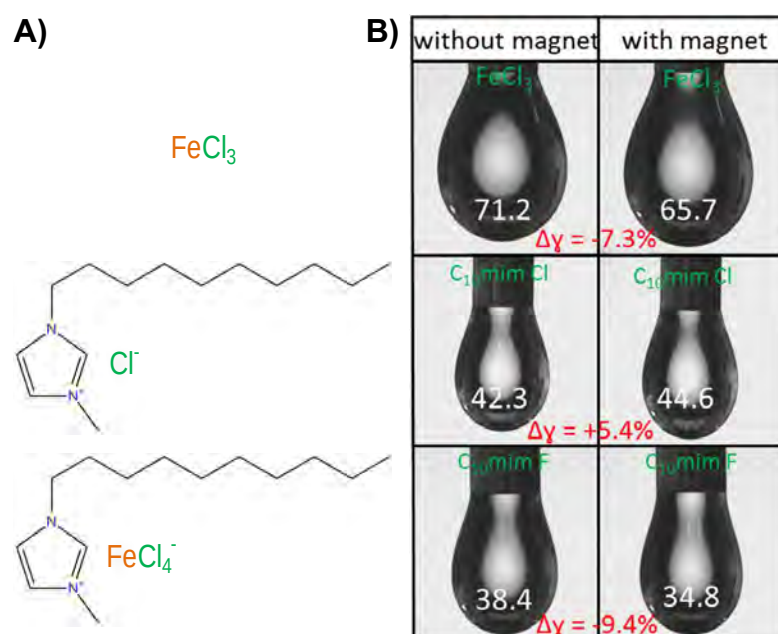


Figure 7.7: “Magnetic surfactants”. A) Molecular structure of the molecules in B; the bottom molecule is a magnetic ionic liquid surfactant. B) Drops of aqueous solutions containing the molecules in A without (left) and after approaching a permanent magnet from the bottom (right). The apparent surface tension measured with the pendant drop apparatus is written for each drop.^[319]

a concomitant effect of both surface activity of the cations, and magnetic activity of the anions, generating magneto-responsive surfactants. Diverse applications were reported, such as: “levitation” of a magnetic emulsion through an immiscible phase and the controlled motion of drops,^[322] magnetic capture of graphene oxide,^[323] proteins^[324] and DNA^[325] for separation purposes, or their inclusion in the synthesis of magnetic mesoporous silica.^[326]

An alternative interpretation of the proprieties of those “magnetic surfactants” was successively reported by Degen *et al.*,^[327] which repeated the experiments in ref^[319] and compared the apparent surface tension under a magnetic field for MILSs and their parent cations and anions. At first they repeated the levitation experiment: transfer of drops formed from a bottom aqueous liquid and passing through an upper oil phase due to magnetic attraction. Both an aqueous solution containing MILS or a mixture of anionic magnetic ions and anionic surfactant was successfully attracted by an approaching permanent magnet; instead, a

solution containing only magnetic ions did not show any visible effect. Therefore, they concluded that an interfacial tension decrease apported by the addition of surfactants was, in the first place, necessary to cause magnetic levitation of an aqueous solution. Successively, they measured the apparent surface tension of various solutions using the pendant drop technique, approaching to the drop a permanent magnet from the bottom. They detected a surface tension decrease for solutions containing magnetic ions irrespective of the presence of surfactants (actually the same result was reported in ref,^[319] as showed in Figure 7.7B). With surfactant the starting surface tension was lower, as expected, but the effect under a magnetic field was of the same order of magnitude. To summarize, they concluded that: «there is nothing special about “magnetic surfactants”». Their effect is actually decoupled: the surfactant decrease the water surface tension; the magneto-active ions, being paramagnetic, are attracted by an increasing magnetic field – which is a well-known and described phenomenon.^[328;329] It is due to this attractive force that, if the interfacial tension is low enough, water levitation could be obtained. With this interpretation, the magnetic effect is not a surface effect, but a bulk one, as it is for drops containing magnetic particles.

7.5 Conclusions

The chapter reviewed various approaches devised to achieve control over the manipulation of drops inside microfluidic channels or on open surfaces. The focus was on external, contactless stimulations, applied with configurations that allow to perform programmable and reconfigurable operations. For the scope, mainly electric, optical and magnetic stimulation were considered, and advantages and drawbacks were underlined. Successively, the attention was pointed towards magnetic field actuation of drops on surfaces (solid or liquid), which mainly rely on dispersing magnetic particles inside the targeted drops. Based on recent findings, an alternative to magnetic particles, using magnetosensitive surfactants to modulate the surface tension of water solutions, was finally considered.

Reports of magnetically-induced surface tension variations of liquid solutions measured the surface tension in non-homogeneous magnetic fields; thus concomitant bulk effects due to attraction/repulsion of the liquid caused by its paramagnetic/diamagnetic character were present as well. Therefore, in order to separate eventual surface effects from bulk effects, in the following chapter I describe a custom-built setup constructed to measure precisely the surface tension of liquids under homogeneous magnetic fields. Successively, in the last chapter, a novel magnetic actuation method for drops floating on liquid surfaces will be presented. The components governing the drops motion, thanks to a series of experiments, the help of the results reported in chapter eight and a theoretical model, will be precisely described.

Magnetic effect on the surface tension of liquid drops

8.1 Abstract

The surface tension of liquids is exploited in numerous phenomena involving continuous fluids or drop manipulation. Therefore, a precise, direct and contactless control over its strength is of utmost importance. The use of magnetic fields for this purpose would offer great advantages: it is adaptable to many environments (compatible to both close and open systems), not affected by several solution parameters (pH, ion concentration, etc.), non-invasive and remote. Finally, depending on the specific requests for a desired application, can be provided by electro- or permanent magnets. Although the magnetic effect on liquids has been studied since a long time, fewer works have been devoted to investigate their surface tension, especially using moderate magnetic fields (~ 100 mT), as the one commonly employed in microfluidic devices. Here we show how a magnetic field gradient affects surface tension measurements by means of the pendant drop technique due to the interference of bulk forces. Therefore, to eliminate bulk magnetic forces occurring in the presence of magnetic field gradients, we constructed a setup where a pendant drop is surrounded by a highly homogeneous magnetic field, the intensity of which we can vary in a controlled manner. In this way we could measure precisely the surface tension of diamagnetic (water) and paramagnetic liquids under uniform fields as a function of the field intensity. We can conclude that the surface tension of water is unaffected in the range of explored intensities; and only a small, negative, variation has been detected for the paramagnetic solution tested. Overall, the proposed setup allows for a more reliable measurement of the surface tension of liquids under magnetic stimulation.

8.2 Introduction

Controlling the properties of fluids in a contactless manner, through the use of external stimuli, offers great advantages in a variety of applications where liquid solutions are involved. Especially, the on-demand variation of their surface/interfacial tension has been proved to be a very efficient method for their handling and manipulation, both in microfluidic channels, or on plain surfaces.^[234] For this purpose, various stimulations have been used, such as thermal,^[330] electrical^[292;331] or optical.^[230;239;271;281;298;299] Compared to the already mentioned stimuli, magnetic control has been proved to be suitable for many practical operations, thanks to its various advantages;^[263;332] among the others: no need of specific substrate modification, relative insensitivity to the variation of solution properties (such as pH, temperature, ionic concentration, turbidity), non-invasive, remote, and offering good spatio-temporal control.

A magnetic field gradient is generated either with electromagnets, or using permanent magnets. Electromagnets can be opportunely switched on/off using an electric impulse for time-controlled stimulation, and, eventually, they can be patterned in desired positions (using micro coils) giving very sharp magnetic field gradients, and ultimately acting as very precise guiding platforms, for example for drops actuation. On the contrary, permanent magnets are sought for different purposes: they do not require any power source to operate, and can be easily manipulated by hand. With the goal to build novel low-cost and portable devices for fluids handling and diagnostic, permanent magnets offer the unique advantages of being affordable, without requiring any equipment implementation, nor necessitating of an electric power source.

On one hand, fluid manipulation using magnetic fields have been typically performed adding magnetic particles inside the target liquids.^[301–303;306;312;313;315] Despite being a very powerful technique, the use of magnetic particles decreases its applicability, increases costs, and causes sample contamination. On the other hand, for complex fluids handling inside microfluidic devices, building up surface tension gradients has already been proved to be suitable in controlling various fluidic operations. Even though a lot of research effort has been put on studying the magnetic effect on water or other liquids^[333–336] (see Chapter 9), fewer studies on their surface tension were reported,^[337–339] especially at relatively low magnetic fields,^[319;327] as the one that can be produced with small permanent magnets used inside microfluidic chips (~ 100 mT at the drop level).

Up to now, surface tension measurements have always been performed using the pendant drop method, with drops placed in a non-homogeneous magnetic field. The pendant drop is one of the most commonly used method to determine the surface tension of liquid/liquid or air/liquid interfaces.^[2] It is based on analysing the shape of drops hanging from a capillary, and deducing the surface tension value with a mathematical model, considering that the drop shape is dictated by the interplay of the forces acting on it (surface tension, gravity and, in this case, magnetic force). Under a non-homogeneous gradient, the magnetic field

8. MAGNETIC EFFECT ON THE SURFACE TENSION OF LIQUID DROPS

exerts a bulk force on the liquid that causes its deformation^[333] (see Chapter 9). Such magnetic force will be attractive if the liquid is paramagnetic (having a magnetic susceptibility, $\chi > 0$), while it will be repulsive if the liquid is diamagnetic ($\chi < 0$). This interaction can deform the pendant drop in a way that is not considered by the instrumental software. Therefore, in these conditions, fitting of the drop shape does not allow to isolate between the bulk and the, eventual, surface effect components that can cause a variation on the surface tension detected by the instrument.^[327] Only an apparent surface tension can be extracted. In order to suppress the bulk component, dependent on the presence of a magnetic gradient,^[328] we constructed an experimental setup where surface tension measurements using the pendant drop could be performed in a homogeneous, variable magnetic field. The setup is composed of two large-sized permanent magnets having a rectangular shape, facing each other in parallel with the opposite poles. Thanks to this setup, we could measure the true effect of magnetic field intensity on the surface tension of diamagnetic (pure water) and paramagnetic solutions (water with dissolved paramagnetic salts). Our results contradicted the data published to now that were obtained in magnetic field gradients. Our technique allows for a more reliable determination of the surface tension of air/liquid surfaces – but could be applied to liquid/liquid interfaces too – under magnetic stimulation, offering a valuable characterization protocol when a magnetic field interacts with fluids.

8.3 Experimental results and discussion

In Figure 8.1 I report the two experimental setups used to measure the surface tension of water solutions by means of the pendant drop technique. In particular, Figure 8.1A shows a sketch of the experimental configuration used to measure the apparent surface tension of drops in a non-homogeneous magnetic field generated by a small permanent magnet approaching from the bottom of the drop. This geometry is similar to the one commonly used in literature.^[319;327] It has been used in order to compare our experiments with the results already published, and with the surface tension of the same solutions as measured in a homogeneous magnetic field of similar intensity. A map of the magnetic field around a drop in this configuration is reported in Figure 8.1B. Both the components of the magnetic field perpendicular and parallel to the magnet surface are highly non-homogeneous at the drop level, with a variation of around 70 mT from the drop neck to its far end only for the perpendicular component of $\mathbf{B}$. In order to obtain a magnetic field homogeneous all over the drop, we optimized a new setup where we placed at a precisely controlled, and variable, distance two large-sized parallel magnetic plates (Figure 8.1C) facing their opposite poles. It is important to note that permanent magnets of this size, when facing each other at relatively short distances (in the order of centimetres) exert a very strong force that attracts them and represent a risk to the experimentalist that should not be neglected. Therefore, a rigid scaffold was constructed in order to keep the two plates at a controlled distance. This apparatus was conceived to

