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Multipolar capillary interactions: Self-assembly and Manipulation

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*To those who wonder,
that they know their path is right.*

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Abstract

Capillary interactions drive the aggregation of floating objects at fluid interfaces. This thesis demonstrates that multipolar capillary interactions can be encoded purely through geometry, both within floating elements and across the liquid interface, to enable programmable complexity in mesoscale self-assembly and controlled micromanipulation.

A multipolar discrete-charge framework is developed to model anisotropic interface deformations and their interactions. We first show that the tilt of a pinned contact line induces dipolar deformations that modify short-range attractions and extend pairwise interaction rules beyond linear superposition. Saddle-shaped particles are then designed and modelled as quadrupolar elements, establishing explicit relations between geometry and orientation-dependent interaction potentials.

This geometric encoding is further extended to flexible chains of connected elements. Energy landscape analysis demonstrates that the capillary sequence controls folded configurations and metastable states, providing a mesoscale analogue of molecular folding.

In a complementary approach, complexity is encoded at the interface level. Arrays of 3D-printed spines generate curved liquid landscapes beyond the capillary length, enabling controlled particle guidance. Dipolar Capillary Actuators introduce dynamic landscape reconfiguration, achieving trapping, directed transport, and non-reciprocal motion.

Résumé

Les interactions capillaires gouvernent l'agrégation d'objets flottants aux interfaces fluides. Cette thèse démontre que des interactions capillaires multipolaires peuvent être encodées uniquement par la géométrie, à la fois au sein des éléments flottants et à l'échelle de l'interface liquide, afin de permettre une complexité programmable en auto-assemblage mésoscopique et en micromanipulation contrôlée.

Un formalisme multipolaire basé sur des charges discrètes est développé pour modéliser les déformations anisotropes de l'interface et leurs interactions. Nous montrons d'abord que l'inclinaison d'une ligne de contact pincée induit des déformations dipolaires qui modifient les attractions à courte portée et enrichissent les règles d'interaction par paires au-delà de l'approximation de superposition linéaire. Des particules de forme selle sont ensuite conçues et modélisées comme des éléments quadrupolaires, établissant des relations explicites entre la géométrie et des potentiels d'interaction dépendant de l'orientation.

Cet encodage géométrique est ensuite étendu à des chaînes flexibles d'éléments connectés. L'analyse des paysages d'énergie montre que la séquence capillaire gouverne les configurations repliées et l'organisation des états métastables, ce qui constitue un analogue mésoscopique du repliement moléculaire.

Dans une approche complémentaire, la complexité est encodée à l'échelle de l'interface. Des réseaux de pics imprimés en 3D génèrent des paysages liquides courbés au-delà de la longueur capillaire, permettant le guidage contrôlé de particules. Des actuateurs capillaires dipolaires permettent de modifier dynamiquement le paysage liquide, assurant le piégeage, le transport dirigé et des déplacements non réciproques de particules.

Publications

The contributions related to this manuscript are shown in blue, as they partially cover Chapters 2 to 7. Other contributions are listed but not included in the scope of this thesis.

- [M. Delens](#), Y. Collard, and N. Vandewalle, *Induced capillary dipoles in floating particle assemblies*, Physical Review Fluids **8**, 074001 (2023).
- [M. Delens](#), A. Franckart, D.M. Harris, and N. Vandewalle, *3D-printed spines for programmable liquid topographies and micromanipulation*, Nature Communications **16**, 4348 (2025).
Editors' highlights: Applied physics and mathematics.
- J. Metzmacher, [M. Delens](#), and N. Vandewalle, *Ring of capillary actuators as trap, tweezers and ratchet for floating particles*, Scientific Reports **15**, 20617 (2025).
- [M. Delens](#) and N. Vandewalle, *Encoding Quadrupolar Capillary Information into Saddle-Shaped Objects for Self-Assembly*, Physical Review Fluids **10**, 104003 (2025).
- S. Ziegler, [M. Delens](#), Y. Collard, M. Hubert, N. Vandewalle, and A.-S. Smith, *Metachronal coordination as a mesoscale phenomenon*, Physics of Fluids, **37**, 121917 (2025).
- F. Novkoski, M. Mélard, M. Delens, F. Wéry, M. Noirhomme, J. Pande, A. Maier, A.-S. Smith, and N. Vandewalle, *GRASPion: an Open-Source, Programmable Brainbot for Active Matter Research*, Review of Scientific Instruments, **97**, 014704 (2026).
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*...and then, I have nature and art and poetry,
and if that is not enough, what is enough?*

-Vincent van Gogh

0

Introduction

Figure 0 illustrates a seemingly simple scene: a pond where vegetation pierces the water surface, small debris or organisms float, and a water-walking insect rests on the interface. At first glance, this landscape appears static. Yet it contains all the physical ingredients that motivate this thesis. Each object visible in the scene deforms the liquid interface. The insect locally depresses the surface under its legs. The plant stem creates a persistent meniscus around its base, which increases as multiple stems pierce the interface and their deformations superpose. Floating particles drift along the surface and accumulate near curved regions, while also clustering together to form aggregates. These deformations store surface energy and generate lateral forces without direct contact, governed solely by the curvature of the liquid surface. Aggregation, trapping, alignment, and transport therefore occur spontaneously.

In natural aquatic environments, such processes play a fundamental ecological role. The interception of floating particles by surface-piercing vegetation is essential for seed dispersal and for the retention of organic matter [1]. Floating pollen grains cluster via lateral capillary forces into rafts that experience a stronger attraction toward the stigma than isolated grains, enhancing pollination efficiency [2, 3]. Buoyant mosquito eggs form well-defined orientational aggregates due to meniscus-mediated forces [4]. The aggregation of floating insects or larvae protects individ-

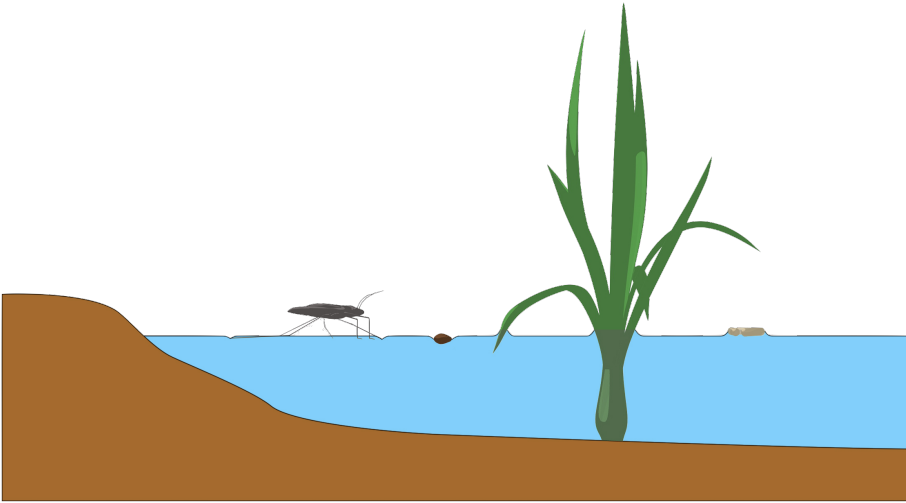


Figure 0: Life on a pond. Vegetation piercing the surface, floating objects and organisms, and a water-walking insect locally deform the liquid interface. Illustration courtesy of Yves-Eric Corbisier de Harbonnier de Cobreville, reproduced with permission.

uals from predators and improves survival rates [5–7]. Water-walking insects actively modify their body posture to increase local surface deformation and climb menisci to reach the shore [8]. Fire ants exploit capillary interactions to assemble into floating rafts during floods, enhancing collective survival through spontaneous self-assembly [9].

The geometry, wettability, and structural design of these plants and organisms are not arbitrary; they result from natural selection and evolutionary optimisation, progressively shaping systems in which capillary forces are harnessed for ecological function.

Capillary self-assembly has been studied extensively since the late 1990s and has been proposed as a versatile route toward functional organisation at fluid interfaces. Because it operates across a broad range of length scales, it enables the formation of static or dynamic structures in two or three dimensions, providing an alternative to conventional fabrication strategies.

Achieving truly functional systems, however, requires precise programmability and increased structural complexity, which are typically introduced through chemical patterning.

The objective of this thesis is:

Encode multipolar capillary interactions purely through geometry, both within floating elements and across the liquid interface, to enable programmable self-assembly and controlled micromanipulation.

To achieve this objective, the thesis develops two complementary strategies, following a progressive structure.

Chapter 1 establishes the physical framework of capillary interactions at fluid interfaces, introducing surface tension, the Young–Laplace equation, the capillary length, and the multipolar description of interface deformations. Chapter 2 develops the discrete-charge and multipolar modelling framework used throughout this thesis to characterise anisotropic interface deformations and their interactions.

Building on this foundation, the first part of the thesis focuses on encoding capillary information directly into the geometry of floating objects in order to achieve controlled **self-assembly**. Chapter 3 demonstrates that when heavy floating spheres approach each other, the tilt of a pinned contact line induces dipolar capillary deformations that generate an additional short-range attraction. Using magnetocapillary experiments combined with modelling, we quantify this induced dipolar interaction and analyse its role in asymmetric particle pairs and in the breakdown of the linear superposition approximation. Chapter 4 introduces shape-encoded quadrupolar interactions using saddle-shaped floating objects, showing how anisotropic curvature leads to orientation-dependent forces and selective self-assembly. Chapter 5 extends these concepts to flexible chains of connected elements. Through discrete-charge modelling, energy-landscape analysis, and experiments with 3D-printed branched components, we demonstrate how a one-dimensional capillary sequence governs both the final folded geometry and the complexity of folding pathways, establishing capillary self-folding chains as a programmable many-body platform.

The second part of the thesis shifts the focus from encoding interactions within particles to programming the interface itself, enabling controlled **manipulation**. Chapter 6 demonstrates how arrays of 3D-printed spines piercing the interface can be combined to generate programmable liquid landscapes whose size exceeds the capillary length. We show how such

engineered topographies can be exploited to guide and control floating particles. Chapter 7 introduces Dipolar Capillary Actuators as elementary building blocks for dynamically programmable liquid landscapes. By actively controlling dipolar interface deformations, we demonstrate trapping, controlled displacement, and directional transport of floating particles.

And finally, Chapter 8 concludes the thesis with a summary of our results and outlines future perspectives.

*Science and everyday life cannot and should not
be separated.*

-Rosalind Franklin

1

Research Context

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In this chapter, we introduce key physical concepts that explain capillary interactions between floating objects. We define and describe capillary menisci and the resulting interactions between neighbouring objects, a phenomenon commonly known as the Cheerios effect. We present how the shape and wettability of floating particles can create capillary multipoles. These interactions can be utilised to facilitate self-assembly at liquid interfaces. Finally, we review recent advances in capillary self-assembly and present the concept of encoding and controlling capillary interactions for mesoscale manipulation.

1.1 Cohesion: Surface tension

Matter is found in three common states: solid, liquid, and gas. In solids, intermolecular interactions are strong enough to constrain molecules to fixed positions, allowing only small oscillations, described by phonons. In gases, molecules are almost free, with negligible interactions and no fixed volume. Liquids represent an intermediate case: molecules are mobile but remain bound by attractive interactions strong enough to maintain a fixed volume, yet weak enough to allow flow. This condensed yet mobile state is therefore characterised by a deformable interface.

Cohesion, which refers to the mutual attraction between molecules of the same substance, is a fundamental property of the liquid state. This cohesion, together with adhesion, denoting the attraction between molecules of a liquid and those of another material or state, is at the origin of most interfacial phenomena, and in particular of capillarity and wetting. Their interplay explains why liquids exhibit unique behaviours such as the formation of droplets, the climbing of liquid along walls, or the menisci observed around floating objects.

In the following section, I will concentrate on the unique interface between a liquid and another non-miscible liquid or gas, which behaves like an elastic skin, holding the liquid in place. This phenomenon, known as surface tension, is a crucial aspect of the present work.

1.1.1 Macroscopic manifestation

Surface tension is a property of condensed matter interfaces, arising from molecular cohesion, and is not restricted to fluids; related interfacial stresses also exist at solid interfaces. In this thesis, we focus on liquid interfaces, where surface tension tends to minimise the interfacial area. Although its origin lies at the molecular level, its consequences extend across scales: it explains why droplets adopt a spherical shape, why water can be stretched around swimmers' faces, and why some insects can walk on water.

A beautiful example, depicted in Figure 1.1(a), is provided by dew drops suspended to a surface: rather than spreading indefinitely, the liquid volume remains localised because the interface resists extension. The spherical geometry of free droplets is the most efficient way to minimise surface area for a given volume and, therefore, the most energetically favourable configuration.

Another striking example, pictured in Figure 1.1(b), is found in the abil-

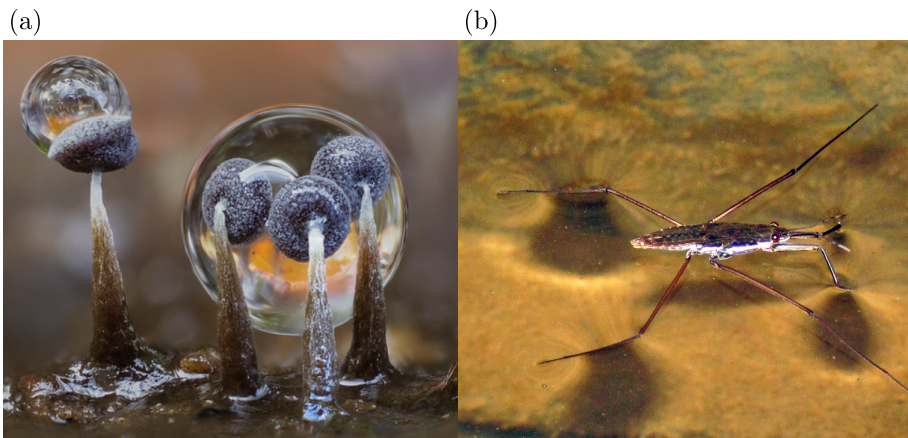


Figure 1.1: Macroscopic manifestation of surface tension. (a) Dew drops sitting on and encapsulating multiple sporangia of the fungus *Physarum album*. The droplets remain nearly spherical owing to surface tension. Photograph courtesy of [Barry Webb](#), reproduced with permission. (b) Water strider *Gerridae* standing on a water surface. The meniscus deformation under each leg creates dark shadows corresponding to the curved liquid interface. Photograph courtesy of [James St. John](#), licensed under CC BY 2.0, via Flickr.

ity of small insects, such as water striders, to stand and move on the water's surface [8, 10]. Their legs, covered in hydrophobic hairs called microsetae, locally deform the interface. Still, as long as the force exerted by surface tension exceeds their weight, the insect remains supported without breaking the surface. This will be formally discussed in the following Section 1.3.