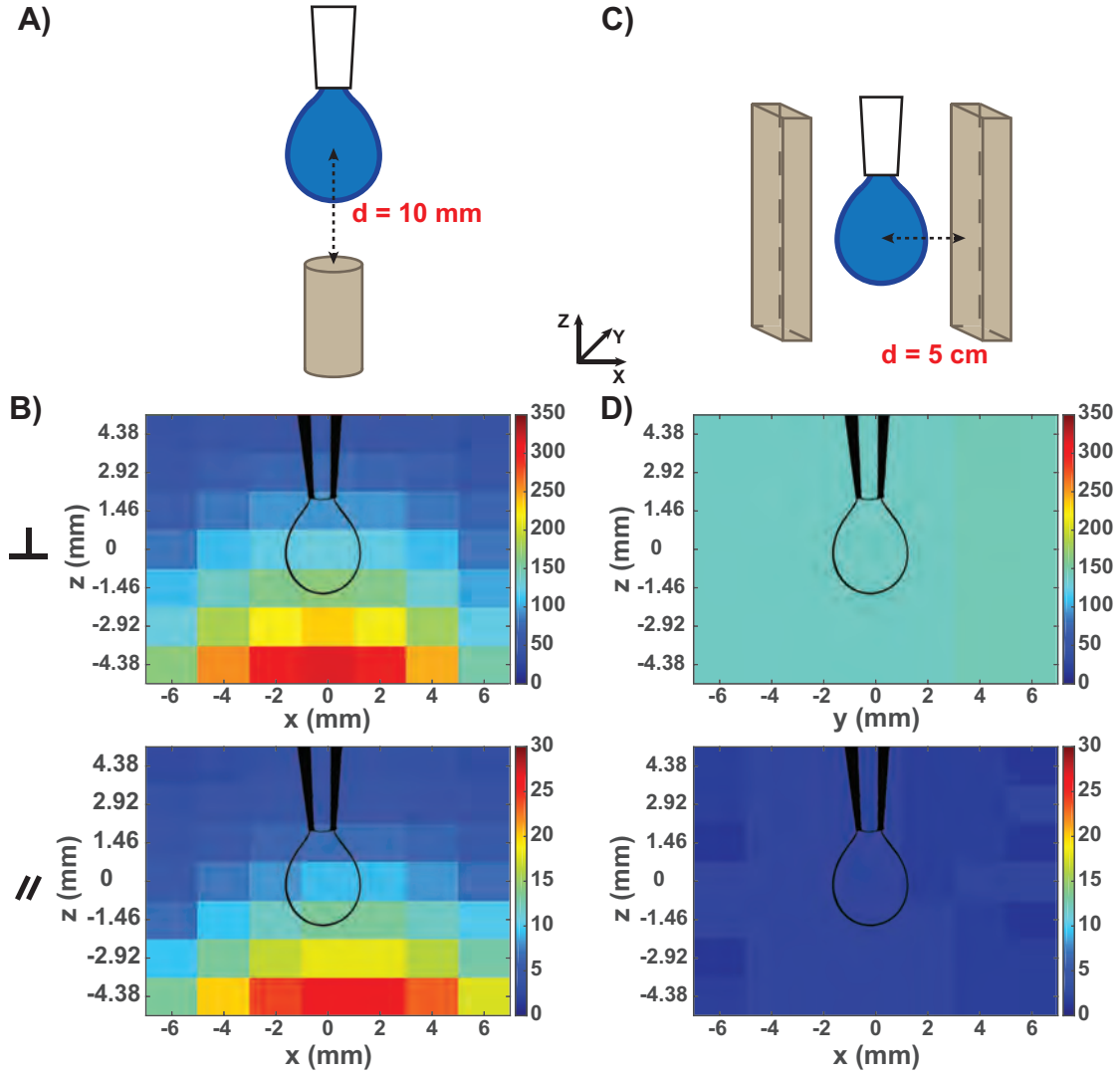


Figure 8.1: Experimental setup and map of the magnetic field around a pendant drop for surface tension measurements. A) Sketch of a pendant drop in a non-homogeneous magnetic field generated by a small permanent magnet placed on the bottom of the drop, at a distance from the centre of the drop of $d = 10 \text{ mm}$. B) Measured map of the magnetic field around the drop as in A); a drawing of the drop contour is added to help visualizing its position. The tip for the magnetic field measurement is perpendicular (top) or parallel (bottom) to the magnet surface. C) Sketch of a pendant drop in a homogeneous magnetic field generated by two parallel magnets placed at a distance of $d = 5 \text{ cm}$ each from the drop centre. D) Measured map of the magnetic field around the drop as in C). The tip for the magnetic field measurement is perpendicular (top) or parallel (bottom) to the magnet surfaces. The x , y , z coordinates refer to A-D.

be compatible with a Kruss tensiometer for surface tension measurements. All the materials used were non-metallic in order to avoid interactions with the strong magnets. In this way, a drop could be produced in the centre of the two parallel plates, where both the perpendicular and parallel components of the magnetic field were highly homogeneous. Figure 8.1D shows the measured map of the magnetic field in the case of a distance (d) between the plates and the centre of the drop equal to 5 cm, the perpendicular component of $\mathbf{B}$ around the drop equals to $141 \pm 0.5 \text{ mT}$. Varying d allowed us to tune the magnetic field intensity while

8. MAGNETIC EFFECT ON THE SURFACE TENSION OF LIQUID DROPS

keeping the field highly homogeneous.

All experiments were conducted at room temperature and constant humidity ($T = 22 \pm 1$ °C; $RH = 35 \pm 5$ %); for each sample solution, an average over at least ten drops was performed to obtain the relative surface tension value. The apparent surface tension (γ^*) provided by the tensiometer of a diamagnetic and a paramagnetic solution measured in a non-homogeneous magnetic field are reported in Figure 8.2A. The diamagnetic solution is

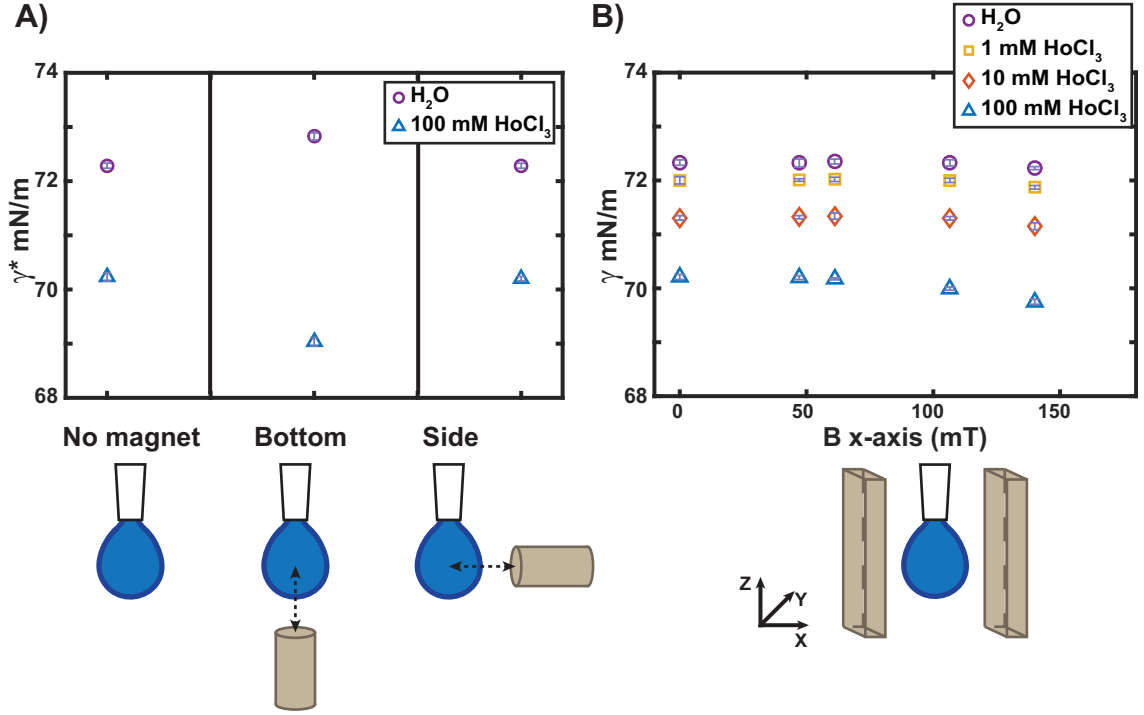


Figure 8.2: Apparent surface tension (γ^*) and surface tension (γ) measurements for diamagnetic and paramagnetic solutions. A) Apparent surface tension (γ^*) measurements for water (violet circles) and a solution of 100 mM $HoCl_3$ (blue triangles) in the absence of a magnetic field (left), with a small permanent magnet approached from the bottom (centre) at a distance $d = 10$ mm (see Figure 8.1 for a map of the corresponding magnetic field), and with a small magnet approached from the side at a distance $d = 10$ mm (right). Symbols and error bars show mean $\pm$ sd from 10 individual experiments. B) Surface tension (γ) measurements for water (violet circles) and increasing concentration of $HoCl_3$ as a function of the magnetic field intensity on the x-axis (perpendicular to the magnets surfaces). The map of the magnetic field in Figure 8.1 corresponds to the points at $B = 140$ mT. Symbols and error bars show mean $\pm$ sd from 10 individual experiments.

pure water, having $\chi = -9.5 \pm 0.4 \cdot 10^{-6}$; while the paramagnetic one is a $HoCl_3$ solution in water at a concentration of 100 mM, having $\chi = 45 \pm 1.7 \cdot 10^{-6}$. On the left side of the graph is reported the actual surface tension (γ) of the solutions in the absence of the magnetic field. We note that the addition of $HoCl_3$ causes a small decrease of the surface tension value of pure water. Approaching a small permanent magnet from the bottom (Figure 8.2A, middle) up to a distance $d = 10$ mm (corresponding magnetic field map in Figure 8.1B) causes a deformation of the drop as described in the introduction: a diamagnetic drop will be repelled (shrunk), while a paramagnetic one will be attracted (elongated). Upon fitting of the drops

8.3 Experimental results and discussion

profiles, the instrument detects an apparent surface tension variation that is quantified as $\Delta\gamma^* = 0.5$ mN/m for pure water (violet circles in the figure), and $\Delta\gamma^* = -1.2$ mN/m for 100 mM HoCl_3 (blue triangles in the figure). Similar $\Delta\gamma^*$ values in a non-homogeneous magnetic field are reported in ref^[327] both for water and a paramagnetic solution (in their case a 200 mM solution of FeCl_3 in water).

To show that the apparent surface tension change, detected for shrunk and elongated drops, is actually due to a bulk effect, and not to a variation of the surface properties of the solutions in the presence of the magnetic field, we placed the magnet at the same distance from the drop, but on its side, so that the magnetic field gradient points now from the left side to the right side of the drop. As a result, the drop is now repelled (if made of pure water solution) or attracted (for 100 mM HoCl_3), but no shrinking or elongation occurs. Consequently, the apparent surface tension detected in this configuration (Figure 8.2A, right) is the same as without the magnetic stimulation for both solutions. The drops deformation, due to a bulk response of a diamagnetic or paramagnetic liquid in a magnetic field gradient, in this geometry does not affect the instrumental software. We can therefore conclude that a setup where a pendant drops is placed in a non-homogeneous magnetic field is not correct for measuring the actual effect of the magnetic field on the surface tension of the solution.

To rule out bulk effects interfering with the surface tension measurements, and in order to extract surface tension values that are dependent on the magnetic field intensity, and not on the direction of its gradient, we exploited our setup depicted in Figure 8.1C. In a homogeneous magnetic field we can assume that eventual drops deformation is due to surface tension only. Figure 8.2B shows the surface tension measured when drops of a diamagnetic or paramagnetic solution is placed inside a homogeneous magnetic field of varied intensities. We quantified the maximum surface tension variation ($\Delta\gamma$) for the solutions studied by comparing γ_0 , the surface tension without magnetic stimulation, and γ_{140} , the surface tension at the maximum magnetic field intensity used ($B_x = 140$ mT). For pure water (violet circles in figure) we obtained $\Delta\gamma = -0.1$ mN/m: a small decrease, well within the experimental error, and not an increase as obtained when a non-homogeneous magnetic field was pointing toward the bottom of the drop. We can therefore conclude that, under moderate magnetic fields up to 140 mT, no measurable effect of the magnetic field on the surface tension is detected when pure water drops are placed inside homogeneous fields. We do not exclude that effect could exist at higher magnetic field intensities, as reported, for example, in ref^[339] when a very strong magnetic field (10 T) is employed.

The same result, $\Delta\gamma = -0.1$ mN/m, is obtained in the case of water solutions containing 1 mM or 10 mM HoCl_3 (having respectively $\chi = -8.4 \cdot 10^{-6}$ and $\chi = -3.4 \cdot 10^{-6}$). A qualitatively similar effect is observed when a paramagnetic drop, composed of 100 mM HoCl_3 , is placed inside a homogeneous magnetic field. In this case, the maximum surface tension difference detected is $\Delta\gamma = -0.46$ mN/m. It is important to note that a small fluctuation in temperature of around two degrees Celsius can cause similar variation in the

surface tension value of water solutions; specifically, a $\Delta\gamma$ of - 0.3 mN/m between 21 and 23 °C.^[340] We can therefore conclude that a 100 mM HoCl₃ solution shows only a very small decrease of its surface tension, in a moderate homogeneous magnetic field, a decrease that is comparable to the variation in surface tension expected by a small fluctuation in temperature.

8.4 Conclusions

We constructed a custom-built setup for the precise measurement of the surface tension of pendant drops inserted into a homogeneous magnetic field of moderate intensities, whose strength is comparable to the one commonly used in microfluidic devices and/or for the magnetic handling of drops. We note that, even though not showed, the liquid/liquid interfacial tension of pendant drops immersed in an outer liquid could be measured as well with our configuration. The surface tension of diamagnetic (water) and paramagnetic solutions could be detected, and compared to previously reported experiments where the drops were placed in non-homogeneous magnetic fields. Being unaffected by bulk effects, our measurement in homogeneous fields offers a correct and more reliable value. We could conclude that, while pure water was unaffected, only a small, negative, variation has been detected for the paramagnetic solution tested (holmium chloride dissolved in water) with the magnetic field intensities used.

This chapter reports a setup that can be of general interest in characterizing systems where a magnetic field can affect the surface/interfacial tension of the liquids involved. Its reliability, and user-friendly characteristic, is based on the homogeneity of the magnetic field used, provided by dm-sized parallel flat permanent magnets (and easily measured by a magnetic probe), and on the well-known pendant drop technique employed to measure the surface tension. Finally, the results obtained for the solutions we analysed here will be useful for the magnetic actuation mechanism subject of the next chapter. In particular, we can state that approaching a permanent magnet to a paramagnetic liquid can cause its deformation (*c.f.* Figure 9.2), but do not generate significant gradients of surface tension, therefore excluding the possibility of magnet-induced Marangoni flows.

Magnetic actuation of drops and liquid marbles using a deformable paramagnetic liquid substrate^{*}

9.1 Abstract

The magnetic actuation of deposited drops has mainly relied on volume forces exerted on the liquid to be transported, which is poorly efficient with conventional diamagnetic liquids such as water and oil, unless magneto-sensitive particles are added. Herein, we describe a new and additive-free way to magnetically control the motion of discrete liquid entities. Our strategy consists of using a paramagnetic liquid as a deformable substrate to direct, using a magnet, the motion of various floating liquid entities, ranging from naked drops to liquid marbles. A broad variety of liquids, including diamagnetic (water, oil) and nonmagnetic ones, can be efficiently transported using the moderate magnetic field (*ca.* 50 mT) produced by a small permanent magnet. Complex trajectories can be achieved in a reliable manner and multiplexing potential is demonstrated through on-demand drop fusion. Our paramagnetofluidic method advantageously works without any complex equipment or electric power, in phase with the necessary development of robust and low-cost analytical and diagnostic fluidic devices.

^{*}This chapter is adapted from *Angew. Chem. Int. Ed.* **2017**, 56, 16565–16570.

9.2 Introduction

Controlling the motion of drops on surfaces is the cornerstone of a broad range of scientific and technological operations.^[254;262] In the large majority of cases, the drop motion is induced by an interfacial energy gradient at a solid/liquid interface (wettability gradient) and/or at a free interface (Marangoni stress).^[234] This has resulted in a plethora of studies to elucidate the fundamental mechanisms that convert such gradients into drop motion^[341] as well as to develop strategies to manipulate drops under the control of various external signals, such as thermal,^[330] electrical^[262;292;331] and optical^[230;239;271;281;298;299] stimuli. Most of these approaches necessitate the implementation of rather complex components, such as electrodes or optical elements, or the development of systems that are intrinsically responsive to the desired stimulus, such as photo- or thermosensitive substrates.^[298;299] This has led to the emergence of a broad variety of powerful drop actuation strategies that work in a laboratory environment, that is, require specific equipment and well-controlled conditions (for example, protection from ambient light or precise control of temperature and surface tension). However, broadly applicable strategies for robust and cost-effective manipulation of discrete liquid entities have yet to be identified. Apart from thermal, optical, and electrical stimulation, magnetic field-induced drop actuation could be the basis to achieve such a goal.^[301;332] In particular, permanent magnets are available in a variety of sizes and shapes at affordable prices and can be easily handled without any specific environmental requirement. However, although drops composed of strongly responsive fluids, such as paramagnetic liquids^[319;342] or ferrofluids,^[249;310;312] are commonly actuated by magnets, the majority of conventional drops are made of diamagnetic liquids (for example, water and oil) and cannot be efficiently manipulated unless a strong magnetic field is applied. To our knowledge, the only strategy for moving discrete diamagnetic liquid entities in air using moderate magnetic fields has consisted in using magnetosensitive particles, dispersed inside the liquid^[306] or coating the liquid to form liquid marbles.^[57;301;307;313;343] Using magnetic particles inside or outside the liquid increases sample cost, reduces applicability, and poses the problem of sample contamination. Moreover, although liquid marbles allow efficient liquid transport,^[52;240] they remain, unlike their drop counterparts, difficult to merge and split apart for digital fluidic operations.^[262]

Herein, we propose a new way to move and merge any kind of discrete liquid entity, including diamagnetic and non-magnetic ones, using external small permanent magnets. Our method does not require the use of any magnetosensitive particles, nor has it any specific restrictions in terms of environmental conditions. It consists in using a paramagnetic liquid as a substrate and exploits the deformation induced by an approaching magnet as the driving force for a floating entity. To our knowledge, although the magnetic field-induced deformation of a paramagnetic liquid is a well-known phenomenon that has been used in various scientific fields,^[328;329] it has never been exploited to transport guest liquid entities. We characterized the deformation induced by small permanent magnets and analysed the resulting motion

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of different floating entities, including oil drops and water-based liquid marbles of various compositions. We also experimentally and theoretically quantified the marked contribution of the substrate deformation to the motion of a floating object under magnetic stimulation. We finally used mobile magnets to perform various operations such as long-term transport along complex trajectories and magnetically controlled drop fusion.

9.3 Experimental results and discussion

The experimental set-up consisted of a Petri dish containing a paramagnetic HoCl_3 solution used as a deformable substrate. The liquid thickness (5.2 mm) was fixed at a value larger than the capillary length of the system (*ca.* 2.7 mm). A portable, permanent NdFeB magnet was released from a fixed position far from the substrate surface to follow a free fall trajectory and reach a second fixed position close to the substrate surface (12.7 mm), resulting in motion of floating objects deposited on the substrate. I first used a 2 μL liquid marble (LM), made of hydrophobically modified silica nanoparticles surrounding a water core,^[240] as the entity to be transported (Figure 9.1A). With the magnet maintained in position 1, no marble motion was detected. Switching the magnet from position 1 to 2 led to an immediate and radial motion of the marble away from the magnet axis (Figure 9.1B). To our knowledge, this is the first reported magnetically induced motion of a liquid marble that does not contain any ferromagnetic or paramagnetic component (in the coating particles or in the inner core). A key component of this motion is the deformation of the substrate resulting from the applied magnetic field (Figure 9.2A). When the magnet was switched from position 1 to position 2, the surface was elevated toward the magnet forming a stationary radially symmetric bump with a maximum height of about 5 μm and a radial extent of about 20 mm (Figure 9.2B), thus creating a slope onto which the marble could slide.^[240] Regardless of the initial distance between the LM and the magnet axis, the LM first rapidly accelerated up to a maximal speed $v_{\text{max}} \approx 2 \text{ mm s}^{-1}$ and then slowly decelerated (Figure 9.2C), symbols). This maximal speed could be increased by simply bringing the magnet closer to the substrate. For instance, decreasing the magnet-to-substrate distance in position 2 from 12.7 mm to 9.8 mm led to $v_{\text{max}} \approx 4.8 \text{ mm s}^{-1}$ (Figure 9.2D).

I hypothesized that the two main components leading to marble motion were the diamagnetic repulsion exerted on the marble and the deformation-induced gravity force, both of which induced a repulsion of the marble from the magnet axis. To quantify the relative contribution of each component, I varied the magnetic susceptibility (χ) of the liquid marble as well as that of the substrate by using HoCl_3 solutions of different concentrations (Figure A.8). The results are summarized in Figure 9.3. I first used a water LM on a water substrate ($\chi = -9.5 \pm 0.4 \cdot 10^{-6}$ for both the LM and the substrate). No significant motion could be detected, which was attributed to the attractive contribution of the surface deformation (depression) counteracting the diamagnetic repulsion (Figure 9.3A, i). The effect of the dia-

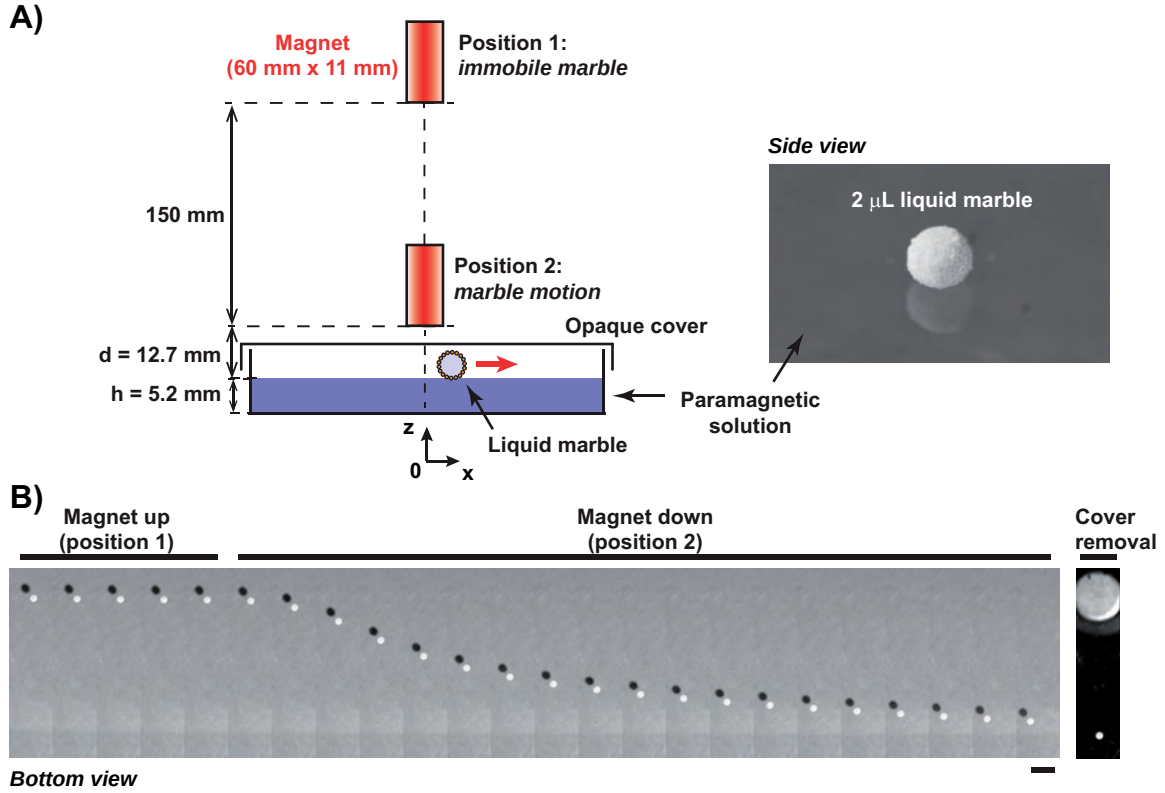


Figure 9.1: Magnetic actuation of a water liquid marble on a paramagnetic liquid substrate. A) Experimental set-up with a 2 μL water liquid marble (diameter 1.6 mm) floating on a paramagnetic solution ($[\text{HoCl}_3] = 100 \text{ mM}$) in a closed Petri dish. The free-fall switch of a permanent magnet from position 1 (far from the substrate surface) to position 2 (close to the substrate surface) induces marble motion. B) Kymograph of the marble (bottom view) upon switching the magnet from position 1 (up) to position 2 (down). The white and black disks are the marble and its shadow, respectively. Frames are separated by 2 s. Scale bar = 5 mm. The last image on the right indicates the position of the magnet that can be seen once the cover has been removed.

magnetic repulsion only on the water LM was assessed by using a 17 mM HoCl_3 solution as the substrate ($\chi = 0.4 \pm 0.1 \cdot 10^{-6}$), so that no surface deformation occurred (Figure 9.3A, ii). The LM then moved at a relatively low speed ($v_{\max} = 0.6 \pm 0.1 \text{ mm s}^{-1}$). In contrast, a much higher speed ($v_{\max} = 1.7 \pm 0.2 \text{ mm s}^{-1}$) was obtained when a 17 mM HoCl_3 LM was used on a 100 mM HoCl_3 substrate ($\chi = 45 \pm 1.7 \cdot 10^{-6}$), that is, in the case of a motion induced by the substrate deformation only (Figure 9.3A, iii). When the water LM was placed on this substrate (same conditions as in Figures 9.1 and Figure 9.2), the strongest response to the magnet was obtained ($v_{\max} = 2.2 \pm 0.2 \text{ mm s}^{-1}$) as a result of the additive contributions of both the diamagnetic repulsion and the substrate deformation (Figure 9.3A, iv). We built an analytical model (Annex A.7.1) for the LM motion including weight, buoyancy, surface tension, drag force, and magnetic repulsion exerted on the LM floating on the liquid substrate, which led to Equation (9.1):

$$\frac{dv}{dt} = -\frac{v_0}{\tau}(\sin\phi)^2\partial_r h - \frac{C\sin\phi}{\tau}v(r,t) + V\frac{\chi}{1+\chi}\frac{\partial_r B^2}{2\mu_0 m} \quad (9.1)$$

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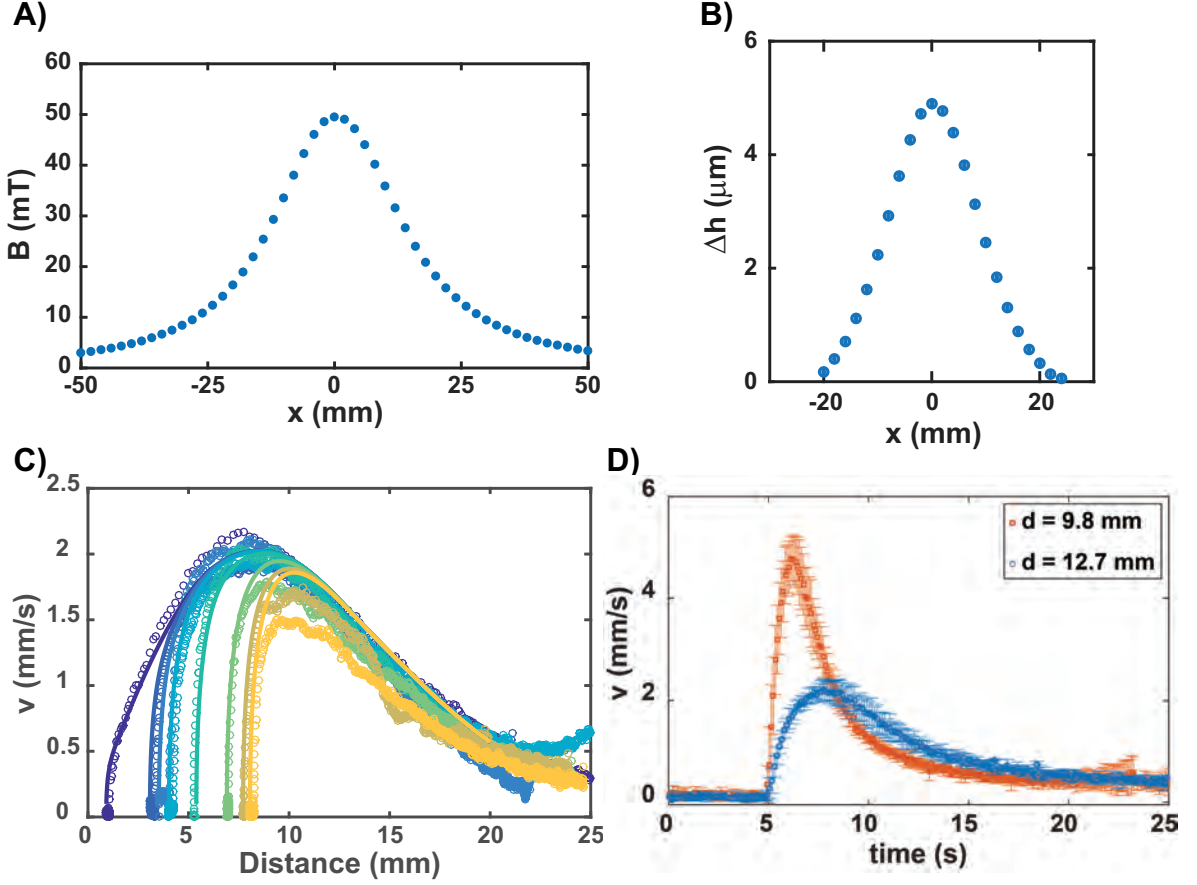