1.1.2 Microscopic origin

The macroscopic manifestations of surface tension originate from the asymmetry of molecular interactions at the interface. As illustrated in Figure 1.2, in the bulk of a liquid, each molecule is surrounded by neighbours and experiences cohesion of comparable magnitude in all directions. At the surface, however, the situation changes fundamentally: molecules lack neighbours on the vapour side. As illustrated in the left side of Figure 1.2, the potential energy landscape of a molecule near the interface thus differs from that in the bulk. Surface molecules occupy a higher-energy environment, even though the instantaneous force on each molecule is zero, $f = -\partial U/\partial r = 0$, at equilibrium. Increasing the interfacial area increases the number of high-energy molecules, thereby raising

the total surface energy. This is the microscopic reason why a liquid tends to minimise its surface area [11].

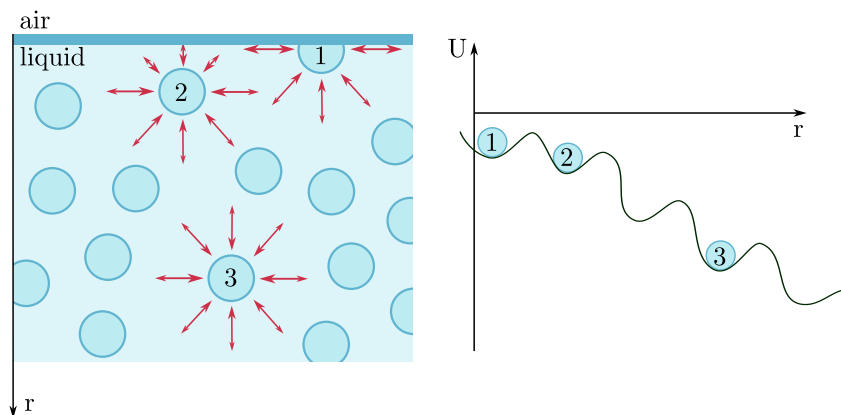


Figure 1.2: Microscopic origin of surface tension. A molecule within a liquid, labelled as 3 in the schematic, is uniformly surrounded by other molecules and experiences cohesive forces equally in all directions, as indicated by the red arrows. In contrast, a molecule located near the interface, such as molecules 1 or 2, lacks a significant fraction of these interactions. The instantaneous potential profile shown on the right illustrates the interaction energy of a liquid molecule with its surroundings as a function of its position. While the interaction energy increases as the molecule approaches the surface, each molecule remains in a local potential minimum, so that the net force acting on it at equilibrium is zero. The local energy barriers indicate that displacing molecules out of equilibrium requires energy. Increasing the number of molecules at the interface, therefore, increases the total surface energy. Figure adapted from [11].

The molecular origin of cohesion depends on the liquid. In most organic liquids, van der Waals forces dominate, leading to moderate surface tensions (typically 20 – 40 mN/m). In water, however, the bent geometry of the H_2O molecule produces a permanent dipole moment: the oxygen atom bears a partial negative charge, while the hydrogen atoms are partially positive. As depicted in Figure 1.3, neighbouring molecules are therefore connected by directional hydrogen bonds. Although individually 10 to 100 times weaker than covalent bonds, hydrogen bonds are numerous and confer on water exceptionally high cohesion. As a result, water possesses one of the largest surface tensions among common liquids, $\gamma \simeq 72 \text{ mN/m}$ at room temperature. Thus, water is the liquid used throughout all the studies presented herein.

This microscopic picture also explains the dependence of surface tension

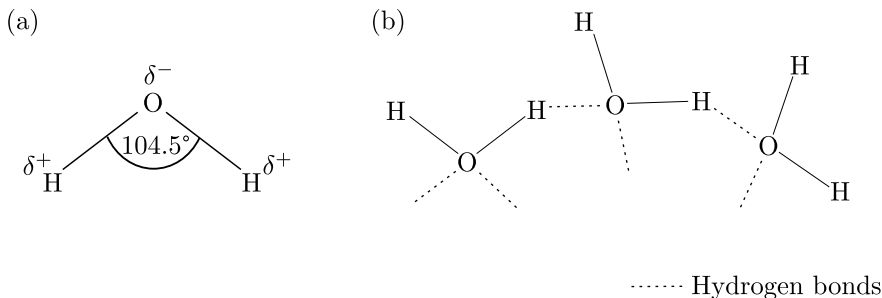


Figure 1.3: The case of water. (a) Polarity of a water molecule. (b) Three H_2O molecules linked through hydrogen bonds.

on temperature. As thermal fluctuations increase, intermolecular bonds are progressively weakened, reducing the cohesive energy and therefore γ . Close to the critical point, where the distinction between liquid and vapour vanishes, surface tension approaches zero.

In summary, surface tension arises because molecules at the interface are in an energetically unfavourable environment compared to those in the bulk. The system responds by minimising its interfacial area. This mechanism, first emphasised in classical capillarity theory and reformulated in modern statistical physics, links the microscopic cohesion of molecules to the striking macroscopic phenomena discussed in the previous section.

1.1.3 Laplace pressure

From elementary fluid mechanics, we know that in a fluid with a flat free surface, the pressures on both sides of the interface are equal, leading to a purely hydrostatic distribution. The situation changes fundamentally if the interface between two fluids is curved, in which case the equality of pressures no longer holds. Indeed, the existence of surface tension implies that a curved surface corresponds to different pressures near the interface in the two media. This pressure jump, known as the Laplace pressure, arises from the thermodynamic equilibrium condition between the two media [11, 12].

Consider the situation of two fluids separated by a surface undergoing an infinitesimal normal displacement δn , as represented in Figure 1.4.

The volume swept between the old and new positions of the surface is $\delta n dA$, where dA is the element of interfacial area. If the pressures in the two media are p_1 and p_2 , and we take δn as positive when the surface moves towards medium 2, then the work associated with the change in

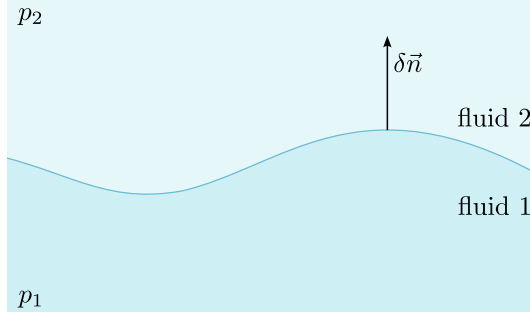


Figure 1.4: Curved interface. A curved interface separating two fluid phases 1 and 2 and characterised by a normal vector $\delta\vec{n}$. Figure adapted from [11].

volume is

$$\delta W_V = -(p_1 - p_2) \delta n dA. \quad (1.1)$$

Additionally, the displacement alters the surface area itself. The change of area is related to the surface mean curvature κ_m through the principal radii of curvature R_1 and R_2 at the considered point of the surface. A displacement δn produces a change in the interface surface

$$\delta S = \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \delta n dA, \quad (1.2)$$

so that the corresponding work due to surface tension is

$$\delta W_\gamma = \gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \delta n dA. \quad (1.3)$$

The total work associated with the displacement of the surface element is therefore

$$\delta W = \left[-(p_1 - p_2) + \gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \right] \delta n dA. \quad (1.4)$$

The condition of thermodynamic equilibrium requires that $\delta W = 0$ for arbitrary δn , hence

$$p_1 - p_2 = \gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) = 2\gamma\kappa_m. \quad (1.5)$$

Equation (1.5) is the Laplace formula [11–13]. The pressure jump is therefore proportional to the mean curvature κ_m of the interface. Convex surfaces (droplets, bubbles) have a positive Δp , while concave menisci

present a negative pressure difference. For a plane surface ($\kappa_m = 0$), the pressures are equal, and we retrieve the usual hydrostatic distribution.

If no external forces act on the fluids, the pressure in each medium is constant. Equation (1.5) then requires that

$$2\kappa_m = \frac{1}{R_1} + \frac{1}{R_2} = \text{constant}. \quad (1.6)$$

Thus, the mean curvature of the surface is uniform. A closed free surface satisfying this condition must thus be spherical, as already concluded from a previous argument.

In particular, if the surface is spherical with radius R , one recovers the familiar result:

$$p_{\text{in}} - p_{\text{out}} = \frac{2\gamma}{R}, \quad (1.7)$$

that can be applied for small droplets and bubbles (with an additional factor 2 because bubbles have two interfaces [13]), and explaining why small bubbles dissolve faster than large ones, why foams coarsen, and why porous materials can sustain large suction pressures.

In summary, Laplace pressure is the bridge between the microscopic cohesion of molecules and the macroscopic curvature of interfaces. It provides the fundamental relation that governs the equilibrium shapes of drops, bubbles, and menisci, and thus lies at the core of capillarity theory.

1.1.4 Young-Laplace equation

In practice, fluid interfaces are rarely completely free from external fields. The omnipresence of gravity makes it impossible to ignore hydrostatic pressure when describing most liquid surfaces. The interplay between capillarity and gravity is therefore central to everyday phenomena, as it explains why water surfaces flatten beyond a few millimetres, and why small insects or floating particles deform the interface only locally.

To account for gravity, let us consider a liquid of density ρ_l in contact with a gas, such as the atmosphere, of constant pressure p_{atm} , as these are the conditions under which all experiments presented in this thesis were conducted. The liquid is incompressible, with a pressure distribution

$$p_l(z) = p_{\text{atm}} - \rho_l g z, \quad (1.8)$$

dictated by the laws of hydrostatics, and where z is the vertical coordinate directed upwards. Together with the Laplace equation of Eq.(1.5),

this yields

$$\rho_l g z = 2\gamma\kappa_m \quad (1.9)$$

Equation (1.9) is the Young-Laplace equation in the presence of gravity. The balance between capillarity and gravity introduces a natural length scale, the capillary length [13] given by

$$\lambda = \sqrt{\frac{\gamma}{\rho_l g}}. \quad (1.10)$$

For water at room temperature subject to the atmosphere, $\lambda \simeq 2.7$ mm. This scale controls deformations of the liquid interface: below λ , surface tension dominates, and curvature effects prevail; above λ , gravity flattens the interface. The Young-Laplace equation (1.9) is nonlinear and thus no exact solution can be found analytically. However, it can be linearised under reasonable assumptions [14].

Let us choose the coordinate plane xy to coincide with this horizontal surface. Let $z = h(x, y)$ be the equation describing the surface of the liquid, also known as the Monge patch. Depending on the surface depression or elevation compared to the horizontal level, due to gravity, h can be positive or negative. In this reference, the mean curvature of the surface is given by [15–17]

$$2\kappa_m = \frac{\left(1 + \left(\frac{\partial h}{\partial y}\right)^2\right) \frac{\partial^2 h}{\partial x^2} - 2 \frac{\partial^2 h}{\partial x \partial y} \frac{\partial h}{\partial x} \frac{\partial h}{\partial y} + \left(1 + \left(\frac{\partial h}{\partial x}\right)^2\right) \frac{\partial^2 h}{\partial y^2}}{\left(1 + \left(\frac{\partial h}{\partial x}\right)^2 + \left(\frac{\partial h}{\partial y}\right)^2\right)^{3/2}}. \quad (1.11)$$

When the interface slope is small, i.e. when,

$$\frac{\partial h}{\partial x} \ll 1, \quad \text{and} \quad \frac{\partial h}{\partial y} \ll 1, \quad (1.12)$$

the mean curvature becomes

$$2\kappa_m = \frac{\partial^2 h}{\partial x^2} + \frac{\partial^2 h}{\partial y^2} = \nabla^2 h. \quad (1.13)$$

Submitting this into the Young-Laplace equation yields its linearised form:

$$\nabla^2 h = \frac{1}{\lambda^2} h, \quad (1.14)$$

which is the Helmholtz equation that can be analytically solved to determine the shape of the liquid interface near a perturbation under the

simultaneous action of surface tension and hydrostatic pressure. It will be the fundamental condition used throughout this thesis to describe menisci and capillary interactions.

1.2 Adhesion: Wetting

Beyond cohesion, liquids also interact with surrounding materials through adhesion. Adhesive forces arise when liquid molecules interact with a solid substrate via van der Waals forces, hydrogen bonds, or electrostatic interactions. The competition between cohesive and adhesive forces determines how a liquid spreads or beads up on a solid surface, as well as the upward rise of water against a vertical glass wall.

The wettability is quantified by the static contact angle θ_c , which measures the inclination of the liquid interface at the triple phase line. At equilibrium, for a perfectly flat and homogeneous solid surface, this angle results from the balance of interfacial tensions according to Young's law [13, 18],

$$\gamma_{sv} - \gamma_{sl} = \gamma \cos \theta_c, \quad (1.15)$$

where γ_{sv} , γ_{sl} , and γ are respectively the solid-vapour, solid-liquid, and liquid-vapour surface tensions. On hydrophilic substrates ($\theta_c < 90^\circ$), adhesion dominates and the liquid tends to spread, while on hydrophobic ones ($\theta_c > 90^\circ$), cohesion dominates and the liquid beads up, forming a droplet with a large contact angle. Similarly, when the liquid meets a vertical solid wall, the same balance of interfacial tensions determines whether the interface rises (concave meniscus) or is depressed (convex meniscus). These situations are illustrated in Figure 1.5.

In practice, the contact line may deviate from Young's ideal law. Surface heterogeneities, roughness, or sharp geometrical features can pin the contact line. Thus, the surface energies for a rough solid surface do not coincide with those for the smooth surface. This changes the Eq. (1.15) and the resulting contact angle, but also leads to contact angle hysteresis [19, 20]. Such pinning allows the meniscus to sustain non-equilibrium shapes, a mechanism widely exploited in the studies presented in this thesis.