Figure 9.2: Substrate deformation and characterization of the marble motion. A) Norm of the magnetic field profile on the liquid surface. The distance between the magnet and the probe was 12.7 mm. Symbols are mean data on triplicates with error bars (sd) smaller than the symbol size. B) Radial elevation of the substrate surface, Δh , when the magnet is switched from position 1 to position 2. Error bars are smaller than the symbol size. C) Speed of the liquid marble as a function of the distance to the central axis of the magnet. Each curve corresponds to a different initial position. Symbols are experimental data and solid lines are theoretical curves calculated using the experimental measurements of both magnetic field profile and surface deformation and the same value of C for all curves (Annex A.7.1). D) Temporal profiles of the speed of a $2 \mu\text{L}$ water liquid marble for two different approaching distances. The magnet was released at $t = 5 \text{ s}$ from position 1 to reach position 2 at 9.8 mm (orange squares) or 12.7 mm (blue circles). Symbols and error bars show mean $\pm$ sd from 6 individual experiments.

where $\tau = m/2\pi\eta a$ and $v_0 = \gamma/\eta$ and χ , v , m , a , V and ϕ are the magnetic susceptibility, velocity, mass, radius, volume, and wrapping angle of the LM, respectively (Annex A.7.1, Figure A.7), and $h(r)$ is the local elevation of the substrate, μ_0 is the vacuum permeability, and C is a numerical prefactor of the drag force (on the order of 1^[344]). ϕ was determined according to Ooi *et al.*^[345] and found to be around 14° . Equation (9.1) was integrated numerically using the experimentally determined values for both $h(r)$ and $B(r)$ ². The only unknown parameter, C , was determined by fitting the data for the water LM on a 100 mM HoCl_3 substrate and was kept constant for all other conditions. The resulting calculated curves reproduced particularly well the experimental data, even in the absence of any adjustable

9.3 Experimental results and discussion

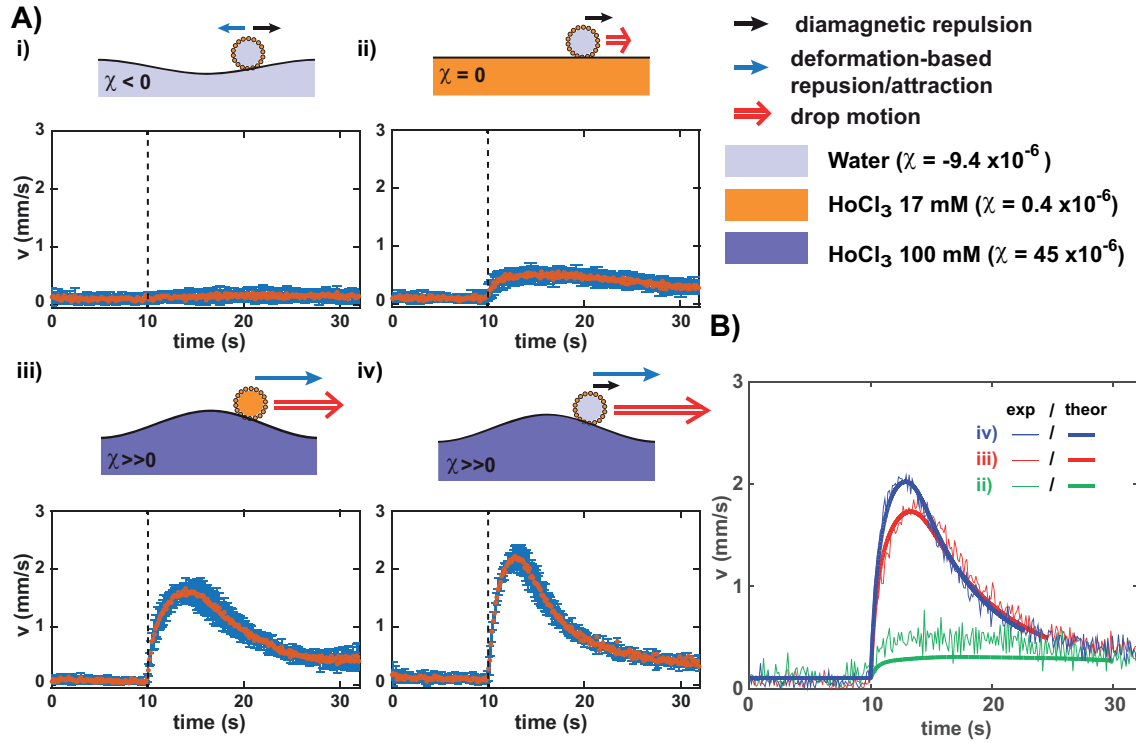


Figure 9.3: The motion is mainly driven by substrate deformation. A) Scheme of the main components of marble motion and speed as a function of time for a 2 μL liquid marble made of water (i, ii, and iv, $\chi < 0$) or 17 mM HoCl_3 (iii, $\chi \approx 0$) on a water substrate containing different amounts of HoCl_3 : 0 mM (i, $\chi < 0$); 17 mM (ii, $\chi \approx 0$); and 100 mM (iii and iv, $\chi \gg 0$, bottom). The marble motion (double red arrow) results from the combination of the diamagnetic repulsion (black arrow) and the substrate deformation-driven gravity force (blue arrow). Each graph shows the experimental speed data (mean $\pm$ sd for 6 independent experiments) with an initial distance between the marble and the magnet axis within the range of 0-5 mm. The dashed line indicates the time at which the magnet was switched from position 1 to 2. B) Three sets of experimental data (thin lines) taken in the three configurations in which marble motion was observed (ii, iii, and iv) and corresponding theoretical curves (thick lines) calculated with the same value of C as in Figure 9.2, using the experimental measurements of both magnetic field profile and surface deformation (Annex A.7.1).

parameter (Figure 9.3B), showing that the marble motion is essentially a combination of substrate deformation-induced and diamagnetic repulsions. Our model thus confirmed the experimental observation that the main contribution to the motion of a marble floating on a paramagnetic substrate was the magnetically induced substrate deformation and not the magnetic effect on the marble itself. Our method thus constitutes a new way to efficiently transport floating objects, even diamagnetic (*i.e.*, water) or non-magnetic (for example, 17 mM HoCl_3) ones. Our model also reproduced well the distance-dependent behaviour (Figure 9.2C, solid lines), emphasizing the interest of using substrate deformation to achieve a long-range actuation of remote objects.

Liquid marbles have the remarkable advantage that they can encapsulate virtually any kind of liquid,^[346] making this method of transport particularly versatile. We then wanted to know whether it can be applied to conventional liquid drops without any specific coating.

9. MAGNETIC ACTUATION OF DROPS AND LIQUID MARBLES USING A DEFORMABLE PARAMAGNETIC LIQUID SUBSTRATE

I thus performed the same experiment as in Figure 9.1 but using a 2 μL oil drop instead of a liquid marble. Interestingly, switching the magnet from position 1 to position 2 led to immediate motion of the drop (Figure 9.4A). To our knowledge, this is the first magnetic

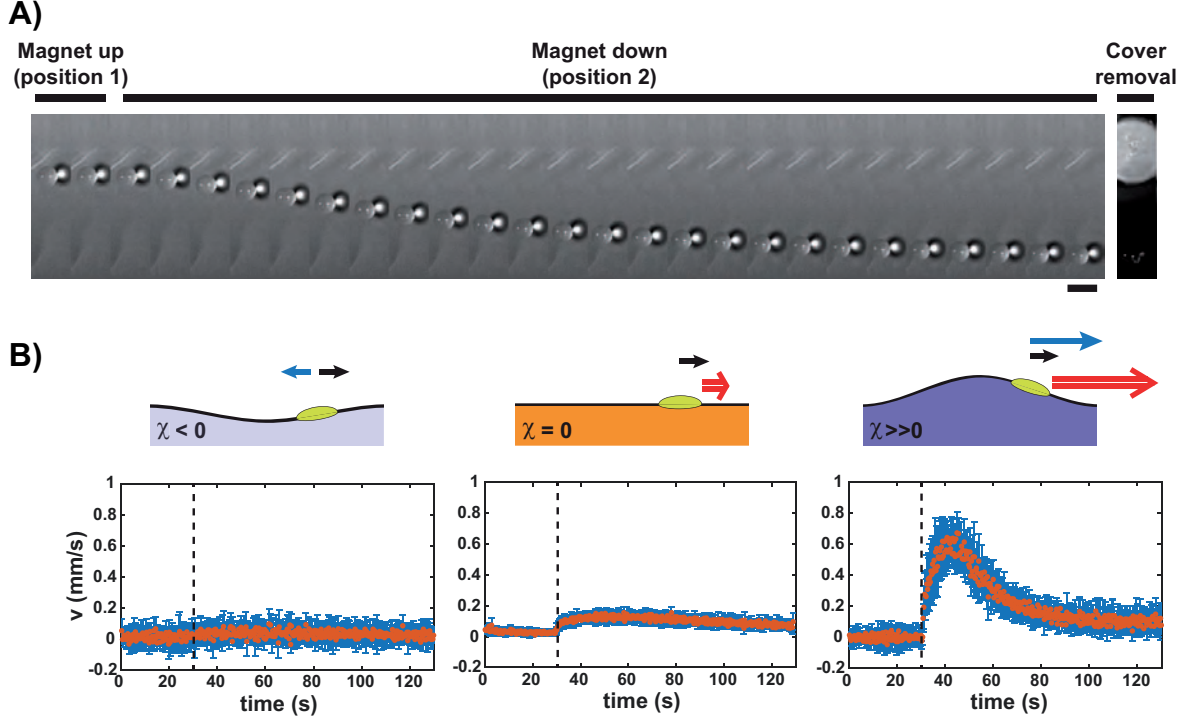


Figure 9.4: Magnetic actuation of an oil drop. A) Kymograph of the magnet-triggered motion of a 2 μL mineral oil drop on a 100 mM HoCl_3 substrate using the same experimental set-up as in Figure 9.1A. The bright spot surrounded by a dark ring is the shadow of the drop. Frames are separated by 1.6 s. Scale bar = 5 mm. B) Scheme (top) and speed as a function of time (bottom) of a 2 μL mineral oil drop on a water substrate containing different amounts of HoCl_3 : 0 mM (left, $\chi < 0$); 17 mM (middle, $\chi \approx 0$); and 100 mM (right, $\chi \gg 0$). Each graph shows the experimental speed data (mean $\pm$ sd for 10 independent experiments) with an initial distance between the drop and the magnet axis within the range of 0-5 mm. The dashed line indicates the time at which the magnet was switched from position 1 to 2.

actuation of a diamagnetic floating liquid drop, which does not rely on any magnetosensitive solid entities such as magnetic particles. To assess the contribution of the substrate deformation to the drop motion, I performed experiments on substrates of various magnetic susceptibilities. Similarly to what was observed with the liquid marble, we could not detect any significant motion when pure water was used as a substrate (Figure 9.4B, left), confirming the importance of the paramagnetic nature of the substrate to achieve significant drop transport. Using a nonmagnetic substrate (17 mM HoCl_3) in which no deformation occurred (Figure 9.4B, middle), resulted in drop motion at a low speed ($v_{\text{max}} = 0.2 \pm 0.04 \text{ mm s}^{-1}$), which was due to the diamagnetic repulsion exerted on the drop ($\chi = -10.3 \pm 0.3 \cdot 10^{-6}$). In contrast, the drop acquired a much higher speed ($v_{\text{max}} = 0.7 \pm 0.1 \text{ mm s}^{-1}$) when a strongly paramagnetic and thus highly deformable substrate (100 mM HoCl_3) was used (Figure 9.4B, right). The same trend was observed when the concentration of HoCl_3 was varied in a sys-

9.3 Experimental results and discussion

tematic manner. Values of v_{max} increased with an increase in $[\text{HoCl}_3]$, that is, when χ and therefore the substrate deformation increased (Figure 9.5A). In the same way as for the liquid

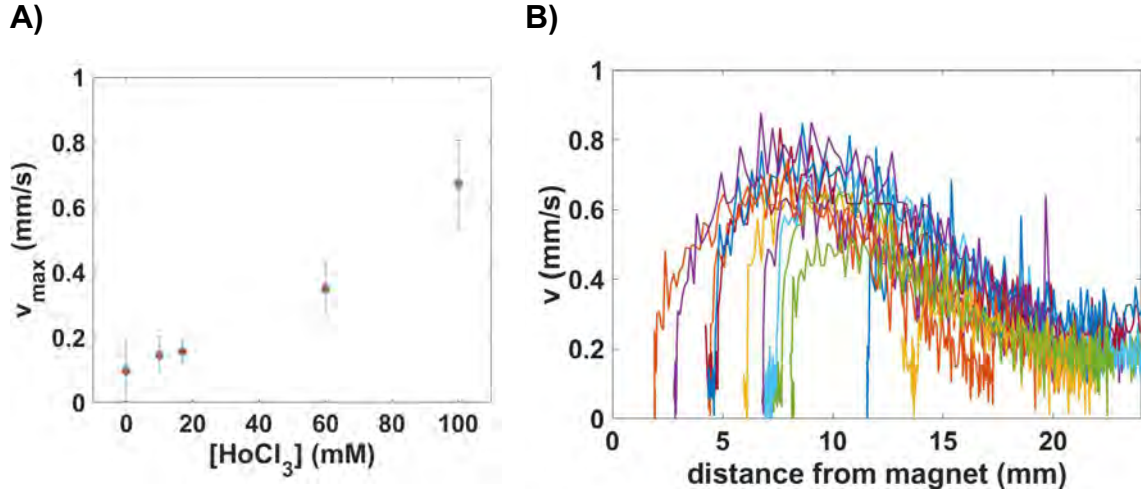


Figure 9.5: A) Maximum speed of a $2\ \mu\text{L}$ oil drop at the air-solution interface, as a function of HoCl_3 concentration. Symbols and error bars show mean $\pm$ sd from at least six independent measurements. B) Speed profile of a $2\ \mu\text{L}$ oil drop on 100 mM HoCl_3 liquid substrate as a function of the initial distance from the magnet axis.

marble actuation, these results showed that the magnetically induced motion of the drop on a paramagnetic substrate (Figure 9.4) was mainly driven by the substrate deformation, to which was added the weak contribution of the diamagnetic repulsion. The behaviour of the velocity as a function of distance to the magnet was also similar to that of liquid marbles (Figure 9.5B). Although the liquid marble and the oil drop had a similar magnetic susceptibility, the maximum speed for the drop was typically half that of the marble, which was attributed to a stronger dissipation at the liquid/liquid interface between the drop and the paramagnetic liquid substrate.