Understanding the concepts of wetting and adhesion is essential for analysing how particles or boundaries affect a liquid surface. In the next section, we extend this framework to describe different types of capillary

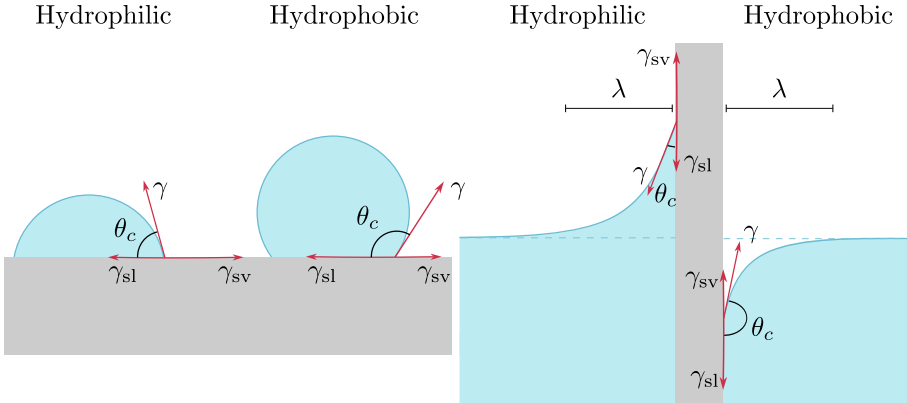


Figure 1.5: Equilibrium contact angle. Illustration of equilibrium contact angles θ_c for hydrophilic and hydrophobic wetting on a horizontal solid surface (left side) and along a vertical wall on the right side (right side). The dashed line on the right side of the figure corresponds to the undisturbed interface. The typical extension of the meniscus is the capillary length λ of Eq. (1.10).

menisci and how their profiles can be calculated from the Young-Laplace equation.

1.3 Menisci

When an object is placed at or pierces a liquid interface, it perturbs the surface and creates a meniscus. This deformation can originate from various physical causes, including the weight of the object compared to its buoyancy, the wettability of its surface, its roughness, or a geometrical constraint such as the pinning of the contact line. These deformations extend into the surrounding liquid over a distance of order the capillary length λ , and can lead to interactions between neighbouring objects. This everyday phenomenon is often referred to as the Cheerios effect, after the tendency of breakfast cereals to aggregate in a bowl of milk [21].

1.3.1 Capillary force and Bond number

Let us first examine the capillary force that enables dense particles, including water striders, to float, and which also contributes to capillary rise in small tubes. Indeed, surface tension pulls the object, freely floating or fixed, along the contact line in directions tangential to the interface

and contained in planes normal to the contact line. The resultant capillary force can be written in the concise form

$$\mathbf{F}_{\text{cap}} = \gamma \oint_{\mathcal{C}} \mathbf{r} \times \mathbf{n} \, dl, \quad (1.16)$$

where $\mathcal{C}$ is the contact line, γ the surface tension, $\mathbf{r}$ the position along $\mathcal{C}$, and $\mathbf{n}$ the local unit normal to the interface [13, 17]. For example, the capillary force acting on an axisymmetric particle that is either freely floating or fixed and piercing the surface, with a circular contact line of radius R_c , can be expressed as a vertical resultant force given by $F_{\text{cap}} = 2\pi R_c \gamma \sin \psi$, where ψ is the inclination of the interface at the contact line.

When surface tension is strong enough, this vertical force allows small objects denser than the liquid to float. The competition between gravity and surface tension is quantified by the dimensionless Bond number,

$$\text{Bo} = \frac{\Delta \rho g R^2}{\gamma}, \quad (1.17)$$

with R a characteristic size of the object, and $\Delta \rho = \rho_s - \rho_l$ the density difference between the object and the liquid [22].

When $\text{Bo} \ll 1$, capillarity dominates and interface slopes are weak ($|\nabla h| \ll 1$). In this regime, the Young–Laplace relation from the previous section linearises. For $\text{Bo} \sim 1$, gravitational and capillary effects are comparable, and the particle’s weight creates a measurable deformation of the interface. In practice, many millimetric systems at the air–water interface operate near $\text{Bo} \sim 1$, where the linear description remains quantitatively accurate for interfacial profiles and for deriving interactions. In the works presented in this thesis, we will focus on such particles. Finally, when $\text{Bo} \gg 1$, gravity dominates, and dense particles sink.

1.3.2 Types of menisci

Let us now discuss the different menisci scenarios that can be distinguished based on the shape and nature of the particles freely floating or fixed at the interface, as schematised in Figure 1.6 [23–25].

1 Smooth floating particles

When a smooth particle, such as a solid, a liquid droplet, or a bubble, floats on the surface, it is deformed through the balance of buoyancy, gravity, and surface tension, with the condition of a fixed contact

angle dictated by the Young equation (1.15). In this scenario, the slope of the meniscus is determined by the vertical force balance at the contact line. When the particle is light, such as a bubble, it is only attached to the surface through capillary forces, causing the interface to bend upwards and create a convex meniscus. Conversely, for heavier particles, which are denser than the liquid, the interface bends downwards, resulting in a concave meniscus. The concavity of the meniscus is crucial for capillary interactions: alike menisci (both convex or both concave) attract, whereas unlike menisci repel, as discussed in depth in Section 1.5. Depending on the shape of the object and its Bond number, the contact line can undulate to satisfy the condition of a fixed contact angle. In this case, the meniscus concavity changes along the contact line, resulting in orientation-dependent capillary interactions.

2 Pinned contact lines on floating particles

Although the balance between gravity and surface tension must still be satisfied, the contact angle may deviate from that imposed by Young’s law. Indeed, as discussed in Section 1.2, surface roughness, chemical patterning, curvature, or sharp geometric features can pin the contact line, thereby creating large contact-angle hysteresis. Controlling the contact line through pinning enables more elaborate anisotropic menisci, which are necessary to ultimately control and program complex capillary interactions.

3 Fixed objects piercing the surface

Finally, some objects are fixed and pierce through the interface, imposing either a fixed contact angle that prescribes the interfacial deformation or pinned boundary conditions that lead to large contact-angle hysteresis, thereby allowing the meniscus to be modulated through the liquid level. These inclusions sculpt well-defined liquid landscapes in which free-floating particles can be trapped, guided, and manipulated.

These three scenarios, all explored in the present thesis, illustrate how different boundary conditions at the triple line govern surface deformations and, thereby, the capillary forces and interactions that emerge between floating or immersed objects.

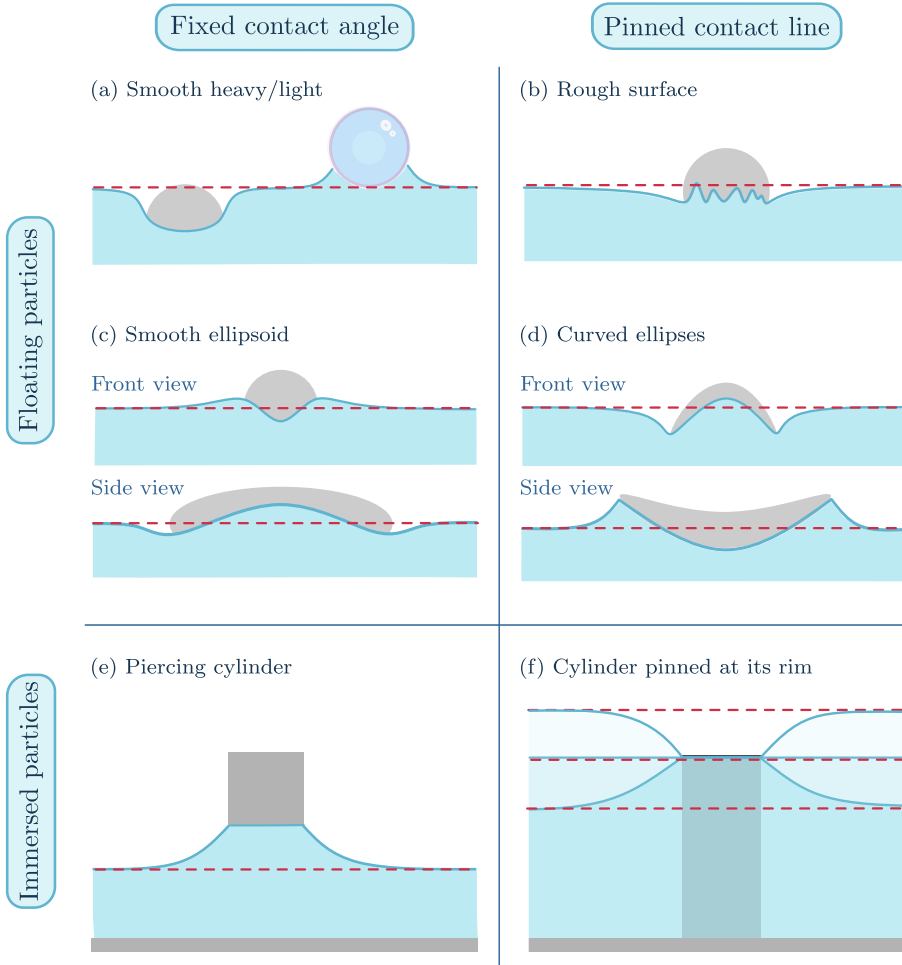


Figure 1.6: Types of menisci. (a,c) Free-floating particles with smooth surfaces and thus fixed contact angles. (b,d) Free-floating particles with pinned contact lines due to rough surfaces or sharp features. (e,f) Immersed solids with fixed contact angles (e) or with pinned contact lines (f), depending on the bath level. In the final case, the bath is rendered transparent to highlight the submerged cylinder as the source of deformation. The bath level is indicated by the red dashed lines.

1.3.3 Liquid profile described as multipolar expansion

In addition to the qualitative descriptions discussed above, the shape of a meniscus can be quantitatively determined from the linearised Young–Laplace equation. For a given contact-line geometry, this equation is

conveniently expressed in polar coordinates (r, θ) centred on the particle:

$$\frac{\partial^2 h}{\partial r^2} + \frac{1}{r} \frac{\partial h}{\partial r} + \frac{1}{r^2} \frac{\partial^2 h}{\partial \theta^2} = \frac{1}{\lambda^2} h. \quad (1.18)$$

Equation (1.18) is a two-dimensional Helmholtz equation describing the equilibrium shape of a liquid interface under gravity and surface tension.

Monopoles

For a spherical or cylindrical particle, the contact line is planar and circular. The deformation is axisymmetric and depends only on r , with no variation along θ . Equation (1.18) then reduces to the modified Bessel differential equation of order 0 [14, 26],

$$\frac{d^2 h}{dr^2} + \frac{1}{r} \frac{dh}{dr} = \frac{1}{\lambda^2} h, \quad (1.19)$$

whose decaying solution is

$$h(r) = Q_0 K_0 \left(\frac{r}{\lambda} \right), \quad (1.20)$$

where K_0 is the modified Bessel function of the second kind of order 0, and Q_0 is an integration constant called the capillary charge. The sign of Q_0 indicates whether the meniscus is concave ($Q_0 < 0$) or convex ($Q_0 > 0$). The capillary charge has length units and indicates the characteristic depth or elevation of the meniscus. This fundamental case defines a monopolar meniscus, directly linked to the particle's Bond number of Eq. (1.17).

Let us determine the amplitude Q_0 of the meniscus formed by a heavy sphere of radius R floating at the air-water interface, as illustrated in Figure 1.7. We will use the principles of vertical equilibrium, similar to the approach taken by Vella and Mahadevan [21]. The vertical position of the sphere is set by the balance between its weight W , buoyancy B , and the vertical component of the capillary force of Eq. (1.16) acting along the contact line. This balance reads [21, 24]:

$$W - B = 2\pi R_c \gamma \sin \psi, \quad (1.21)$$

where R_c is the radius of the contact line and ψ is the angle between the interface and the horizontal at that point. The equilibrium position of

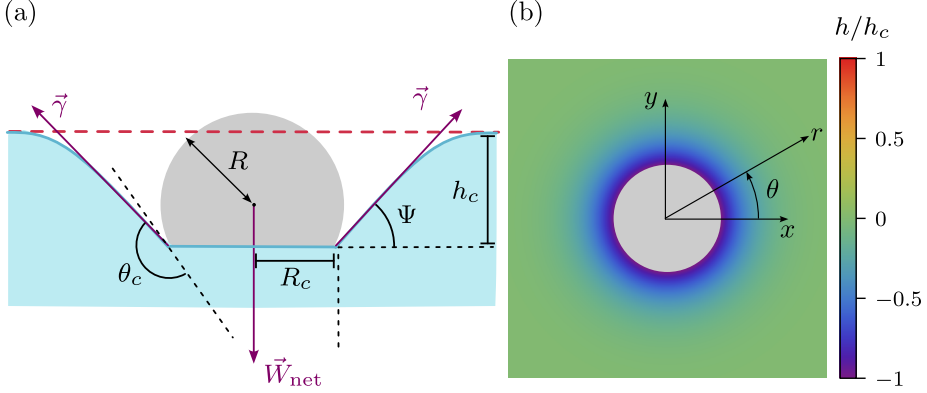


Figure 1.7: Meniscus around a spherical heavy particle. (a) Geometry and force balance on a sphere placed at a liquid-air interface. Slope angle Ψ and contact angle θ_c are defined, as well as the contact line radius. The dashed red line represented the undisturbed liquid level. Figure adapted from [27]. (b) Typical density-plot diagram for the monopolar meniscus in polar coordinates (r, θ) , calculated from Eq. (1.20).

the sphere is therefore determined by the interface slope ψ at the contact line.

Noting h_c the interface height at the contact line and h'_c its derivative, we have $\sin \psi \simeq \tan \psi \simeq h'_c$ in the small-slope regime. Using the solution of the linearised Young–Laplace equation, $h(r) = Q_0 K_0(r/\lambda)$, we find that the amplitude of deformation is related to the slope at the contact line by

$$h'_c = -\frac{Q_0}{\lambda} K_1(R_c/\lambda) \simeq -\frac{Q_0}{R_c}, \quad (1.22)$$

where the final approximation holds for $R_c \ll \lambda$. Hence, the capillary charge can be expressed as

$$Q_0 = -R_c h'_c, \quad (1.23)$$

linking the meniscus amplitude directly to the local slope at the contact line. Submitting this last result in the force balance of Eq. (1.21), we can approximately express the capillary charge as

$$Q_0 = -\frac{W_{\text{net}}}{2\pi\gamma}. \quad (1.24)$$

A negative Q_0 corresponds to a downward (concave) meniscus, typical of heavy spheres, whereas a positive Q_0 describes an upward (convex)

meniscus, as around light particles or bubbles.

As calculated by Martínez-López *et al.* [28] and by Vella and Mahadevan [21], for a heavy spherical bead of density $\rho_s > \rho_l$, Q_0 is proportional to the particle volume V and is given by

$$Q_0 = \frac{R^3}{\lambda^2} \left(\frac{2\rho_s/\rho_l - 1}{3} - \frac{\cos(\theta_c)}{2} + \frac{\cos(\theta_c)^3}{6} \right), \quad (1.25)$$

with θ_c , the contact angle as defined from Eq. (1.15).

Multipoles

The monopolar solution, Eq. (1.20), represents the simplest case of an axisymmetric deformation. However, as illustrated in Figure 1.6, most contact lines deviate from perfect circularity due to particle anisotropy, roughness, or partial pinning. A typical multipolar meniscus, here a quadrupolar one, is illustrated in Figure 1.8. In such cases, the deforma-

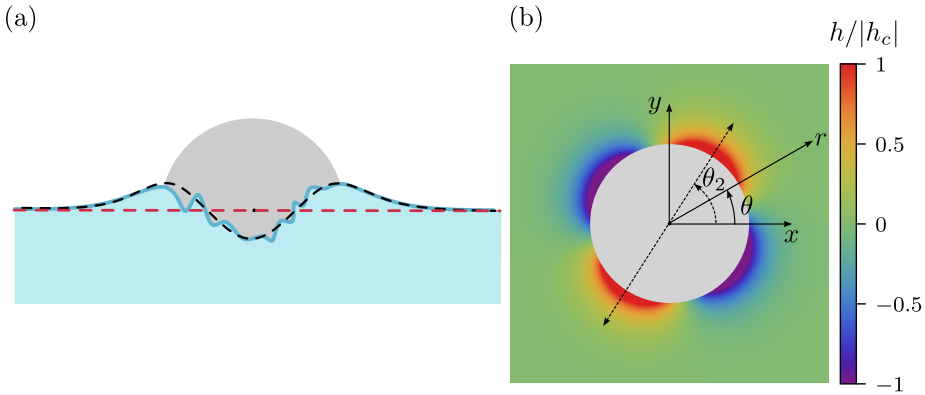


Figure 1.8: Meniscus around an anisotropic particle. (a) Typical meniscus distortion when the contact line is pinned to surface heterogeneities along the contact line. The real contact line is depicted in blue while the black dashed line is its approximation by a quadrupole moment described by Eq. (1.32) where $m = 2$. (b) Typical density-plot diagram for the quadrupolar meniscus based on the same equation with definition of the quadrupolar orientation θ_2 in the polar coordinates of the system.

tion acquires angular dependence. Because Eq. (1.18) is linear, its general solution can be expressed as a superposition of independent modes each satisfying the same differential equation with different angular symmetries [27, 29].

We therefore seek separable solutions of the form

$$h(r, \theta) = R(r) \Theta(\theta). \quad (1.26)$$

Substituting this form into Eq. (1.18) and dividing by $R\Theta$ yields

$$\frac{r^2}{R} \left(\frac{d^2 R}{dr^2} + \frac{1}{r} \frac{dR}{dr} - \frac{R}{\lambda^2} \right) + \frac{1}{\Theta} \frac{d^2 \Theta}{d\theta^2} = 0. \quad (1.27)$$

Since the first term depends only on r and the second only on θ , each term must equal a constant with opposite sign. We introduce a separation constant m^2 , with $m \in \mathbb{Z}$, thus leading to two independent ordinary differential equations [27]:

$$\frac{d^2 \Theta}{d\theta^2} + m^2 \Theta = 0, \quad (1.28)$$

$$r^2 \frac{d^2 R}{dr^2} + r \frac{dR}{dr} - \left(\frac{r^2}{\lambda^2} + m^2 \right) R = 0. \quad (1.29)$$

The first equation gives the angular dependence

$$\Theta(\theta) = A_m \cos(m\theta) + B_m \sin(m\theta), \quad (1.30)$$

while the second, Eq. (1.29), is the modified Bessel equation of order m , similarly to the circular and planar contact line case. Its finite, decaying solution for $r \rightarrow \infty$ is the modified Bessel function of the second kind, $K_m(r/\lambda)$. The complementary solution $I_m(r/\lambda)$ diverges at infinity and is therefore excluded to satisfy $h(r \rightarrow \infty) = 0$.

The general expression for the meniscus shape then reads

$$h(r, \theta) = \sum_{m=0}^{\infty} [C_m \cos(m\theta) + S_m \sin(m\theta)] K_m(r/\lambda), \quad (1.31)$$

which can be conveniently written as

$$h(r, \theta) = \sum_{m=0}^{\infty} Q_m K_m \left(\frac{r}{\lambda} \right) \cos[m(\theta - \theta_m)]. \quad (1.32)$$

Here $Q_m = \sqrt{C_m^2 + S_m^2}$ is the amplitude, or capillary charge, associated with the mode of order m , and θ_m its orientation. The term “capillary charge” for these integration constants arises from a formal analogy with two-dimensional electrostatics [24, 27, 29, 30]. In the far-field regime, where the interparticle distance is much larger than the capillary length ($r \gg \lambda$), the modified Bessel functions behave as $K_m(r/\lambda) \propto (r/\lambda)^{-m}$, and the surface deformation $h(r, \theta)$ plays the role of a potential, while the coefficients Q_m correspond to the amplitudes of the associated multipole

moments. The first few terms of this capillary multipole expansion thus directly mirror the hierarchy of electrostatic multipoles: the monopole ($m = 0$) describes an isotropic depression or elevation of the interface, the dipole ($m = 1$) a tilted meniscus, the quadrupole ($m = 2$) a saddle-like deformation, and higher orders ($m \geq 3$) increasingly complex anisotropic shapes. The multipole expansion provides the natural extension of the single K_0 solution, the zeroth-order term given in Eq. (1.20), to arbitrary contact-line geometries.

It is important to note that a dipole moment $m = 1$ only exists in the presence of an external field [27, 29–31]. Indeed, the capillary force, in opposite directions on the left and right sides of the particle, spontaneously rotates a freely floating particle to annihilate its capillary dipole moment unless it is balanced by external forces, such as gravity when it is significant [32], or by a magnetic field, for example [33, 34].

The amplitude Q_0 is determined by balancing the vertical forces. In contrast, the amplitudes Q_m of the higher-order modes can be theoretically obtained by applying boundary conditions at specific locations (r, θ) along the actual contact line. Experimental determination of the liquid interface height field can be achieved by fitting the reconstructed profile, obtained through techniques such as Schlieren methods profilometry [35, 36], with Eq. (1.32). This procedure yields the coefficients $\{Q_m, \theta_m\}$, which quantitatively represent the deformation of the interface.

1.4 Linear Superposition Approximation

When several particles are present at the interface, the governing Young–Laplace equations become coupled through the nonlinear curvature of the menisci. However, when the interface slopes are small, and the particles are separated by distances larger than their size, the overlap between neighbouring menisci remains weak, allowing the system to be treated linearly. In this limit, the total interfacial deformation can be approximated as the sum of the individual deformations that each particle would produce in isolation. This simplifying principle is known as the Linear Superposition Approximation (LSA).

The LSA was first used by Nicolson in 1949 [14], who studied the lateral capillary interactions between bubbles at a liquid interface by superposing their isolated meniscus profiles. Later, multiple studies [37–39] demonstrated that the error introduced by the linearisation of the Young–Laplace equation remains small for small particles, i.e. small Bond

numbers, and extended the approach to floating cylinders and spheres. Kralchevsky and co-workers [40, 41] formalised the LSA within the framework of capillary multipoles.

Mathematically, if $h_i(\mathbf{r})$ denotes the deformation generated by particle i , the total interface profile is expressed as

$$h(\mathbf{r}) \simeq \sum_i^N h_i(\mathbf{r}), \quad (1.33)$$

where each h_i satisfies the linearised Young–Laplace equation independently. The LSA thus enables analytical expressions for the total interface shape and for the pairwise interaction energy arising from the overlap of individual meniscus fields, as we will discuss formally in the next section 1.5. The approximation holds as long as the meniscus slopes remain small and neighbouring particles do not perturb the boundary conditions at each contact line.

For objects ranging from millimetric to larger scales at liquid interfaces, the linear superposition approximation provides an excellent and robust description of both the interfacial shape around a single particle, using multiple monopolar charges to describe the meniscus, and the resulting capillary forces, as we will discuss in depth in Chapter 2. This so-called discrete-charge formalism is a cornerstone of this thesis.

1.5 Capillary interactions

When several particles float at a liquid interface, the deformation around each particle is no longer axisymmetric. The total interface shape results from the superposition of the individual menisci, and the overlap of these deformations leads to lateral capillary forces that drive attraction or repulsion between particles. The interaction between particles can be understood from simple energy considerations. From an energetic perspective, a particle trapped at the interface always moves in the direction that minimises its potential energy. For instance, a heavy sphere, denser than the liquid, depresses the surface and tends to move downward. If another heavy sphere is placed nearby, it will slide down the meniscus created by its neighbour, leading to attraction. Suppose instead a light particle or bubble producing an upward meniscus is placed nearby. In that case, the heavy sphere still moves downhill along the interface, thus away from the bubble, resulting in repulsion. This behavior is schematically illustrated in Figure 1.9.

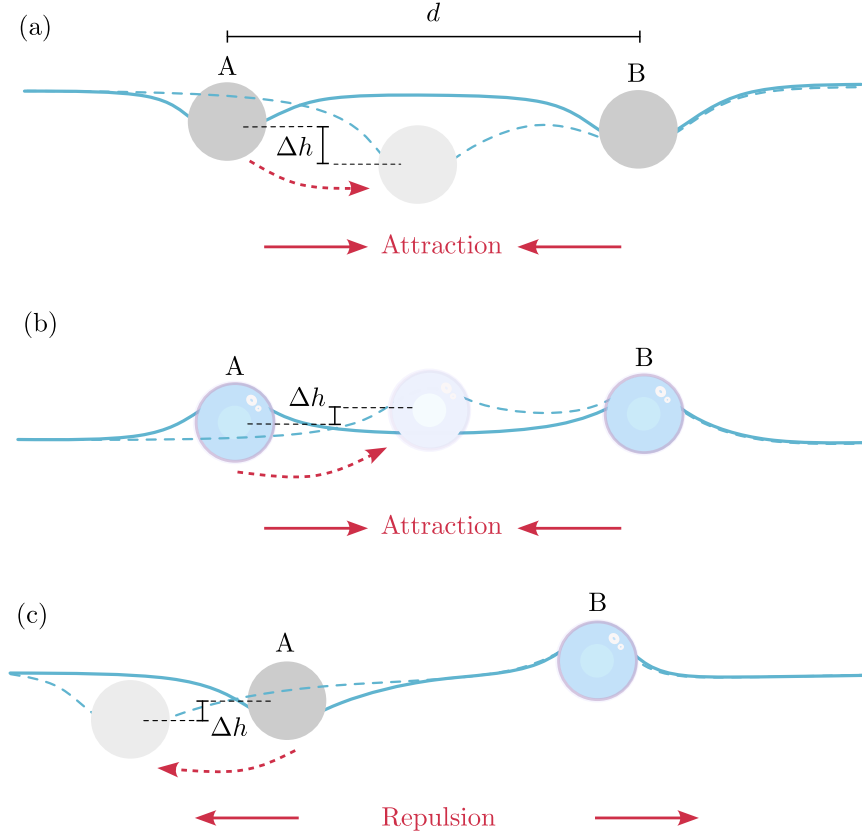


Figure 1.9: Capillary interaction. Schematic representation of the lateral capillary interactions between two floating particles, labelled A and B, and initially separated by a distance d . In all panels, particle A is shown in full opacity at its initial position, while its position after a natural displacement along the interface created by the neighbouring particle B is indicated by a semi-transparent particle. The dashed profiles and Δh respectively represent the interfacial deformation and the height difference experienced by particle A after this displacement. One observes (a) attraction between two heavy particles, (b) attraction between two light particles, and (c) repulsion between a heavy and a light particle.

This qualitative approach provides a simple way to quantify capillary interactions and forms the basis of most analytical treatments that follow, including the monopolar and multipolar cases described in the following sections.

1.5.1 Interaction between capillary monopoles

As proposed in the pioneering work of Nicolson [14] to model the interaction between floating bubbles, the horizontal force between two floating particles can be computed using the linear superposition approximation introduced previously. The assumption that the liquid profile between particles is the sum of the isolated profiles, although seemingly simplistic, is supported by numerical simulations showing that it yields quantitatively accurate results even at moderately short separations. Indeed, since then, this approximation has been used to establish analytical solutions for the interaction between parallel infinite cylinders [38, 42], and to particles floating at liquid interfaces [15, 25, 37, 39, 43, 44].

A more rigorous approach to compute the interaction between two floating particles is provided by the reflection method [45]. In contrast to the linear superposition approximation, which neglects modifications to boundary conditions caused by neighbouring particles, the reflection method iteratively enforces these modifications on all objects, yielding progressively more accurate solutions. It converges rapidly and reproduces the LSA as its leading-order limit, while remaining valid at smaller separations. For completeness, the exact solution of the two-body problem can be obtained by expressing the linearised Young–Laplace equation in bipolar coordinates, which naturally satisfy the circular boundary conditions imposed by each particle [29, 37]. This approach provides a closed-form analytical expression for the interface shape and capillary force at any separation, but its complexity limits its practical use. Since the systems investigated in this thesis involve small slopes and moderate separations, the linear superposition approximation remains accurate and is therefore adopted throughout.