Finally, we explored how this new universal principle for magnetically induced motion of discrete liquid entities can be exploited for more complex operations of drop manipulation. First, using a mobile and portable magnet, drop motion could be maintained for extended periods of time and complex trajectories including curves (Figure 9.6A) and self-crossing points (Figure 9.6B) were easily achieved with precision. Liquid marbles were also successfully transported along complex trajectories, such as “S” and “J” shapes (respectively, Figures 9.6C and D). To program drop fusion, I simply used a pair of mobile magnets to move two drops toward each other and therefore guide their fusion (Figure 9.6E).

9. MAGNETIC ACTUATION OF DROPS AND LIQUID MARBLES USING A DEFORMABLE PARAMAGNETIC LIQUID SUBSTRATE

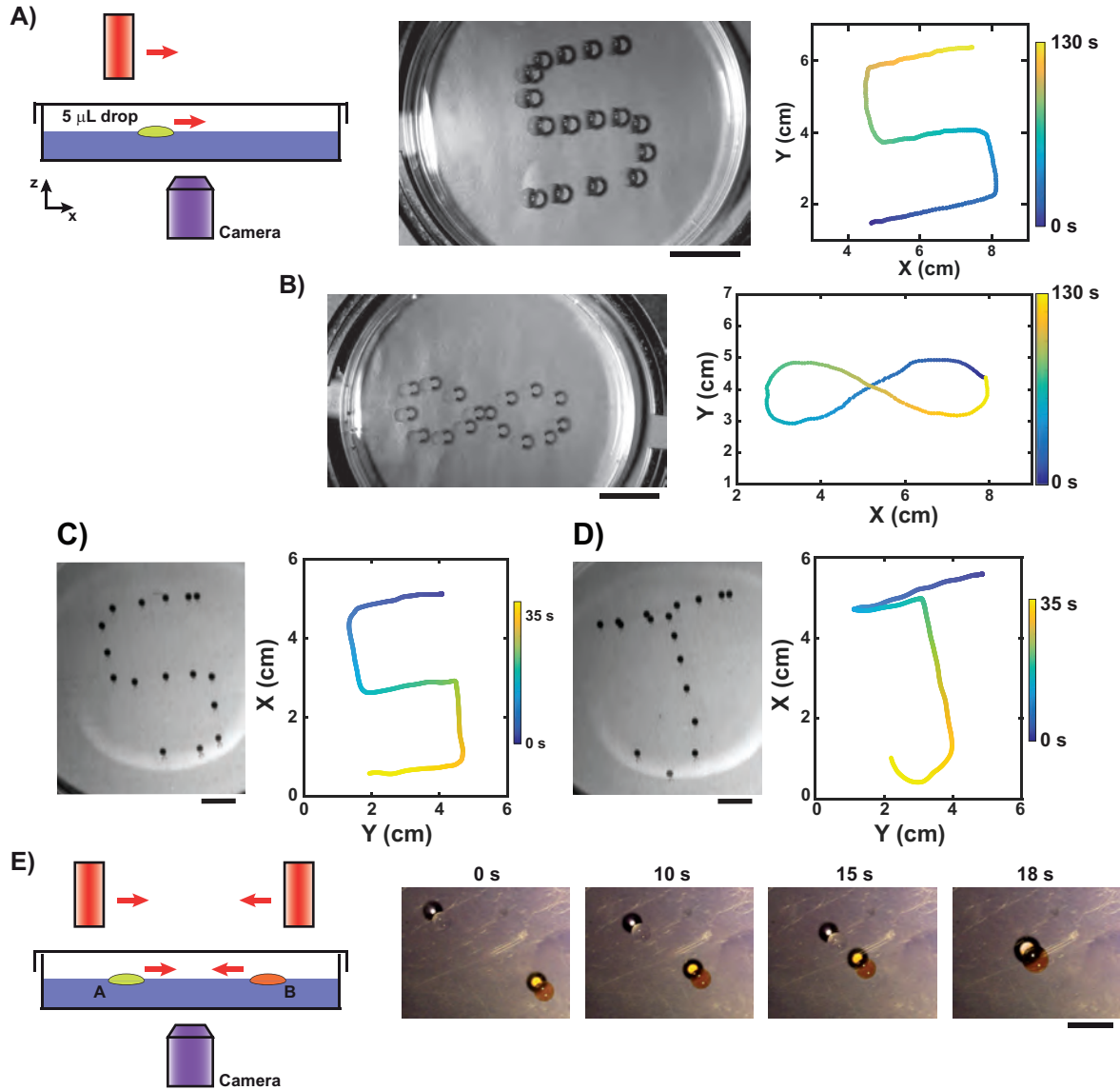


Figure 9.6: Digital magnetofluidic operations: complex transport and fusion. A) The magnet was placed at a distance of 12 mm from the surface of a 100 mM HoCl_3 substrate and manually moved to direct the motion of a 5 μL mineral oil drop (left). Superposition of images (middle, each image separated by 8.6 s) and XY positions of the drop as a function of time (right) for an imposed S-shaped trajectory. B) The magnet is moved along an ∞ -shaped pathway to transport a 5 μL oil drop on a 100 mM HoCl_3 liquid substrate. Left panel: superposition of images showing the drop motion (one image per 8 s). Right panel: plot of the position of the drop as a function of time. C-D) Magnetic transport of a liquid marble along various trajectories. The magnet is moved along a pathway having shapes of letters S (C) and J (D) to transport a 2 μL water liquid marble on a 100 mM HoCl_3 liquid substrate. Left: superposition of images showing the liquid marble motion (one image per 2.3 s). The marble and its shadow (black disk) are both visible. Right: plot of the position of the liquid marble as a function of time. E) Two identical magnets were placed at a distance of 10 mm and moved manually to direct the motion of two 5 μL mineral oil drops, without (drop A) and with (drop B) Sudan II dye, and induce their fusion (left). Images show the magnetically induced drop fusion (right). Scale bars are: 2 cm for A-B; 1 cm for C-E.

9.4 Conclusions

In summary, we described a new mode of interfacial transport in which magnetic field-induced liquid substrate deformation was used to actuate floating objects. This is the first method that allows the magnetically controlled actuation and manipulation of discrete liquid entities in air, which does not rely on the use of magnetosensitive particles. It was demonstrated to be particularly versatile as it is compatible with both conventional drops and liquid marbles; and any liquid, including most common diamagnetic liquids such as oil and water, can be actuated. Deformation-based forces, especially capillary interactions, have been widely exploited to assemble or organize objects at interfaces,^[155] but deformation-based fluidic transport^[240] has been a much more rarely explored principle.^[3] From a fundamental point of view, we showed that the contribution of the substrate deformation, even within a range of only a few microns, largely dominated that of the magnetic force exerted on the transported object. This made it possible to actuate the system with cost-effective permanent magnets, paving the way for a new generation of microfluidic devices powered by miniature magnets and which are able to work without complex elements such as pumps, valves, or electrodes. This electric power-free principle can also contribute to expanding the possibilities of low-cost microfluidics and diagnostics,^[259;260] making solutions developed in laboratories more broadly available to people and societies.

Conclusions

Throughout this thesis I studied various soft matter systems involving liquid interfaces, from the behaviour of colloidal particles (of micrometer- and nanometer-size) to the manipulation of small (microliters) floating drops. The design of systems able to respond to external stimuli in order to modify on demand their constituting interactions, properties and response is the *trait d'union* that moved our research perspectives.

In **Part I**, focusing on mixtures of anionic particles and cationic surfactants at concentrations typically 10^3 smaller than their critical micellar concentration, we critically expanded the potential of surfactants to induce the adsorption of particles at the air/water interface and, at the same time, control their two-dimensional organization. Generally used to modify particle charge and hydrophobicity or to decrease interfacial energies, we have shown here that surfactants, added in minute quantities, can also promote the adsorption of particles at the liquid interface while keeping most of their charge. Consequently, we proved that they can be used to directly govern colloidal crystallization at the air/water interface. A series of experiments varying important parameters, such as particle and surfactant concentration, allowed us to investigate the main components governing particle organization, namely the short-range repulsive potential (in case of negatively charged particles), and the long-range attractive potential due to the collective deformation of the interface by the weight of the adsorbed particles, and to draw a phase diagram where various organization states could be reached (amorphous aggregates, polycrystalline or gel structures). Successively demonstrated with two types of conventional cationic surfactants, four different particle types and both micrometer- and nanometer-sized colloids, we expect our strategy/approach to be readily applicable to a wide range of surfactant/particle systems of scientific or industrial interest.

In **Part II**, we reported two systems where, to our knowledge for the first time, light stimulation was used to direct the organization states of ensembles of particles adsorbed at the air/water interface. Those experiments started from the results described in Part I, and took advantages from both our new practical method to prepare 2D colloidal crystals, and the understanding of the underlying mechanism dictating the way particles organized once adsorbed at the air/water interface. On-demand switching between ordered and disordered two-dimensional structures was achieved in two conceptually different ways. The system described in Chapter 5 exploits the energy dissipation of absorbing particles heated up by light irradiation to reversibly switch from the crystalline state (stable in the absence of any

stimulation) to a disordered one (upon irradiation). Interestingly, at a lower irradiation power, the long-range ordered structure was not destroyed, instead it was possible to increase under light command the particle-particle distance up to hundreds of nanometres. With these findings we described a powerful system where both inter-particles distances and the organization state could be controlled dynamically and externally with a ms to s response time. In Chapter 6, the light response of common passive particles was provided by the light-induced isomerization of a photosensitive surfactant. By exploiting the out-of-equilibrium adsorption/desorption dynamics of the surfactant isomers at/from the water surface we could control the structural properties of the particle assembly in a fast and reversible fashion. Cycles between disordered (without stimulus) and highly crystalline (under light) colloidal structures were achieved with a single wavelength switch, without being hindered by the very slow thermal relaxation of the excited surfactant isomers. Ultimately, the emergent polycrystalline structures formed under light irradiation are a key characteristic of a self-assembled dissipative system, where the long-range ordering is achieved, and maintained, only through consumption of the energy supplied by the incoming irradiation. Therefore, this system expands the field of currently known dissipative systems, in phase with the developing of man-made devices with emergent, adaptive and reconfigurable properties.

Part III was devoted to the development of a new method to manipulate microlitre drops floating on a liquid surface. Since many approaches were already reported, by our laboratory and others, to control drop motion using light, we challenged the possibility to use a magnetic field instead but, contrary to all methods reported to now, without any magnetic particles dispersed within or outside the drops. Our method was based on the magnetic field-induced deformation of a paramagnetic liquid substrate to precisely actuate floating entities such as drops or liquid marbles. Relying on the moderate magnetic fields provided by small permanent magnets, it is targeted to the development of cost-effective microfluidic devices, able to work in an electric power-free manner. The flexibility of the method was demonstrated through the actuation of drops and liquid marbles, and the complex manipulation and on-demand fusion of multiple drops. Liquid marbles, together with an analytical model and the precise surface tension measurements carried out in Chapter 8, were instrumental in understanding the underlying mechanism. Varying their content (and accordingly their magnetic response), we were able to extract the contribution of the substrate deformation, which largely dominated that of the magnetic force exerted on the transported object. This emphasized how the method is versatile in actuating diamagnetic or non-magnetic solutions.

Future research perspectives have been opened by each part of this thesis. A first obvious direction could be the study of the adsorption and two-dimensional structural organization of various other colloidal particles. I believe our method, thanks to the multiple controlled interactions involved in dictating the final particle organization, would allow to obtain further interesting results (especially regarding the assembly of polycrystalline architectures). Soft

microgel particles (with which an additional *in situ* control over their size could play an important role), metal nanoparticles (for which a lot of work is still required), or patchy particles (presumably giving less straightforward two-dimensional arrangements) are the first examples of suitable building blocks for further research that come to my mind. In addition to this material science perspective, the well-controlled effect of each component acting on the system (particle, surfactant and meniscus curvature) permits fundamental studies on the two-dimensional particle structuring, exempt of uncontrolled effects due, for example, to contaminations (such as the one coming by the use of external solvents). Therefore, further experimental findings (*e.g.* measurement of the surface potential of the adsorbed particles), possibly coupled with simulations, will be of great scientific interest.

Part II reports two light-responsive systems of particles at a liquid/liquid interface, where the colloidal structural organization can be tuned on demand, with a fast response time, between ordered and disordered structures (and *vice versa*). Both systems are proof of principles and still in their infancy. The implementation of specific properties in the particle structure (such as reflectivity, sensing or catalytic properties) that could be conveniently switched by light is a interesting direction, opening the way to the design of smart responsive two-dimensional “soft” devices. In addition, my curiosity once more point at studying particles with a soft outer layer, whose diameter could be varied as a function of temperature or light. I believe interesting properties coming from tiny variation in the centre-to-centre particles distances, as the one that can be obtained using soft particles, can arise. Finally, the use of an IR laser, instead of UV-visible light, to locally heat up the water surface, could be tested for a novel system where neither specific particles nor photosensitive surfactant would be required to design tunable colloidal structures.