Within the LSA, consider the two spherical floating particles A and B, similar to those in Figure 1.9, separated by a finite distance d . When particle A moves along the interface, it follows the deformation created by particle B, leading to a change in its gravitational potential energy relative to infinite separation. This change provides a direct estimate of the interaction energy between the two particles. It can be written as the product of the net weight of particle A, W_{net} , and the vertical

displacement of its centre of mass compared to infinite separation, which is simply given by $h_B(d)$, the interface deformation created by particle B at distance d :

$$U_{AB} = W_{\text{net}} h_B(d). \quad (1.34)$$

The capillary interaction energy therefore reduces to the product of W_{net} and the local meniscus height generated by the neighbouring particle. By introducing the previous expressions linking the monopolar capillary charge to the net weight (Eq. (1.24)) and the interface profile created by a spherical particle (Eq. (1.20)), the potential of the capillary interaction between two spheres, i.e., two monopoles, takes the form

$$U_{AB} = -2\pi\gamma Q_A Q_B K_0\left(\frac{d}{\lambda}\right). \quad (1.35)$$

The product $Q_A Q_B$ determines the sign of the interaction: identical signs, i.e., similar menisci, correspond to attraction, while opposite signs lead to repulsion. This expression is again formally analogous to the potential energy between two charges in two-dimensional electrostatics, but with the sign of the interaction inverted [30].

Experimental measurements of capillary interactions have been conducted using various methods, which all emphasise the limitations of the LSA. Velez *et al.* [46] conducted one of the earliest direct measurements of lateral capillary forces between vertical capillary tubes using an optical lever force balance. Ho *et al.* [47] directly quantified the lateral capillary force between floating particles by monitoring their relative motion under controlled initial separations. Khattak *et al.* [48] used a micropipette probe to directly measure the lateral capillary force on microscopic droplets by tracking the calibrated deflection of the pipette as the droplet was displaced along the interface.

A method closer to the one developed in this thesis was introduced by Helseth and Fischer [49], who inferred capillary forces between floating magnetic colloids by balancing them against a well-calibrated magnetic repulsion. In our work presented in Chapter 3, we adopt a similar strategy: we determine the capillary interaction by balancing it with a tunable magnetic force, allowing for a direct and quantitative measurement of the capillary attraction between heavy spheres of different sizes [32].

1.5.2 Interaction between capillary multipoles

Polar multipoles

When the contact line is undulated, the interfacial deformation acquires angular structure, and the meniscus is naturally expanded in capillary multipoles, as already introduced in Eq. (1.32). Research on the interactions between such anisotropic particles has been conducted both theoretically and experimentally for nearly three decades. This type of interaction is indeed particularly appealing because it introduces orientational effects in addition to the usual attractive or repulsive forces, providing a powerful mechanism for controlled and directional self-assembly. As we will see, the sign and magnitude of the interaction depend on the mutual orientation defined by the phases $\theta_{A,m}$ and $\theta_{B,n}$ in Eq. (1.32). This class of capillary interactions represents a crucial ingredient for the design of functional mesoscale materials [50].

Consider the situation illustrated in Figure 1.10, where two particles A and B generate multipolar, here quadrupolar, menisci described by Eq. (1.32). Their centres are separated by a distance d and the angles $\theta_{A,m}$ and $\theta_{B,n}$ correspond to the relative orientations of the m - and n -poles of particles A and B , respectively, with respect to the line of centres. Both angles are counted positive from the line to the pole's direction.

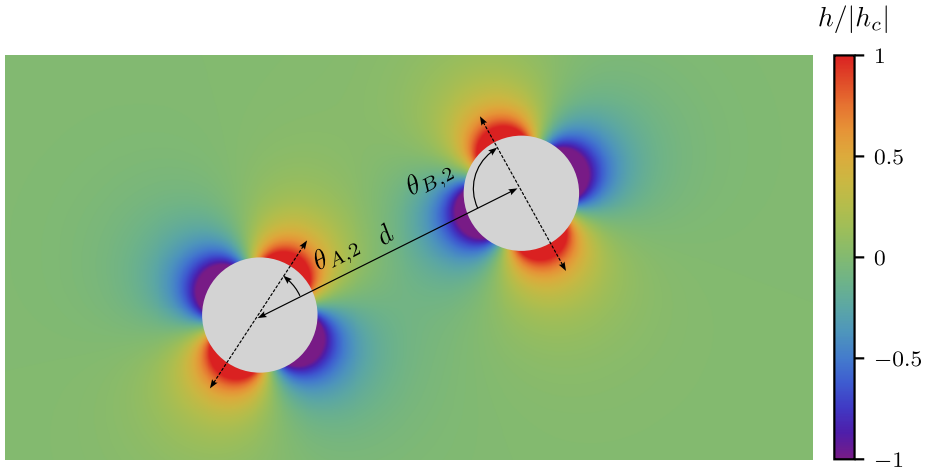


Figure 1.10: Interaction between two multipoles. Two identical multipolar, here quadrupolar, objects at a distance d and theoretical elevation of the liquid profile around them, following Eq. (1.32). Relative angles $\theta_{A,2}$ and $\theta_{B,2}$ are defined.

Compared to the monopole-monopole case of the previous subsection 1.5.1,

multipolar coupling is more complex: it is not set by net weight alone, and the simple gravitational-energy estimate used previously no longer applies. When gravity can be fully neglected, i.e. for small particles ($R_c \ll \lambda$), the classical short-distance asymptotics ($d \ll \lambda$) predict $E \propto d^{-(m+n)}$ for an m - n pair [27, 29], but this result lies at the edge of applicability and often fails for mesoscale particles where gravity cannot be neglected and d can be comparable to λ [51]. A general and accurate framework, valid from short- to long-range, was developed by Danov and Kralchevsky [51]. The key idea of their work is to evaluate the lateral capillary force by integrating the tensor of capillary interaction over the midplane between the particles, where the slope is small even if it is steep near the contact lines. In that midplane, the Young–Laplace equation is linear, so the superposition approximation holds: the midplane height is $h = h_A + h_B$ with h_Y the isolated meniscus of particle Y expressed by Eq. (1.32). One then expresses the force as a line integral of that tensor (constructed from h_A , h_B , and their gradients) and integrates the force with respect to separation to obtain the interaction energy. This procedure reproduces the known charge–charge result of Eq. (1.35) and yields compact formulas for charge–multipole and multipole–multipole couplings in terms of the modified Bessel functions K_m that already appear in the meniscus description of Eq. (1.32):

Monopole–monopole ($m = n = 0$). The integration of the midplane force recovers the expression obtained in the previous subsection, even from different assumptions.

$$E_{00}(d) = -2\pi\gamma Q_{A,0}Q_{B,0}K_0\left(\frac{d}{\lambda}\right). \quad (1.36)$$

Charge–multipole (0 - m , $m \geq 1$). The energy of a monopole interacting with an m -pole is

$$E_{0m}(d) = 2\pi\gamma Q_{A,m}Q_{B,0}K_m\left(\frac{d}{\lambda}\right)\cos\left[m(\theta_{A,m})\right]. \quad (1.37)$$

This expression shows that the introduction of a single multipolar component already induces preferred orientations, selected by the minimisation of the angular term $\cos[m(\theta_{A,m})]$ and the respective signs of $Q_{A,m}$ and $Q_{B,0}$.

Multipole–multipole ($m, n \geq 1$). The general pair energy for capillary multipoles of arbitrary order $m, n \geq 1$ is

$$E_{mn}(d) = -\frac{\pi\gamma}{2} Q_{A,m} Q_{B,n} \left[\mathcal{G}_{m+n+1} \left(\frac{d}{\lambda} \right) \cos(m\theta_{A,m} - n\theta_{B,n}) + \mathcal{G}_{m-n-1} \left(\frac{d}{\lambda} \right) \cos(m\theta_{A,m} + n\theta_{B,n}) \right], \quad (1.38)$$

where $\mathcal{G}_j(x) := \int_x^\infty K_j(\xi) d\xi$. One should note $\mathcal{G}_{-j} = \mathcal{G}_j$ and $\mathcal{G}_1(x) = K_0(x)$, while the recurrence $\mathcal{G}_j(x) = 2K_{j-1}(x) - \mathcal{G}_{j-2}(x)$ eliminates $\mathcal{G}$ in favor of K 's if desired [51]. The overall sign convention follows the monopolar case: like meniscus curvature (both upward or both downward) yields attraction; opposite curvatures repel [30]. In the short-distance small-particle limit, Eq. (1.38) reduces to the power law $E_{mn} \propto d^{-(m+n)}$ found independently by Stamou *et al.* [27] and by Danov *et al.* [29], with the identical orientation factor.

Let us look at the specific cases of dipoles and quadrupoles. Using the definition of $\mathcal{G}_j$ in terms of K -functions, and recalling that $K_4(d/\lambda) \gg K_2(d/\lambda) \gg K_0(d/\lambda)$ for distance $d \lesssim \lambda$, the leading terms of the interactions become:

Dipole–dipole:

$$E_{11}(d) \simeq -\pi\gamma Q_{A,1} Q_{B,1} K_2 \left(\frac{d}{\lambda} \right) \cos(\theta_{A,1} - \theta_{B,1}). \quad (1.39)$$

Quadrupole–quadrupole:

$$E_{22}(d) \simeq -\pi\gamma Q_{A,2} Q_{B,2} K_4 \left(\frac{d}{\lambda} \right) \cos(2\theta_{A,2} - 2\theta_{B,2}). \quad (1.40)$$

The orientation dependence introduces directional binding: dipoles favor $\theta_{A,1} = \theta_{B,1} = 0$, meaning both aligned with the line of centers, while quadrupoles exhibit preferred configurations either end-to-end or side-by-side ($\theta_{A,2}, \theta_{B,2} \in \{0, \pi/2\}$) and rotate in opposite directions under torque, preserving mirror symmetry. This aligns with the predictions of Stamou *et al.* [27].

In summary, Eqs. (1.36)–(1.38) provide the hierarchy of capillary multipoles where the monopole governs the isotropic long-range attraction, while higher-order terms ($m \geq 1$) introduce directionality and torques that drive selective orientation and ordered self-assembly. This formalism has proven powerful in rationalising experimentally observed pairwise binding and collective organisation of anisotropic floaters [27, 30, 31, 51, 52].

Elongated multipoles

Mosquito egg rafts and more generally, ellipsoidal or rod-like particles trapped at fluid interfaces produce anisotropic deformations that are dominated by a quadrupolar mode, but strongly modified by their elongation and contact-angle boundary conditions [52, 53]. For small aspect ratios, the deformation can still be described by a polar quadrupole, leading to the interaction potential of Eq. (1.40). However, as the eccentricity increases, the contact line deviates from a circle, and the deformation becomes better represented by an elliptic quadrupole, which concentrates the curvature near the particle tips [53]. The difference in the liquid landscape between polar and elongated quadrupoles is illustrated in Figure 1.11(a,b).

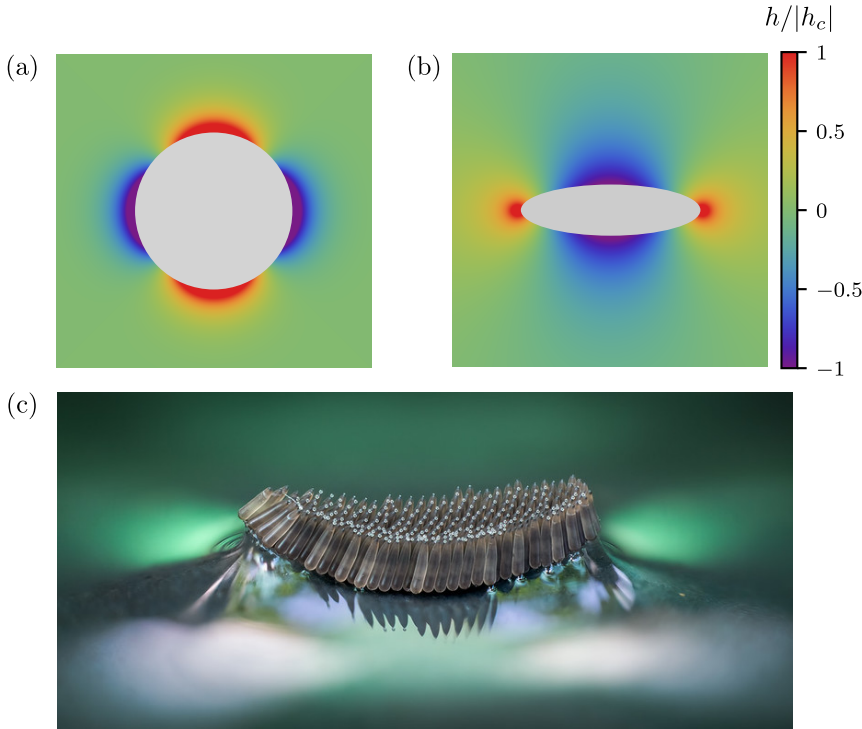


Figure 1.11: Elongated quadrupoles. Typical interface height around polar (a) and elongated (b) quadrupoles. While polar ones produce a symmetric four-lobed deformation, elongated quadrupoles concentrate curvature near their tips, breaking the mirror symmetry of the polar case. (c) Picture of a mosquito egg raft, a natural example of an elongated quadrupole. Photograph courtesy of [Barry Webb](#), reproduced with permission.

This elliptic distortion introduces higher-order harmonics that break the perfect mirror symmetry of Eq. (1.40) and generate a torque aligning the long axes of the particles. As shown by Lehle *et al.* [53] for ellipsoidal colloids with fixed contact angle, the polar quadrupole approximation fails for distances smaller than about four major axes, where coupling between elliptic multipoles becomes important, and the side-by-side configuration becomes slightly more favourable than tip-to-tip. In this intermediate regime, the capillary force no longer follows a pure power law but exhibits an effective decay between d^{-4} and d^{-5} , consistent with experimental results from Loudet and co-workers for ellipsoids with aspect ratios of 3–5 [54].