Last but not least, as already mentioned, the magnetic actuation method of the last chapter needs to be exported to real-world microfluidic devices. Our novel methodology is now well characterized and shall be ready to be developed for useful applications. One possible direction is controlling the deformation of liquid/liquid interfaces in close chips, with the objective to realize a new generation of low-cost, flexible and easy-to-handle microfluidic devices solely powered by cost-effective permanent magnets.

Appendix A

Annexes

A.1 Materials and Particles synthesis/modification

Ultrapure water (resistivity 18.2 M Ω ·cm) was used for all experiments. The suspensions of negatively charged polystyrene particles (diameter: 5.1 μ m), bearing sulphate and a high density of carboxyl functional groups on their surface, were purchased from Life Technologies. All the suspensions of negatively charged silica particles having various diameters, bearing silanol groups on their surface, were purchased from microParticles GmbH. The suspensions of negatively charged polystyrene particles (diameter: 4.5 μ m), having carboxyl functional groups on their surface and iron oxide inclusions in the particle core, were purchased from microParticles GmbH. Suspensions of silver and gold nanoparticles were purchased from nanoComposix, Inc. Silver nanocubes, having a diameter of 103 ± 7 nm (CV = 6.7%), have Poly(vinylpyrrolidone) (PVP) on their surface, and are dispersed in ethanol. Two gold nanospheres batches were used: one with a diameter of 100 ± 13 nm (CV = 13.2%), Lipoic acid on the surface, dispersed in Milli-Q water; the other with a diameter of 99.4 ± 3 nm (CV = 3.1%), Poly(ethylene glycol) (PEG)-Carboxylic acid on the surface, dispersed in aqueous 2mM Citrate.

Although all suspensions were designated as pure, I followed a washing procedure that was found to be essential for obtaining reproducible results. A suspension of the particles at $C_p = 10$ mg/mL underwent typically five to six centrifugation cycles where the supernatant liquid was exchanged with ultrapure water each time. Prior to each experiment, each particle suspension was mixed by vortexing (2 min), sonicated in an ultrasound bath (2 min) and vortexed again for another min.

Dodecyltrimethylammonium bromide (DTAB, purity $\geq 98\%$, Sigma-Aldrich) hexadecyltrimethylammonium bromide (CTAB, purity $\geq 99\%$, Sigma-Aldrich), sodium dodecyl sulfate (SDS, purity $\geq 99\%$, Fluka) and triethoxy monoocylether (C8E3, purity $\geq 98\%$, Sigma Aldrich) were used as received. Azobenzene trimethylammonium bromide (AzoTAB) was synthesized as described in reference.^[231]

A.1.1 Particles surface modification

The surface of the negatively charged silica particles (4.6 μm in diameter) was modified by adsorption of positively charged polymers. In an eppendorf tube containing a water solution of poly-L-lysine (PLL) or poly(diallyldimethylammonium chloride) (PDADMAC) at a concentration of 10 mg/mL and 100 mM salt (NaCl), were added the silica particles up to a final concentration of 10 mg/mL and a final volume of 1800 μL . After 2 hours of vigorous stirring, the polymer-modified particles were separated by centrifugation at 15 000 rpm for 20 min. The particles were then purified six times by addition of 1400 μL of water followed by separation by centrifugation.

The polymer-modified particles were characterized by ζ -potential measurements to ensure the absence of aggregation and to quantify the surface charge modification. Each particles mixture was diluted to 0.1 mg/mL and three independent values were recorded. The PLL-modified particles gave a ζ -potential value of 44.0 ± 0.1 mV, while the PDADMAC-modified particles gave a ζ -potential value of 53.7 ± 1.4 mV.

A.1.2 Janus particles synthesis

Janus particles were synthesized following the procedure in.^[347;348] The glass slides used for particles deposition were cleaned by 10 minutes sonication in alkaline solution, 10 minutes sonication in MQ water, and copious rinsing with MQ water. They were successively dried under vacuum overnight. Monolayers of silica particles (2.4 μm in diameter) were prepared by drop casting 200 μL of a 0.5 mg/mL mixture on the clean glass slides. Thanks to the high density of the silica particles, all the particles sediment during evaporation and no multilayer were found after drying. Monolayers of polystyrene particles (carboxylate modified latex, 1.1 μm in diameter) were prepared by using a convective deposition set-up to avoid multilayer formation during drop evaporation. Experimentally the deposition was carried at 1.33 A, setting the cooling water bath at 20°C, with a substrate speed of 0.1 mm/s, and depositing a 20 μL drop of 4 mg/mL particles mixture.

An adhesion layer of titanium (~ 4 nm, at 125 mA for 30s) was deposited on the templates by sputter deposition, followed by a thin film of platinum (~ 20 nm, at 125 mA for 60s). After the deposition of the metal film, the particles were released from the surface by sonication for 30 minutes in MQ water.

A.1.3 Gold nanoparticles synthesis

Gold nanoparticles were synthesized following the procedure in.^[349] 100 mL of a 0.5 mM solution of HAuCl_4 in water was prepared and heated up to boiling under reflux. 5 mL of a 1 wt% citrate solution was added in one shot in the HAuCl_4 solution under vigorous stirring. Boiling was continued for 15 minutes, than the obtained red solution was let cool down to room temperature. The Gold nanoparticles were characterized by absorption spectroscopy

and AFM imaging. For AFM imaging 15 μL of the nanoparticles solution were adsorbed on a Mica plate previously treated with Polylysine.

A.2 Setups for microscopy imaging coupled with various light irradiation configurations

A.2.1 Setup for upright microscopy imaging and coupled light irradiation

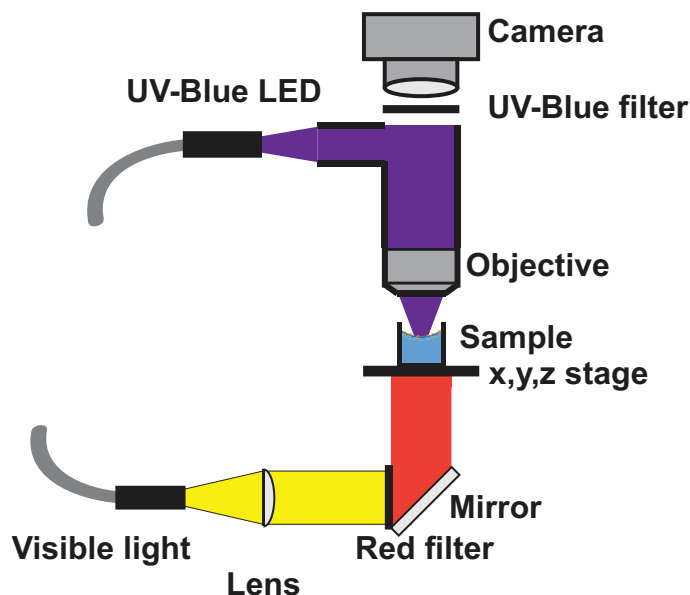


Figure A.1: Schematic of the custom built upright microscope for transmission and reflection microscopy images. The UV-Blue LED is coupled to the tube system of the microscope via a side port; alternatively, a light guide for visible light is placed there for reflection images.

The great majority of microscope images (if not stated otherwise) were acquired using a home-built upright microscope, which could operate both in transmission and reflection mode. The microscope mainly consisted of a 12X Zoom Lens System (Navitar), the appropriate microscope objective (a 20X, $NA = 0.42$ and a 5X, $NA = 0.14$ for respectively low and high magnification, both from Mitutoyo) and an XYZ translation stage on which the sample cell was placed. White light (or red light if required by the experiment, as in Chapter 6) illumination was provided by a flexible light guide coupled to a cold white light source (KL 2500 LED, Schott). For transmission imaging the light was brought from the bottom of the sample cell after passing through a diffuser, a red filter if required, and a mirror. For reflection imaging the light guide was inserted on a side port of the tube system of the microscope. A colour CCD camera (Basler acA1600-20uc, resolution 1626 pixels x 1234 pixels, 12 bits) was used for image acquisition, applying a UV-blue filter before it to avoid blinding from the excitation light.

UV ($\lambda = 365$ nm) or blue ($\lambda = 440$ nm) irradiation was applied using a light-emitting diode (LED) source coupled to a liquid light guide (pE-2 excitation system, CoolLED), as

A.2 Setups for microscopy imaging coupled with various light irradiation configurations

in Figure A.1. The light guide was inserted coupled directly to the tube system of the microscope (*via* a side port), passing through the 20X objective. The beam diameter was about 4 mm at the focal plane focused on the air/water interface of the sample; the power of the applied irradiation could be modulated directly from the excitation system depending on the intensity required, and each time was measured at the sample position.

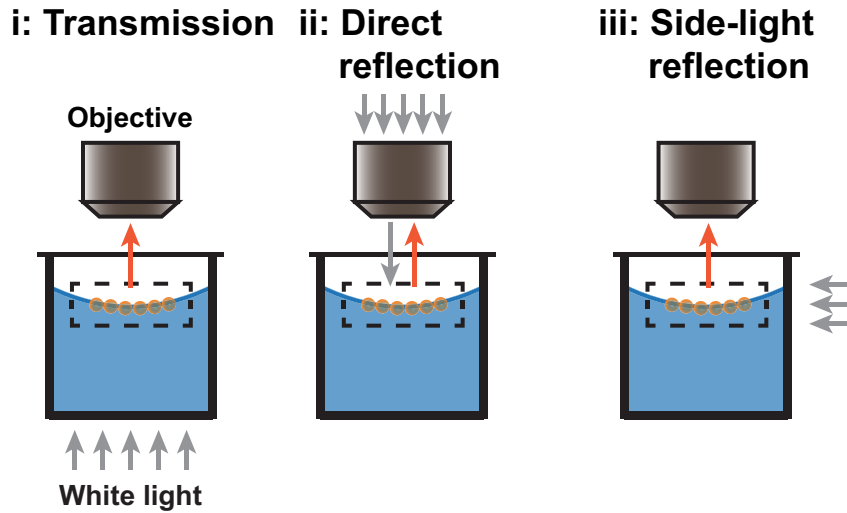


Figure A.2: Light configurations used, coupled with the optical setup in Figure A.1, to image particles at the air/water interface. i) transmission; ii) direct reflection; iii) side-light reflection with a white light source parallel to the water interface.

A.2.2 Setup for focussed light irradiation

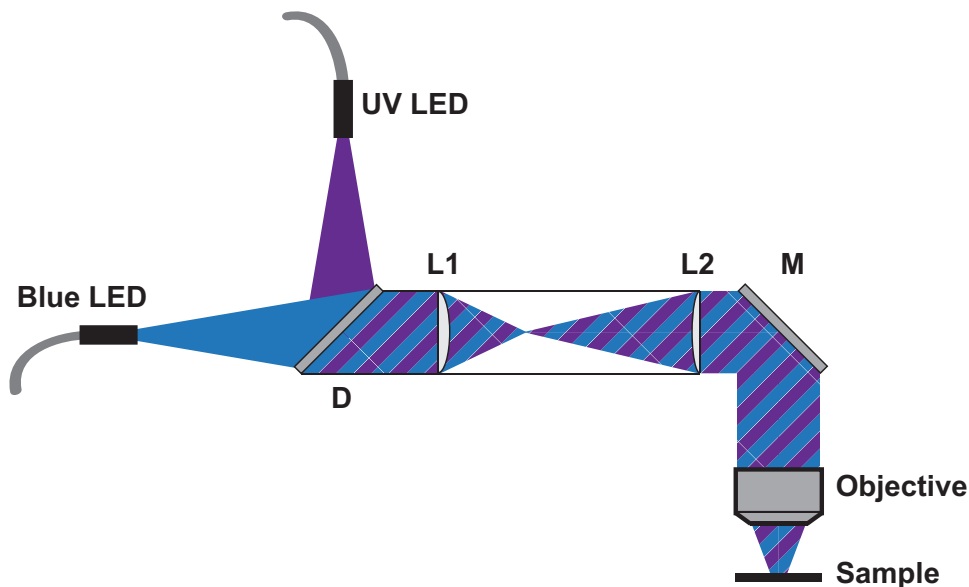


Figure A.3: Schematic of the custom built optical setup used to produce light patterned focussed irradiation coupled to an inverted fluorescent microscope (not shown). D: dichroic mirror; L1 and L2: lenses; M: mirror.

A custom built optical setup was built to produce a light pattern focussed on the sample.

A schematic illustration of the setup used is shown in Figure A.3. UV light (wavelength 370 ± 10 nm, maximum power = 1.2 W) and blue light (wavelength 410 ± 5 nm, maximum power = 1.4 W) were provided by two LED sources. Since the output of each LED source was highly diverging, it was important to make the source size smaller (considered as a point source) for better focusing of the light. To realize this, each LED was positioned at a distance of 8 cm from a dichroic mirror (D). The blue LED was positioned in the optical axis of the experiment, while the UV source was positioned at 90° and reflected by the dichroic mirror into the optical axis of the experiment. The diverging beam was allowed to pass through a Keplerian telescope formed by the lenses L1 ($f = 2.5$ cm) and L2 ($f = 10$ cm) placed at a separation of about 13 cm. This arrangement yielded a nearly collimated output beam with a diameter of 2.5 cm. This beam overfilled the input aperture of the focusing objective (LMU-5X-NUV, 325 - 500 nm, NA = 0.13, Thorlabs), and resulted in a spot diameter of about 100 μm at the focal plane. The maximum blue light power after the objective was found to be 11.14 μW , while for UV 24 μW . The optical assembly used for irradiation was coupled to an inverted fluorescent microscope (Axio Observer Z1, Zeiss) equipped with an EMCCD camera (Evolve, Photometrics). A filter-set was modified in order to record reflection images of the samples using only red excitation light.