At larger distances, the deformation recovers the polar quadrupolar form, and the far-field interaction again follows the orientation dependence $\cos[2(\theta_{A,2} - \theta_{B,2})]$ of Eq. (1.40) with equal attraction by the tips or by the sides. This theoretical framework rationalises the directional assembly of elongated particles into tip-to-tip chains, side-by-side doublets, and open square or ring structures, depending on their initial orientation and contact-angle asymmetry. The elliptic-quadrupole picture thus provides a unified bridge between the analytic quadrupolar theory of Danov and Kralchevsky [51] and the experimentally observed assemblies of strongly anisotropic colloids. This extension successfully explains the experimentally observed rotation of ellipsoids and the formation of ordered chains, rings, and capillary “arrows”, which are all hallmarks of anisotropic quadrupolar capillary interactions [52, 55].

Despite its success in describing elongated and microscopic anisotropic particles at fluid interfaces, the elliptic quadrupole framework remains largely phenomenological.

No general analytical theory currently exists to predict the full interaction potential between two elliptic quadrupoles, because the coupling between higher-order modes prevents the superposition principle from holding [52, 53].

As a result, the far-field interaction can still be approximated by an effective quadrupolar potential, but at intermediate distances the interaction force becomes only quasi-conservative and must be evaluated numerically. This framework still needs to be further developed for mesoscopic particles as well as for elliptic contact lines due to pinning.

To address these limitations and effectively model both elongated quadrupoles and more complex anisotropic objects, we will develop a discrete-charge approach in Chapter 2. This method involves geometrically arranging a set of capillary monopoles to replicate the interfacial deforma-

tion of higher-order multipoles. Additionally, this approach can adapt to changes in the contact line arising from the proximity of other objects, via what we refer to as “induced charges,” especially when the superposition approximation is no longer applicable [32].

1.6 Recent advances

The theoretical framework given in the previous sections demonstrates the potential of capillarity as a versatile route to organise, reconfigure, and manipulate matter at fluid interfaces across scales, from micron-sized colloids to millimetric components. In this final section, we review essential advances that have paved the way for the present thesis, with an emphasis on capillary self-assemblies driven solely by interfacial forces, external-field-assisted assemblies where capillary interactions are coupled to magnetic or electric actuation, and finally programmable liquid landscapes, where fixed or actuated boundaries sculpt the liquid topography to achieve deterministic micromanipulation.

1.6.1 Capillary self-assemblies

The notion that interfacial forces can spontaneously organise floating objects dates back to the pioneering work of Nicolson [14], who initially investigated the stability of bubble rafts. When of identical sizes, the bubble raft takes the form of a two-dimensional hexagonal lattice and has thus been used as an analogue model for atomic crystals [56, 57]. As already stated, such aggregation is observed in our everyday life, for instance, with cereals floating in milk, and capillary interaction has therefore been nicknamed the “Cheerios Effect” [21].

Nature provides numerous examples of even more complex capillary self-organisation, as illustrated in Figure 1.12. Fire ants, for instance, interlock their legs and exploit capillary cohesion to build floating rafts that self-heal and reconfigure under perturbations [9]. Such a raft is presented in Figure 1.12(a). Mosquito egg rafts and whirligig beetles present an undulated meniscus that can be represented by an elongated quadrupole and thus align in chains or attract themselves by their tips at the air–water interface to reduce surface energy by matching their meniscus curvature to that of their neighbors [4, 7]. The resulting complex assemblies are shown in Figure 1.12(b-c).

In all these examples, the efficiency of self-assembly arises from anisotropy:

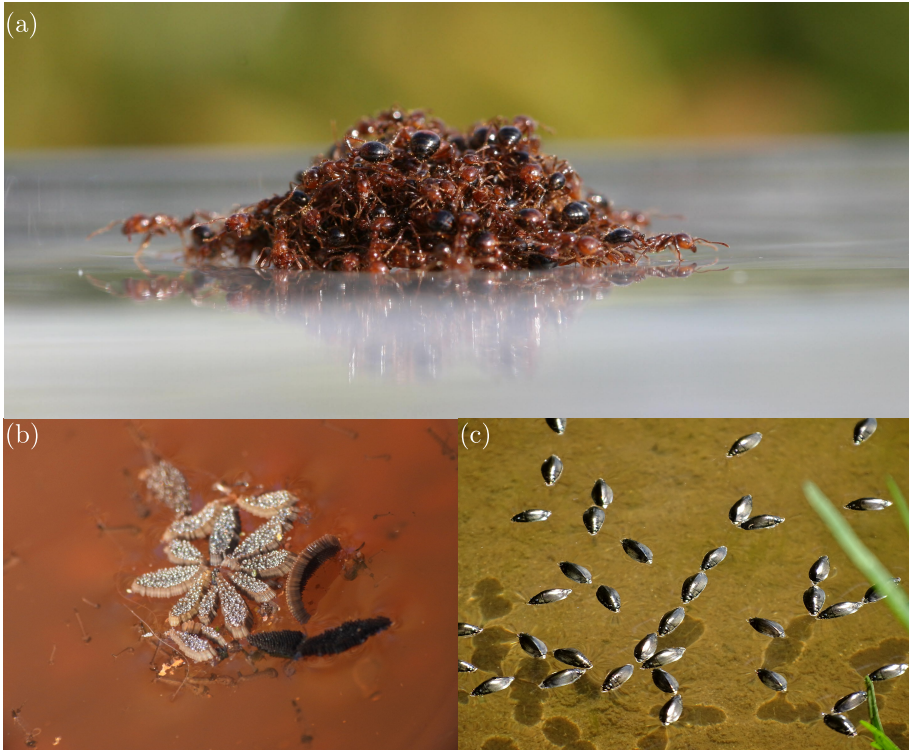


Figure 1.12: Natural examples of capillary self-assemblies. (a) A raft of 500 fire ants. Photograph courtesy reprinted from [9]. (b) Aggregation of multiple mosquito egg rafts. One can observe that the assembly bears some symmetries due to the multipolar shape of the mosquito egg rafts. Photograph courtesy of Mirella Zeeders, reproduced with permission. (c) Whirligig beetles, whose deformation is also described by an elongated quadrupole, assembled head-to-tail to minimise energy following the orientational term of Eq. (1.40). Photograph courtesy of Gary Myers, reproduced with permission.

each organism presents an elongated shape, can bend, or has a heterogeneous surface that creates directional menisci combining attraction and repulsion. Anisotropy thus emerges as a prerequisite for achieving selective, programmable interactions at liquid interfaces.

The first deliberate use of capillarity and anisotropy as design principles for mesoscale self-assembly was proposed by Bowden *et al.* [58, 59]. As illustrated in Figure 1.13, they showed that millimetric polymer or metal plates, with patterned hydrophilic and hydrophobic faces, placed on a liquid interface can spontaneously align, rotate, and bind through meniscus-mediated forces [60]. By tailoring the shape and surface proper-

ties of each component, the authors produced ordered lattices and chains. Rothmund [61] independently framed self-assembly as an algorithmic process in which each building block carries information through its geometry and binding rules. These ideas were then popularised and unified by Whitesides and co-workers [62, 63], who introduced the concept of programmable self-assembly. Their central idea is to encode local interaction rules (geometry, chemistry, roughness) so that a target global structure emerges without serial pick-and-place operations. They propose capillary interactions as a reliable and versatile tool for bottom-up fabrication at mesoscopic scales, bridging the gap between molecular self-assembly and macroscopic manufacturing [64]. Indeed, capillary multipoles tile into lattices with symmetry determined by the dominant order: quadrupoles favour square-like motifs; higher-order patterns can stabilise more complex tilings or open networks [58].

Different strategies have been developed to encode such anisotropy. Chemical patterning or heterogeneous wetting can create local variations in contact angle that bias meniscus shape and directional forces [58–60]. Surface roughness introduces pinning sites that fix the three-phase line and stabilise asymmetric deformations [27]. Geometrical design offers another path: ellipsoids or cylinders with fixed contact angle produce quadrupolar menisci [53–55, 67]. In contrast, objects with pinned contact lines imposed by curvature generate multipolar deformations that can be precisely tuned by their edge geometry [31, 65, 66, 68–70]. An example, shown in Figure 1.13(b) is given by the 3D-printed cross-shaped particles with curved branches, introduced by Poty *et al.* [65] to encode capillary charges and direct multipolar assemblies.

Finally, stimuli-responsive objects introduce a dynamic degree of freedom: shape-memory or thermoresponsive components can reversibly change curvature, switching their capillary signature and reconfiguring the assembly under external cues [66, 69]. As illustrated in Figure 1.13(c), Bae *et al.* [66] demonstrated hydrogel particles whose programmed 3D shape changes with temperature, enabling reversible control over capillary multipoles and their assemblies.

1.6.2 External field–assisted assemblies

Combining additional forces, such as magnetic or electric, with capillary interactions creates assemblies capable of on-demand reconfiguration, locomotion, and robust pattern selection.

Magnetically responsive particles at fluid interfaces provide a robust han-

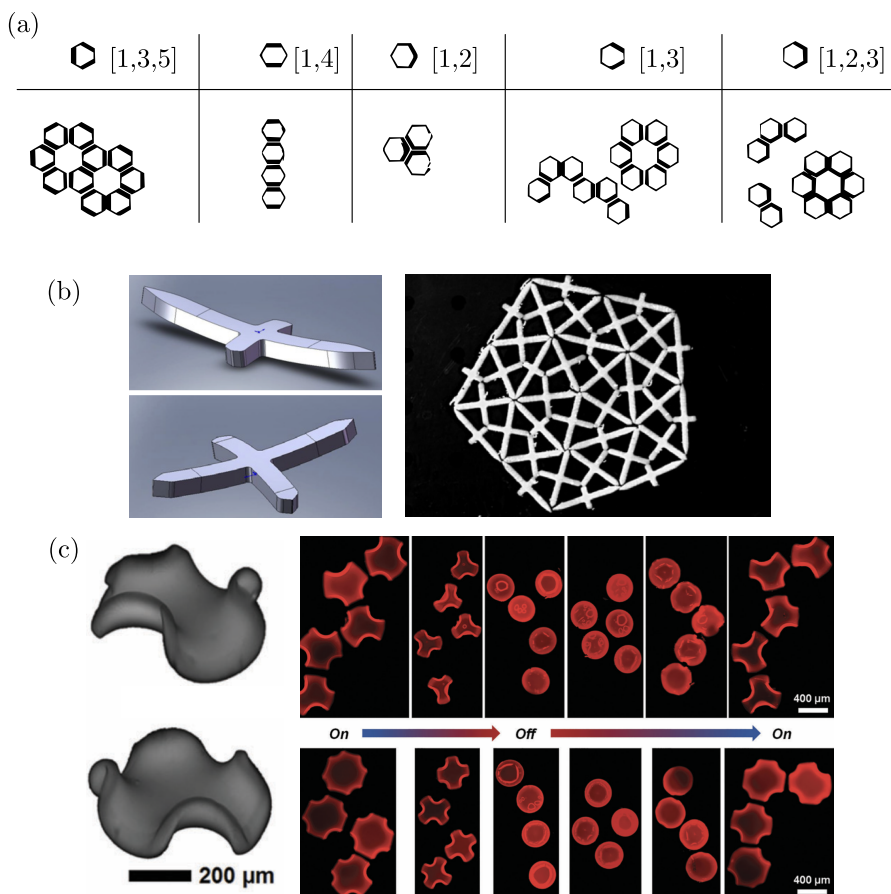


Figure 1.13: Encoded anisotropy to tune capillary assemblies. (a) Capillary assemblies obtained with millimetre-sized hexagonal plates with different configurations of hydrophilic and hydrophobic edges. The thick lines represent the hydrophobic edges and the thin lines the hydrophilic edges. Figure adapted from [60]. (b) Two objects with different branch lengths and opposite curvature form a giant self-assembled pentagon made of 35 objects. Figure reprinted from [65]. (c) Thermo-responsive hydrogel particles with programmed multipolar interactions defined by their prescribed 3D shapes, enabling a switchable assembly when the temperature is varied. Multipolar capillary interactions are turned “off” and “on” by heating to 54°C and cooling to 25°C, respectively. Figure adapted from [66].

dle to tune interactions on demand. As first emphasised by Grzybowski *et al.* [71], dynamic self-assembly arises when competing interactions and external driving combine to produce adaptive, far-from-equilibrium structures. In this context, magnetic fields provide a versatile way to modulate interfacial capillary interactions.

Wen and co-workers showed that paramagnetic colloids confined at an interface form planar magnetic colloidal crystals whose lattice constant and ordering are tunable by the applied field [72].

Complementing this, Golosovsky and co-workers demonstrated the formation of planar dipolar lattices at the air-water interface, induced by an external magnetic field. They showed that the spacing and symmetry of these lattices depend on the field's strength and orientation [73]. In a following study, they quantified the energetics and collective dynamics of these self-assembled magnetic structures, resolving normal modes and lattice rearrangements under field modulation [74].

Another magnetocapillary system, developed within the GRASP lab, uses micrometre soft-ferromagnetic beads placed on the liquid surface. This system is reproduced in Figure 1.14(a). The balance between capillary attraction and magnetic dipolar repulsion produces reconfigurable “bonds,” few-body assemblies, floating crystals, and locomotive units [75–77]. Time-dependent magnetic fields further actuate coordinated deformations and phase-locked rotations that break temporal symmetries, leading to collective propulsion and metachronal coordination [78, 79].

Davies and co-workers [33, 82] demonstrated that a uniform magnetic field can tilt anisotropic ellipsoids at the interface, generating controlled capillary dipoles whose mutual alignment and orientation determine reversible bonding and assembly pathways.

Metzmacher *et al.* [68] introduced the concept of smart floating objects, whose geometry and embedded magnetic elements allow the same component to reversibly switch its configuration under an applied field. These controllable units combine magnetic torques and capillary interactions to assemble or disassemble, providing a model system for field-responsive mesoscale materials. Altogether, these studies illustrate how magnetic actuation enables the transition from passive capillary self-assembly to fully programmable, dynamical organisation at fluid interfaces.

A complementary route is to embed magnetisation in the particles. By patterning the subsurface magnetic field, Hooshanginejad *et al.* [80] controlled the effective pair potential between magnetic floaters from fully attractive to “mermaid” particles exhibiting short-range attraction and long-range repulsion (SALR), and finally to fully repulsive regimes. The

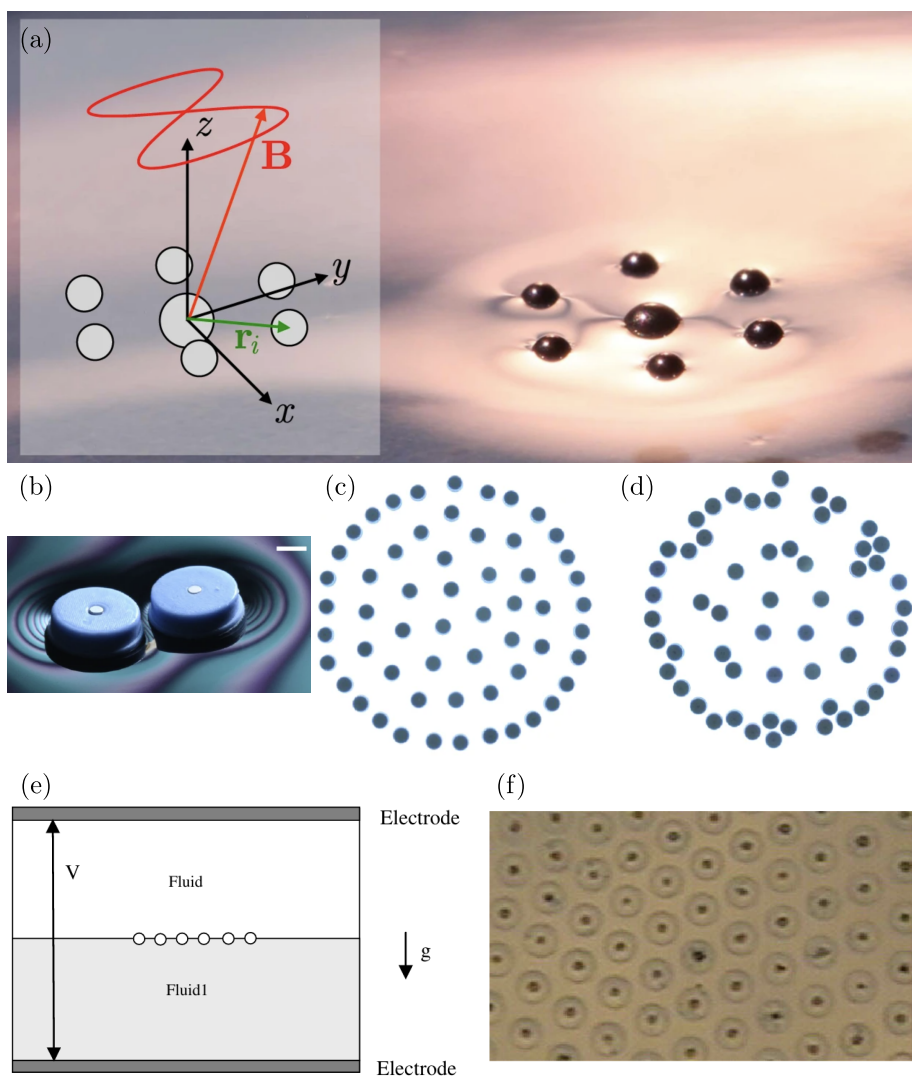


Figure 1.14: External field-assisted assemblies. (a) A 7-bead magnetocapillary assembly, with one large and six intermediate particles, with the direction of the magnetic field when the system is actuated to create metachronal coordination. Figure reprinted from [78]. (b) Two magnetocapillary disks embedded with a permanent magnet. In certain configurations, called mermaid, disks find an equilibrium state defined by a finite spacing. The scale bar indicates 2 mm. Equilibrium situation for packed fully repulsive (c) and mermaid (d) disks. Figures (b-d) reprinted from [80]. (e) Schematic of the electric-field-assisted assembly. The distance between neighbouring particles is controlled by adjusting the applied voltage. (f) Assembly of glass spherical particles obtained by using the device shown in (e) at an air-oil interface and with a voltage of 4000 V. Figures (e,f) reprinted from [81].

“mermaid” behavior is illustrated in Figure 1.14(b-d). This tunability programs the self-assembly of specific patterns: labyrinthine domains, clustered aggregates, or crystalline lattices, depending on the particle packing and magnetic-field parameters.

Electric fields also align and assemble particles at interfaces. Aubry and Singh analysed the underlying physics and showed how uniform fields can generate long-range ordering with very low defect densities [83, 84], as illustrated in Figure 1.14(e,f). Subsequent work demonstrated field-induced alignment and chaining of rods or nanowires at oil–water interfaces [81]. These systems complement magnetic approaches by providing fast, reversible control independent of particle magnetisation.

1.6.3 Programmable surface landscapes

Instead of modifying interactions directly through the properties of the building blocks or adding external fields, one can shape the interface so that passive floaters experience a designed energy landscape. This approach exploits the fact that the interface deformation $h(\mathbf{r})$ acts as a potential energy landscape for objects bearing a capillary charge Q_0 , with an interaction energy $E \simeq -2\pi\gamma Q_0 h(\mathbf{r})$. Controlling the geometry of $h(\mathbf{r})$ therefore provides an indirect yet powerful way to control particle motion and assembly.

Curvature gradients along non-planar interfaces can bias the orientation, migration, and assembly of particles with anisotropic or pinned contact lines [85]. Lewandowski *et al.* [86] first demonstrated that ellipsoids adsorbed on gently curved droplets spontaneously rotate and align along the principal curvature directions of the host interface. Cavallaro *et al.* [87] extended this principle, showing that rod-like particles migrate along curvature gradients toward regions where their meniscus best matches the local curvature, resulting in curvature-driven assembly. This type of manipulation is illustrated in Figure 1.15(a,b) when the overall curvature is created by a cylinder piercing the interface. More recently, Liu *et al.* [88] generalised this idea to nematic and elastic films, where anisotropic surface stresses create effective curvature fields that trap and orient inclusions, further illustrating how shaping the host interface dictates the assembly rules. Peng *et al.* [89] pushed this concept further using a microfabricated slippery oil-infused pillar array with a controlled height gradient shown in Figure 1.15(c). In their system, a continuous variation in pillar height generates a spatially varying meniscus curvature and total height that drives the directional self-transport

of bubbles.

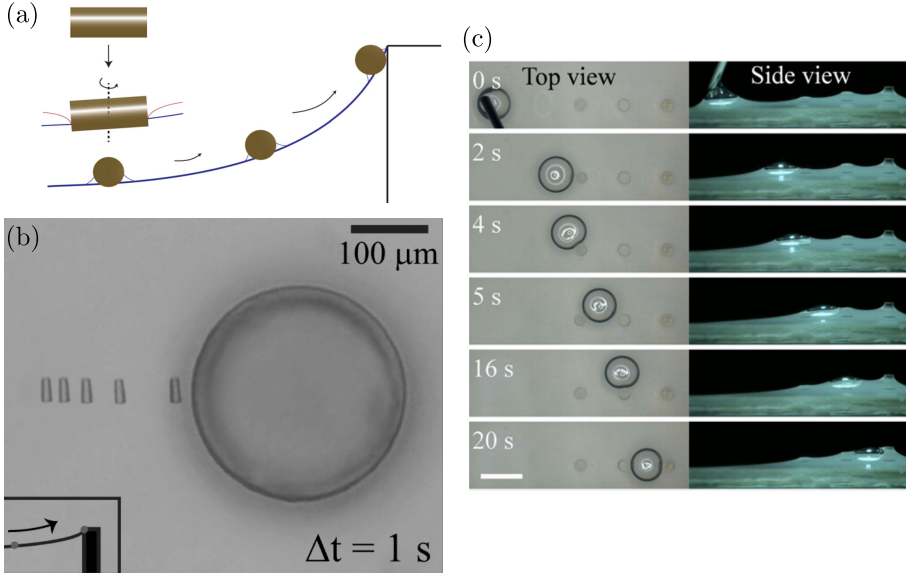


Figure 1.15: Curvature-driven transport and manipulation. (a) Reorientation of a rod-like particle on a curved interface, here created by a cylinder, due to the particle’s quadrupolar moment. (b) Time-lapsed images of a microrod’s position every 1.0 s when approaching the cylinder. Figures (a,b) reprinted from [87]. (c) The self-transport of a 6 μL bubble along a line of micropillars with increasing height, spaced 3 mm apart. The scale bar indicates 3 mm. Figure reprinted from [89].

Beyond naturally curved surfaces, modern microfabrication techniques allow the direct design of interfacial curvature through patterned or responsive substrates. A notable example was reported by Zeng *et al.* [90], who created three-dimensional printed structures that can actively reshape a liquid interface to manipulate microscopic objects without contact. By utilising wetting patterning, these so-called “capillary machines” can trap, transport, and self-assemble microbeads, ultimately braiding micrometre-scale filaments.

Two practical consequences emerge for engineering interfacial devices: superposition of multiple perturbations and breaking spatial/temporal symmetries. As long as slopes remain small, the total $h(\mathbf{r})$ is additive, allowing landscape composition from different building blocks. Encoding directionality may rely either on anisotropic or on time-dependent protocols that break spatial/temporal symmetries to generate transport. These principles will be used in the present thesis to design capillary multipoles and micromanipulation tools.

Capillary self-assembly has thus evolved from bubble rafts into a programmable method for assembling complex patterns and manipulating floating objects. By tuning curvature, wetting, or actuation, one can sculpt energy landscapes with desired symmetries, enabling both static self-organisation and dynamic transport. The next chapters leverage these ingredients to encode information, control interactions, and realise functional self-assemblies and passive micromanipulation at the water–air interface.

Simplicity is the ultimate sophistication.

-Leonardo da Vinci

2

Capillary multipoles as discrete charges

2.1	Discrete charges to modelize menisci	42
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In this chapter, we introduce the discrete-charge model used to represent complex capillary menisci. We show how anisotropic floating objects can be described by a small number of localised monopolar charges and justify this approximation using Graf's addition theorem. We then explain how to compute the resulting liquid surface by superposition and how interactions arise from the pairwise contributions between charges carried by different objects. This framework provides a compact and intuitive description of capillary interactions for complex particle geometries and serves as the theoretical basis for the systems studied in the following chapters.

2.1 Discrete charges to modelize menisci

The multipolar description of the menisci introduced in the previous chapter in Eq. (1.32) provides an exact continuous solution of the linearised Young–Laplace equation for any boundary condition along a polar contact line. As stated earlier, it is much more complex for elongated or arbitrary contact lines. Nevertheless, when several localised meniscus perturbations coexist, or when the contact line of a unique object can be approximated by a set of well-defined regions of positive or negative curvature, the interface deformation can be described in a simpler and physically transparent way using discrete monopolar capillary charges.

A key justification for replacing the continuous multipolar expansion of Eq. (1.32) by a small number of localised monopoles comes from Graf’s addition theorem. This theorem ensures that the multipolar modes of order m that appear in Eq. (1.32) can be generated by combining monopoles placed at different positions along the contact line. In other words, a set of appropriately located displaced monopoles is able to reproduce the same angular modes $\cos(m\theta)$ as the multipolar expansion. More precisely, Graf’s theorem states that the field of a monopole located at $\mathbf{r}_\alpha$ can be rewritten as a full multipolar series around the particle centre. Consequently, by inverting this perspective, the dominant multipolar components of a complex meniscus can be represented by placing a finite number of monopoles at the locations $\mathbf{r}_\alpha$ where the contact line exhibits strong upward or downward curvature. Because the contributions of higher-order multipoles decay rapidly, only a few such localised charges are sufficient to reconstruct the essential features of the interface. This establishes that the discrete-charge model is a mathematically justified reduction of the continuous multipolar description.

2.1.1 Single object

As discussed extensively in the previous chapter, objects with highly anisotropic features (shape, roughness, or heterogeneous wettability) exhibit undulated contact lines composed of regions where the interface either rises or dips. In the multipolar framework, these variations appear as a superposition of capillary multipoles. In the discrete-charge approach, we encode each localised rise or dip of the interface as a point capillary charge $\pm Q_\alpha$ located at $\mathbf{r}_\alpha$ on the interface.

In the small-slope regime, the linear superposition principle holds, and

the total deformation around a single object is written as

$$h(\mathbf{r}) = \sum_{\alpha} Q_{\alpha} K_0 \left(\frac{|\mathbf{r} - \mathbf{r}_{\alpha}|}{\lambda} \right), \quad (2.1)$$

which is the sum of monopolar contributions centred at the charge locations. In the simplest case of a circular floating object, a single monopolar charge at the centre reproduces the axisymmetric profile of Eq. (1.20). For anisotropic objects, however, this central charge only accounts for the net weight, and additional charges are required to encode the local curvature of the contact line. Figure 2.1 illustrates several examples.

Figures 2.1(a,b) show a Janus particle whose asymmetric boundary conditions generate a dipolar deformation. Likewise, the saddle-shaped particle of Figures 2.1(c,d) produces a quadrupolar meniscus with two upward and two downward lobes. A more complex example is provided in Figures 2.1(e,f), where each branch produces a dipolar deformation composed of a rise at the tip and a compensating depression at the base. The global meniscus is thus a superposition of three oriented dipoles, to which a central monopole must be added to account for the object's net weight. These elementary distributions of charges reproduce the dominant $m = 1$, $m = 2$, and higher multipolar terms of Eq. (1.32) while offering a compact and physically interpretable encoding of the contact-line geometry.

Experimentally, the amplitudes and signs of the charges Q_{α} can be extracted from optical profilometry, e.g. Schlieren or FCD methods [35, 36], by fitting the reconstructed height field with Eq. (2.1). The resulting set $\{Q_{\alpha}\}$ quantitatively encodes the local curvature and symmetry of the meniscus.

This framework will be used throughout the following chapters to describe dipolar, quadrupolar, and higher-order capillary systems.

2.1.2 Multiple particles

Extending the superposition principle to N objects, the total interface deformation generated by particles located at $\mathbf{r}_i$, each carrying charges $\{Q_{i,\alpha}\}$, is

$$h(\mathbf{r}) = \sum_{i=1}^N \sum_{\alpha \in i} Q_{i,\alpha} K_0 \left(\frac{|\mathbf{r} - \mathbf{r}_{i,\alpha}|}{\lambda} \right). \quad (2.2)$$

This expression directly applies to the computation of capillary interactions, since the overlap of the field h_i determines the interaction energy between neighbouring objects.