A.3 Sample preparation for SEM imaging

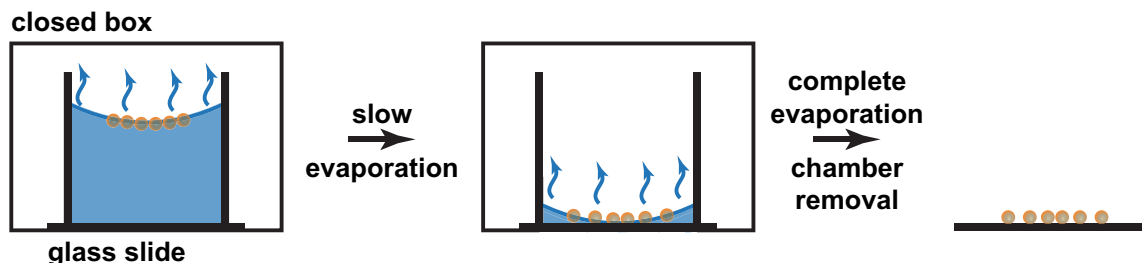


Figure A.4: *Sketch of the procedure to prepare a sample for SEM imaging. After particles adsorption at the air/water interface, modified cells having a glass slide as the bottom surface were placed in a close chamber, without the coverslip on top, and slow evaporation of the water solution was allowed. After complete evaporation, the glued cells were removed, leaving glass slides with the aggregates prepared at the air/water surface transferred on them for SEM imaging.*

Sample preparation for SEM images: I used modified chambers for achieving particles adsorption at the air/water interface. A sketch of the sample preparation for SEM images is reported in Figure A.4. The bottom of the wells was cut and the wells, now open on both sides, were glued on a glass slide using an UV-curing glue. Prior to use, the glued wells were copiously rinsed with MQ water and ethanol and left for two days in a water bath in order to remove any unreacted monomer or other surface-active molecules. After loading the cells with the sample mixture, the particles were adsorbed at the air/water interface in the same manner as described previously. Successively the cells were placed in a close chamber, without

A.4 Calculation of the particle contact angle from confocal reflection microscopy

the coverslip on top, and slow evaporation of the water solution was allowed. Complete evaporation required around five days. Finally, the glued cells were removed, leaving glass slides with the aggregates prepared at the air/water surface transferred on them for SEM imaging.

A.4 Calculation of the particle contact angle from confocal reflection microscopy

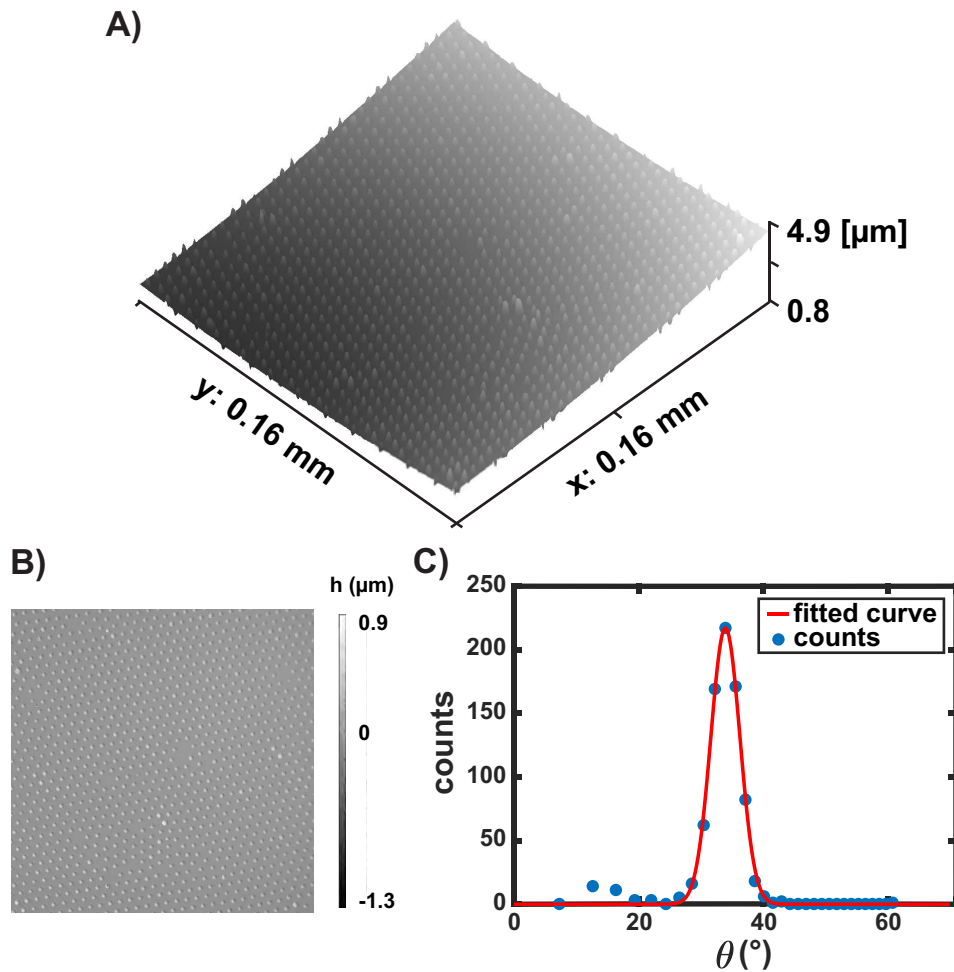


Figure A.5: Calculation of the particle contact angle (θ) from fast confocal reflection microscopy at the air/water interface. A) Three dimensional image of the particles adsorbed at the air-water interface with $C_p = 5$ mg/mL and $C_s = 10$ μ M. B) Same image as in (A) after leveling, showing the height (h) of each particle protruding from the air-water interface. C) Distribution of contact angle values (θ) for all individual particle in (B) as calculated using the equation: $\theta = \arccos((D - 2h)/D)$. The data were fitted with a Gaussian curve to obtain the mean contact angle value and the standard deviation as displayed, for instance, in Figure 2.8C.

The images were obtained by Manos Anyfantakis by using a fast white-light confocal profilometer comprising a 100W XBO illumination source, a rotating multi-pinhole disk and a CCD camera with 512x512 pixels (μ surf, NanoFocus AG), to map the topography of the

particle-laden air/water interface. A long working distance (WD) objective (Olympus LM-PLFL100X M Plan Fluorite, NA = 0.80 WD = 3.40 mm) was used.

In the following paragraph I describe the procedure that I used to calculate the contact angle (θ) of the adsorbed particles. Each acquired image, containing around 1000 particles, was first levelled using the *μsoft* software (Nanofocus AG) to correct for the curvature of the LG interface and was further analysed with the *Gwyddion* software. A threshold by height was applied and a distribution of the maximum height (h) protruding from the interface by each particle was obtained. The contact angle was calculated with the following formula:

$$\theta = \arccos\left(\frac{D - 2h}{D}\right) \quad (\text{A.1})$$

where D is the particle diameter. Further analysis was carried out with *Matlab* software: the distribution was fitted with a Gaussian function to extract the centre of the peak and the standard deviation. In the case of a double peak in the contact angle distribution, a double Gaussian function was used for fitting and the obtained contact angles were averaged, weighted by the intensity of each peak.

A.5 Meniscus shape of DTAB solutions in the experimental chambers

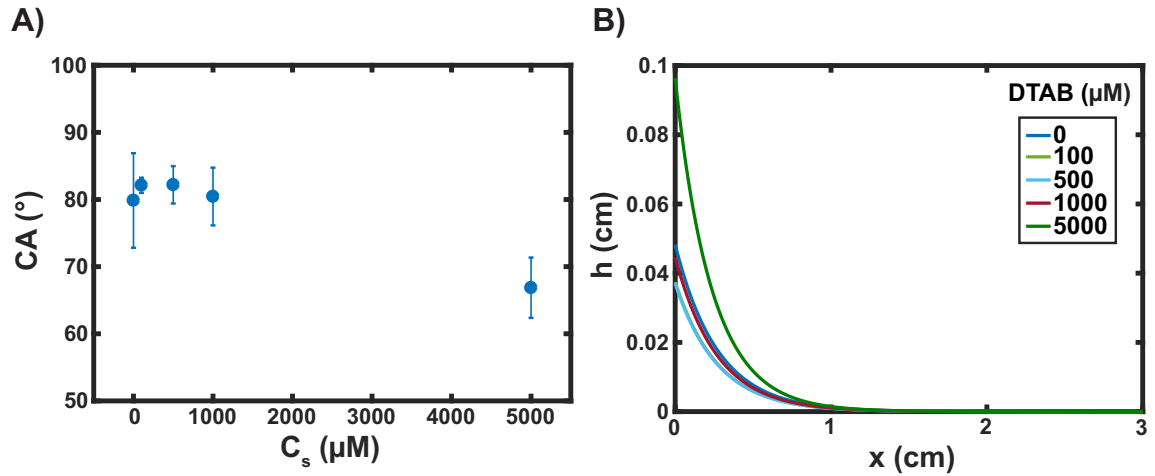


Figure A.6: A) Static contact angle (CA) of drops of solutions at various DTAB concentrations (C_s) deposited on the wall of the experimental chambers. Symbols and error bars show mean values $\pm$ sd from at least 4 individual experiments. B) Numerical solution of the shape of the meniscus (h), for solutions at various DTAB concentrations, in contact with a vertical wall positioned at $x = 0$. The shape was computed knowing the experimental values for the contact angle of the solution and the surface tension values from the reference.^[350]

A.6 Image analysis

Quantitative analysis of the images was carried out using the *ImageJ* software and a custom written *Matlab* (The MathWorks) code. The area of the 2D colloidal patches was obtained

by manually fitting its shape with an ellipse. The total number of particles in each patch was computed by counting the number of particles in the corresponding high magnification image, and multiplying it by particle density which was assumed to be constant across the whole patch. From high magnification images as in Figure 2.4A top row (typically containing roughly 1700 particles), the centre of each particle in the image was detected with the “find maxima” process of the *ImageJ* software. Prior to apply the “find maxima” process, each image was separate into RGB images; then normally the green image was chosen due to a brighter light spot in the centre of each particle, and it was treated with the “subtract background” process and a Gaussian blur. This post-processing allows to detect the centre of all the particles in the images, with a minimum (normally nothing) detection of the background image. Successively, knowing the positional data of the particles enabled us to calculate the radial distribution function (RDF), which describes the number of particles sitting at a (center-to-center) distance r away from a given reference particle, using the “radial distribution function” macro of the *ImageJ* software. A custom written modification of the macro allowed us to analyse multiple frames from a movie, obtaining a RDF per frame. Alternatively, the coordinates of each particle (from smaller images as in Figure 5.1) were imported in a custom written *Matlab* code to extract the first nearest neighbours distance for each image.

For Chapter 9, all videos were analysed using the *ImageJ* software. A threshold was applied, and the “Analyze particles” function was used to determine the position of the moving liquid entity in each frame. Further analysis to obtain the speed at different distances from the center of the magnet was done using the *Matlab* software.

A.7 Complementary information for Chapter 9

A.7.1 Theoretical description of liquid marble motion

Equation of motion for the liquid marble obtained by Nikita Kavokine. We consider a liquid marble (LM) of volume $V = 2 \mu\text{L}$ deposited on the surface of a paramagnetic fluid having a surface tension γ . We describe the position of the liquid marble at time t by the radial coordinate $r(t)$. Under the effect of a magnetic field $\mathbf{B}(r)$, the liquid surface is deformed. The local elevation of the surface is denoted $h(r)$. Under the combined effect of gravity and diamagnetic repulsion, the LM is expected to move down along the deformed interface with a speed $v(r, t)$, t being time. Here we derive the equation of motion of the liquid marble. The forces acting on the LM are:

- The effective weight $\mathbf{P}_{eff} = \mathbf{P} + \mathbf{\Pi}$, where $\mathbf{P}$ is the weight and $\mathbf{\Pi}$ is the buoyancy.
- The tension force $\mathbf{f}_\gamma$, which is normal to the interface. In the hypothesis of a perfectly non-wetting LM, we have

$$f_\gamma = 2\pi r_c \gamma \sin \phi \quad (\text{A.2})$$

where we define r_c the radius of the contact line, γ the surface tension and ϕ the wrapping angle.

- The diamagnetic repulsion force $\mathbf{F}_B = \nabla(\mathbf{M} \cdot \mathbf{B})$, where $\mathbf{M} = V \frac{\chi}{\mu_0(1+\chi)} \mathbf{B}$, is the magnetisation of the liquid marble. Here V and χ are respectively the volume and the dimensionless magnetic susceptibility of the liquid marble (identified to that of the liquid inside the marble); μ_0 is the vacuum permeability. This can be re-written as

$$\mathbf{F}_B = V \frac{\chi}{1+\chi} \frac{\nabla(\mathbf{B}^2)}{2\mu_0} \quad (\text{A.3})$$

- The drag force $\mathbf{f}_{drag}$, which is parallel to the interface and which is expected to be of the form

$$f_{drag} = -2\pi C \eta r_c v(r, t) \quad (\text{A.4})$$

where C is a numerical coefficient that is expected to be of the order of 1, and η the viscosity.

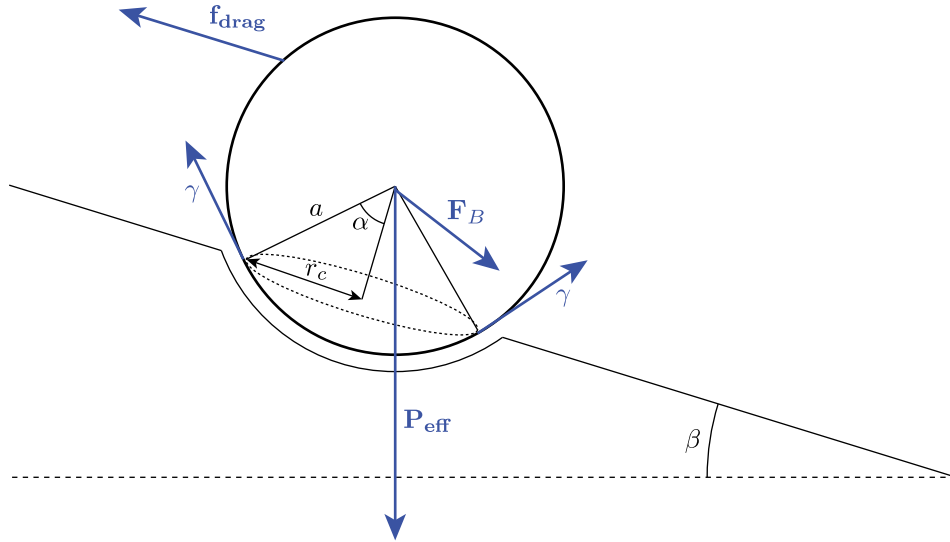


Figure A.7: Forces acting on a liquid marble floating at the air-solution interface, and geometrical parameters characterising its position.

The directions of the forces and the relevant geometrical parameters are specified in Figure A.7. We assume in the following that $\beta = \partial_r h$ is small. Given the geometry of our system, the gradient of the magnetic field along the vertical direction is expected to be of the same order of magnitude as along the vertical direction. Moreover, a simple calculation^[328] shows that, when neglecting surface tension effects, the surface deformation due to the magnetic field is approximately

$$h(r) \approx \frac{\chi}{1+\chi} \frac{\mathbf{B}(\mathbf{r})^2}{2\mu_0 \rho g} \quad (\text{A.5})$$

where ρ is the density of the fluid and g is gravity. Hence the gradient of $\mathbf{B}^2$ along the horizontal direction is of order $\beta = \partial_r h$, and so is the gradient of $\mathbf{B}^2$ along the vertical

direction. Thus it can be neglected in the force balance along the direction normal to the surface, which we write at order 0 in β as

$$P_{eff} = -2\pi r_c \gamma \sin \phi \quad (\text{A.6})$$

Newton's second law projected on the tangential direction reads

$$m \frac{dv}{dt} = P_{eff} \partial_r h + f_{drag} + F_B \quad (\text{A.7})$$

that is

$$\boxed{\frac{dv}{dt} = -\frac{v_0}{\tau} (\sin \phi)^2 \partial_r h + V \frac{\chi}{1 + \chi} \frac{\partial_r \mathbf{B}^2}{2\mu_0 m} - \frac{C \sin \phi}{\tau} v(r, t)} \quad (\text{A.8})$$

with $\tau = m/(2\pi\eta a)$ and $v_0 = \gamma/\eta$.

Equation (A.8) is our main result: it can be integrated numerically in order to predict the motion of the liquid marbles in various conditions. It still contains however an undetermined geometrical parameter: the wrapping angle ϕ of the LM. The shape of the liquid-air interface around a floating LM has been specifically studied by Ooi *et. al.*^[345] Briefly, the height of the meniscus ξ can be expressed using the balance between weight, buoyancy and surface tension as

$$\xi = \frac{a}{3 \sin^2 \phi} \left(1 + 3 \cos \phi - \cos^3 \phi - \frac{6\ell_c^2}{a^2} \sin^2 \phi \right) \quad (\text{A.9})$$

Another expression of ξ can be obtained from the Young-Laplace equation for the shape of the liquid-air interface. This equation usually has no closed analytical solution, however, Ooi *et. al.* find that for $a \sin \phi / \ell_c \leq 0.2$ an approximate solution is

$$\xi = a \sin \phi \sin \beta \left(\ln \left[\frac{4\ell_c}{a \sin \phi (1 + \cos \beta)} \right] - C_{EM} \right) \quad (\text{A.10})$$

where $C_{EM} \approx 0.5772$ is the Euler-Mascheroni constant and $\tan \beta = \sin \phi$. Eliminating ξ between eqs. (A.9) and (A.10) yields an equation for ϕ , which can be solved numerically to obtain, with our system's parameters, $\phi \approx 14^\circ$. This corresponds to $a \sin \phi / \ell_c = 0.07$, which justifies the use of the approximate solution (A.10).

Comparison to experimental data. Equation (A.8) was numerically integrated with a time step $dt = 1$ ms and space discretisation $dr = 0.1$ mm, using the experimentally obtained values of the magnetic field and the surface deformation. The experimental data were linearly interpolated up to the desired space discretisation. The value of the constant C was adjusted so as to fit to the data from liquid marbles made of water moving on a 100 mM HoCl_3 substrate ($C = 3.84$). The same value of C was used for all the displayed curves. The curves in Figures 9.2 and 9.3 were obtained by integrating eq. (A.8) having set B to 0 or $\partial_r h$ to 0.

A.7.2 Experimental methods

Preparation of liquid marbles. Hydrophobized fumed silica nanoparticles were prepared as previously described in reference.^[240] A spatula full of silica particles was placed in a mortar and was spread in order to cover the surface; afterwards a 2 μL drop of ultrapure water (except in the case of Figure 9.3C, where a 2 μL drop of 17 mM HoCl_3 was used) was carefully deposited on top of the particle layer and was rolled in all directions in order to completely cover the drop surface with the hydrophobic particles. The obtained liquid marble was transferred onto a watch glass to remove the excess of powder, and then placed onto the liquid surface used for the experiment.

Magnetic manipulation of liquid entities. For all experiments, 30 mL of HoCl_3 solution of a given concentration were placed in a plastic Petri dish (8.6 cm diameter). Subsequently a liquid marble, or a mineral oil drop of the desired volume, was carefully placed on top of the surface, in the center of the Petri dish to avoid interaction with the meniscus formed at the walls. All experiments were carried out at room temperature.

The magnet (NdFeB, 12 mm x 60 mm, Supermagnete) at the beginning of the experiment was placed along the axis perpendicular to the center of the Petri dish, at a distance from the liquid surface greater than or equal to 150 mm (position 1), where no actuation effects were detected. Then the magnet underwent free fall to approach the liquid surface in position 2. In all experiments position 2 corresponded to 12.7 mm distance, except in Figure A.8 where the distance was 9.8 mm. Videos of the actuation of the drop or liquid marble was recorded with an EOS 5D Mark II camera (Canon), placed below the Petri dish perpendicular to the magnet axis. During the experiments, an opaque cover was placed on the Petri dish, and at the end of the video recording it was removed to obtain the magnet position.

In the case of drop manipulation, the magnet was placed at a distance of about 12 mm from the surface, and was moved manually following the desired trajectory. For the drop fusion experiment, two magnets were used to manually direct to the center of the Petri dish both oil drops; one of the drops was marked with the Sudan II dye.

Measurements of the surface deformation. 30 mL of HoCl_3 solution (100 mM) were placed in a plastic Petri dish (8.6 cm diameter). A He-Ne laser beam (wavelength 543.5 nm, power 0.5 mW, diameter 0.8 mm) impinged on the surface of the solution at an angle of incidence of about 57° . For the calculation of each experimental point Δh in Figure 9.2B, two videos of the position of the reflected beam on a white screen were recorded (for 5 s at 30 fps) and the average position of the reflected spot was obtained. The first video was acquired with the magnet at 150 mm distance from the liquid surface (position 1), the second one with the magnet at 12.7 mm distance (position 2). The local slope of the interface at distance r from the center of the magnet axis was calculated as in reference.^[240] The 2 mm steps between

each point Δh were realized with a linear translation stage (0.01 mm resolution, Edmund Optics).

Measurements of the magnetic field. The magnetic field on a surface at a distance of 12.7 mm from the magnet, with 2 mm steps, was measured with a GM08 Gaussmeter (Hirst Magnetic Instruments Ltd.), equipped with a Standard Transverse Hall Probe.

Measurements of the magnetic susceptibility. The volume magnetic susceptibility of aqueous HoCl_3 solutions as a function of HoCl_3 concentration was measured using a magnetic susceptibility balance Mark1. For each concentration, the average of three independent measurements was obtained.

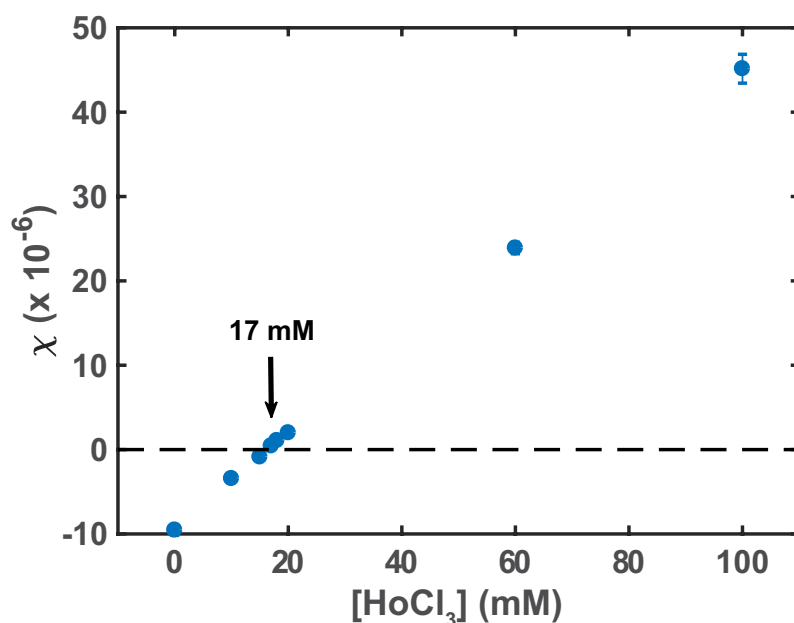


Figure A.8: Volume magnetic susceptibility (χ) of HoCl_3 aqueous solutions as a function of HoCl_3 concentration. Symbols and error bars show mean $\pm$ sd from three independent measurements. The arrow indicates the concentration ($[\text{HoCl}_3] = 17$ mM) used for experiments with $\chi \approx 0$.

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List of publications

originated from this thesis

Original research articles

- (I) “Magnetic actuation of drops and liquid marbles using a deformable paramagnetic liquid substrate”
J. Vialetto, M. Hayakawa, N. Kavokine, M. Takinoue, S. N. Varanakkottu, S. Rudiuk, M. Anyfantakis, M. Morel and D. Baigl*, *Angew. Chem. Int. Ed.* **2017**, 56, 16565–16570. Selected as “**Very Important Paper (VIP)**” and Journal **back cover**.
- (II) “Adsorption and crystallization of particles at the air-water interface induced by minute amounts of surfactant”
M. Anyfantakis†*, J. Vialetto†, A. Best, G. K. Auernhammer, H.-J. Butt, B. P. Binks and D. Baigl*, *under review*.
- (III) “Photoswitchable dissipative 2D colloidal crystals”
J. Vialetto, M. Anyfantakis, S. Rudiuk, M. Morel and Damien Baigl*, *ready for submission*.
- (IV) “Magnetic effect on the surface tension of diamagnetic and paramagnetic liquids”
M. Hayakawa, J. Vialetto, S. Rudiuk, M. Morel and Damien Baigl*, *ready for submission*.
- (V) “Photothermally reconfigurable colloidal crystals at air/water interface”
J. Vialetto, M. Anyfantakis, S. Rudiuk, M. Morel and Damien Baigl*, *under preparation*.
- (VI) “Surfactant-induced assembly of silica and metal nanoparticles at the air/water interface: organization and structural colours”
J. Vialetto, S. Rudiuk, M. Morel and Damien Baigl*, *under preparation*.

In conferences

- (I) 4th International Soft Matter Conference, Grenoble, France, 2016. Poster presentation: “Optical and magnetic actuation of liquid marbles using surface flows and deformation”.
- (II) International Flow17 conference on Fundamentals and Applications of micro- and nanofluidics, Paris, France, 2017. Poster presentation: “Magnetic actuation of discrete liquid entities with a deformable paramagnetic liquid substrate”.
- (III) 91st annual meeting of the American Chemical Society Division of Colloid and Surface Chemistry, New York, US, 2017. Poster presentation: “Magnetic actuation of discrete liquid entities with a deformable paramagnetic liquid substrate”. Winner of the **Soft Matter poster award**.
- (IV) Designer Soft Matter Conference, Singapore, Singapore, 2018. Poster presentation: “Light responsive 2D colloidal crystals”. Winner of the **poster award**.

Grazie!

I will never forget that this work would not have been possible without the people mentioned here.

Damien. You really made me enjoyable working in your lab, helping me and guiding me in the research projects and at the same time giving me carte blanche in several cases. Under your supervision I really learned a lot, I was coming from a somehow different research subject and you made me discover tons of “new” science. After a degree in chemistry I didn’t know I could have liked all those different research subjects as the one you are following, and each time with so much passion.

Many many thanks to all the members of the lab, past and present, for helping me during all my time spent here. I want to thank you for practical help in everyday life, for all things in the lab that were going wrong (or that simply I didn’t know how to do!), for thesis correction, and for making me discover amazing research projects (DNA stuff are really exciting!). So thank you Mathieu, Manos, Sergii, Caroline, Li, Subramanyan, Masa, Koyomi and Vincent. Pur les français, merci beaucoup pour m’avoir enduré malgré ma limité de connaissance de la langue!

A special ευχαριστώ πολύ for Manos, that made me discover the beautiful world of colloidal particles, and initiated me in the work as a PhD student. Basically, most of the work here was possible thanks to your help and all the discussion we had together. But, most important, thank you for making me discover Crete, of course the most beautiful place in the world!

Finalmente!

È finalmente giunto il momento di ringraziare tutti voi che avete condiviso con me bevute, aperitivi, feste, corse, vacanze e quant’altro. La vita a Parigi non sarebbe stata così senza di voi! Grazie “Bizio” Raffaele, Federica, Claudia, Antonio, Lorenzo ed Anna. Danke schön Elke, et merci encore une fois, Vincent.

Sono molto felice di ringraziare Mamma Papà e Nonna, siete la mia famiglia, quindi che dire... grazie per tutto!

Ovviamente non potevi mancare! Mariachiara, dirti solamente grazie mi sembra veramente troppo riduttivo. Mi ricorderò per sempre quanto mi sei stata vicina dal momento in cui sono arrivato qua, e per tutti i tre anni; come hai fatto a farmi stare bene e sopportarmi per tutto il tempo lo sai solo te.