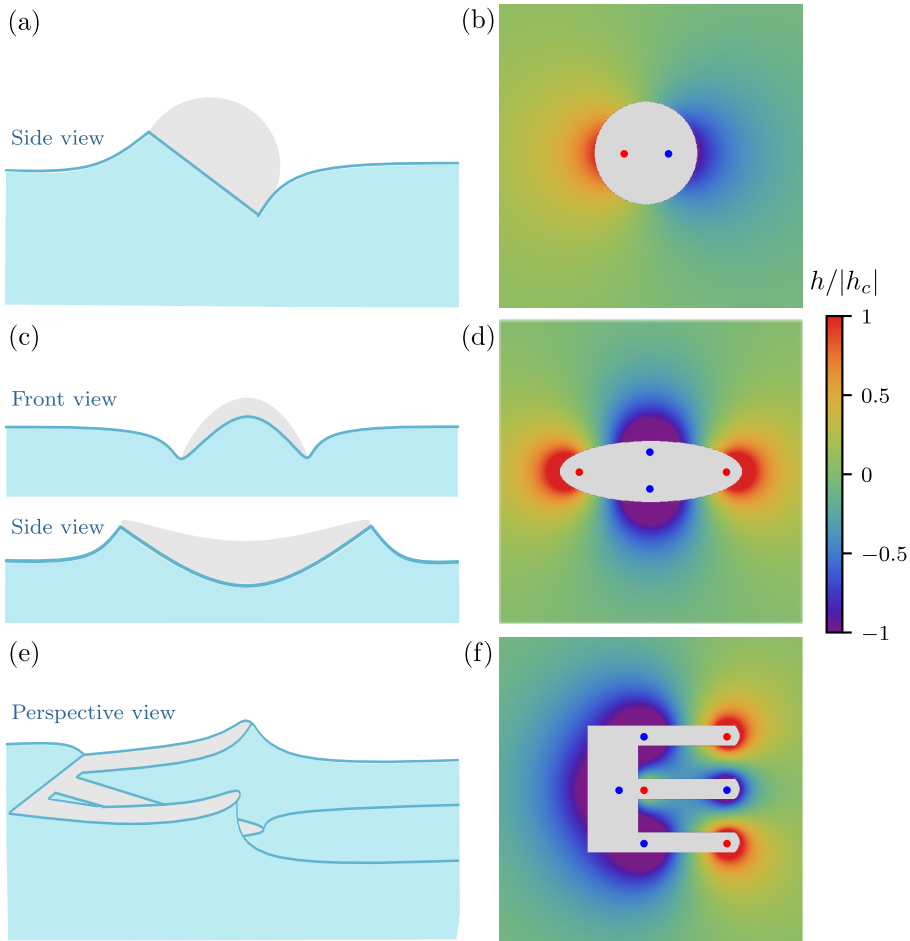


Figure 2.1: Discrete-charge representation of complex menisci. (a) Schematic side view of the interface around a Janus particle. (b) Modelling using two opposite capillary charges, i.e., a dipole. (c) Schematic front and side views of the interface created by a saddle-shaped particle. (d) Modelling using four alternating charges, forming a quadrupole. (e) Highly anisotropic object with three curved arms and an undulated contact line. (f) Discrete-charge representation using three dipoles (one per branch) plus a central monopole accounting for the object's weight. In all cases, the interface shape is reconstructed using Eq. (2.1).

2.2 Capillary interactions

The discrete-charge formulation introduced above provides a compact description of the total interface created by multiple complex floating objects. Building on the theoretical framework developed in Chapter 1, Section 1.5, we can derive the corresponding capillary interactions. The key idea remains the same as for spherical particles: capillary interactions arise from the modification of the gravitational energy of one object by the meniscus created by another. The only difference is that the meniscus is now generated not by a single axisymmetric capillary charge, but by a set of localised monopoles encoding the anisotropy of the contact line. Inserting Eq. (2.2) into the general expression for the gravitational energy given by Eq. (1.34) and extending for N particles yields

$$U = -2\pi\gamma \sum_{i < j}^N \sum_{\alpha \in i} \sum_{\beta \in j} Q_{i,\alpha} Q_{j,\beta} K_0 \left(\frac{|\mathbf{r}_{j,\beta} - \mathbf{r}_{i,\alpha}|}{\lambda} \right). \quad (2.3)$$

This expression provides the complete interaction energy within the discrete-charge model. The competition between all pairs of charges defines the global energy landscape experienced by complex objects. In this framework, all lateral capillary forces and torques experienced by an object follow directly from the derivatives of the total interaction energy,

$$\mathbf{F}_i = -\nabla_{\mathbf{r}_i} U, \quad \tau_i = -\frac{\partial U}{\partial \theta_i}. \quad (2.4)$$

In all applications developed in the next chapters, the interaction energies, forces, and torques are computed directly from Eq. (2.3) by summing over the discrete charges associated with each object. The anisotropy, orientation dependence, and emergent collective behaviour arise solely from the spatial distribution of these charges.

I

Self-assembly

This first part addresses capillary-driven self-assembly by showing how particle geometry, thickness, and contact-line anisotropy determine the interactions between floating components. Monopolar, dipolar, quadrupolar, and higher-order capillary contributions control both translational and orientational degrees of freedom, enabling selective bonding and directional attraction. These interaction rules establish design principles for mesoscale building blocks, resulting in robust and predictable self-assembled structures.

Research means that you don't know, but are willing to find out.

-Charles F. Kettering

3

Dipolar capillary interactions

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In this chapter, we show that as heavy floating spheres approach each other, the pinned contact line tilts, inducing dipolar capillary deformations that generate an additional short-range attraction. Using magnetocapillary assemblies to control and probe particle separations, we combine experiments and modelling to quantify this induced dipolar interaction and clarify its role in asymmetric particle pairs and in the breakdown of the linear superposition approximation.

The results presented in this chapter are partially published as

M. Delens, Y. Collard, and N. Vandewalle, *Induced capillary dipoles in floating particle assemblies*, Physical Review Fluids **8**, 074001 (2023).

3.1 Motivations

In Chapter 1, we showed that the deformation of the interface around a floating spherical particle can be encoded in a single capillary charge, and that the resulting monopolar interaction quantitatively describes the Cheerios effect at large separations. We also stressed that this description relies on the linear superposition of individual menisci. However, when spherical particles come into close proximity or differ significantly in size or immersion depth, these assumptions are no longer valid. Ho *et al.* [47] showed that flat disks tend to tilt near contact, creating an additional attraction compared to the monopolar interactions. Additionally, Poty *et al.* [91] have shown that the simple capillary-charge representation fails to capture the interaction when particles have markedly different sizes or depths. Numerically, Cooray *et al.* [92] studied spheres at fluid interfaces with pinned contact lines and found that the onset of tilting and partial sinking produces a substantial increase in attraction compared to the prediction of the pure monopole model.

To our knowledge, there have been no analytical models or experiments examining the tilt of the contact line between spheres, which motivates the need for a simple physical framework capable of capturing this effect. In this section, we build on these observations: we collect accurate force data for magnetocapillary bead pairs and develop an extended framework in which induced capillary dipoles capture the breakdown of the monopole model.

3.2 Magnetocapillary pair

To probe the limitations of the monopolar description in a controlled way, we use a simple magnetocapillary pair: two soft ferromagnetic beads that reach equilibrium between capillary attraction and magnetic repulsion when subjected to an external vertical magnetic field, as introduced in Chapter 1. Our experimental setup, sketched in Figure 3.1, is the following. Spherical beads of alloy AISI 52100, a soft ferromagnetic alloy, are deposited on a water-air interface where they float thanks to the surface tension. The density ρ_s of the particles is 7800 kg/m^3 . Three diameters are used: $d = 400 \text{ }\mu\text{m}$, $500 \text{ }\mu\text{m}$ and $800 \text{ }\mu\text{m}$. Due to their high density, the beads are more than 90% submerged, so the contact-line radius is approximately $a \approx d/4$. More precisely, we measured the contact line radius to be approximately $80 \text{ }\mu\text{m}$, $180 \text{ }\mu\text{m}$, and $230 \text{ }\mu\text{m}$ for particle di-

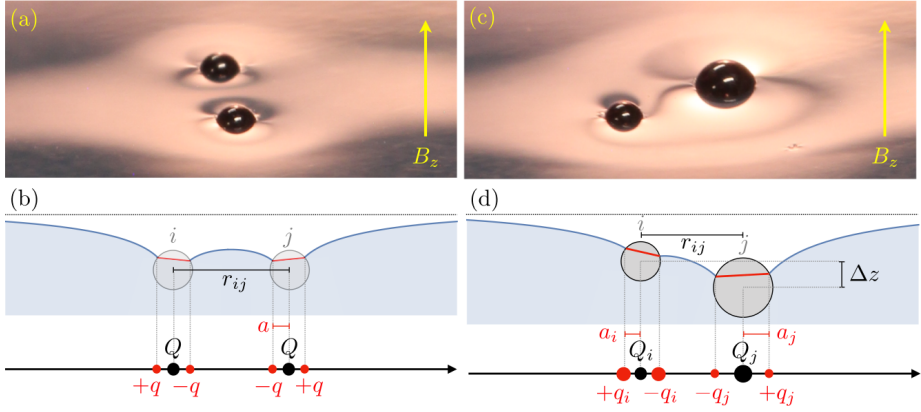


Figure 3.1: Symmetric and asymmetric magnetocapillary pair. (a) Picture of two 400 μm soft ferromagnetic beads floating on the water-air interface under a vertical magnetic field B_z . (b) Sketch of the equilibrium situation for two identical beads. The contact line, denoted in red, is pinned and has a radius a . Each particle is described by a capillary charge Q and dipolar components $\pm q$. (c) Picture of a 400 μm and an 800 μm bead at equilibrium. (d) Equilibrium distance r_{ij} between non-equivalent spheres involves a depth difference Δz but also locally steeper slopes. Each particle i is described by a central charge Q_i and dipolar components $\pm q_i$ at a distance a_i from its centre.

ameters of 400 μm , 500 μm , and 800 μm , respectively. A picture of an 800 μm bead and its contact line is shown in Figure 3.2. The particles have an apparent magnetic susceptibility χ close to 3. The water bath is surrounded by a pair of Helmholtz coils, creating a spatially uniform vertical magnetic field B_z that induces vertical magnetic moments in the particles. In that case, the bead attraction can be counterbalanced by magnetic dipole-dipole repulsion. This repulsion can be precisely tuned by the magnetic field, thanks to the soft ferromagnetic properties of the particles. When the field B_z is larger than a threshold typically of a few tens of Gauss, the magnetocapillary binding leads to an equilibrium distance r^* larger than the bead diameters, avoiding contact [75, 93]. Figure 3.1 shows pictures of equilibrium situations for identical particles (a) and an asymmetric pair (c).

Measuring the equilibrium distance provides an elegant way to evaluate the capillary attraction between floating spheres with high precision.

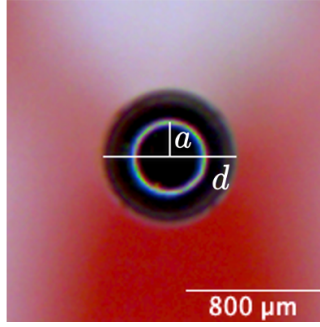


Figure 3.2: Contact line visualization. Top view of an 800 μm bead floating on a water-air interface. A ring light highlights the contact line, enabling accurate measurements. The bead diameter d and contact line radius a are depicted in white.

3.3 Limit of the superposition approximation

Because the objects are spherical and isotropic, their far-field menisci are purely monopolar. In the LSA, the capillary interactions therefore take the simple charge-charge form of Eq. (1.35) introduced in Chapter 1, i.e., the Cheerios effect. For our magnetocapillary beads, the interaction potential between two particles i and j at distance r_{ij} can then be written as

$$U_{\text{Mc}} = -2\pi\gamma Q_i Q_j K_0\left(\frac{r_{ij}}{\lambda}\right) + \frac{\mu_0}{4\pi} \frac{\mu_i \mu_j}{r_{ij}^3}, \quad (3.1)$$

where the first term is the capillary attraction between monopoles only from Eq.(1.35) and the second term is the magnetic repulsion U_M induced by a vertical magnetic field B_z . The magnetic moment μ_i is directly proportional to the field strength B_z and to the volume V_i of particle i , so that both terms in Eq. (3.1) are proportional to the product of particle volumes.

This potential can be rewritten in dimensionless form as

$$u_{\text{Mc}} = -K_0(x_{ij}) + \frac{\text{Mc}}{x_{ij}^3}, \quad (3.2)$$

where $x_{ij} = r_{ij}/\lambda$ and

$$\begin{aligned}
\text{Mc} &= \kappa B_z^2 \\
&= \frac{\chi^2 V_i V_j}{8\pi^2 \mu_0 \gamma Q_i Q_j \lambda^3} B_z^2 \\
&= \frac{2\chi^2 \lambda}{9\gamma \mu_0 \left(\frac{2\rho_s/\rho_w - 1}{3} - \frac{\cos\theta}{2} + \frac{\cos^3\theta}{6} \right)^2} B_z^2
\end{aligned} \tag{3.3}$$

is the magnetocapillary number capturing the competition between capillary and magnetic effects [75, 76, 94–96]. The prefactor κ is independent of particle size, which means that, within the monopole approximation, the dimensionless potential u_{Mc} is also size-independent. For $\theta = 75^\circ$, we find $\kappa = 2.62 \times 10^{-5} \text{ G}^{-2}$. The potential u_{Mc} has a minimum corresponding to the equilibrium distance $r^* = \lambda x^*$. The only control parameter remaining in Eq. (3.2) is therefore the field strength B_z via Mc , which is precisely the feature that makes these systems attractive for self-assembly studies.

We measured the equilibrium distance r^* between two particles for all combinations of diameters $d_i \in \{400, 500, 800\} \mu\text{m}$. In Figure 3.3, the corresponding centre-to-centre distances r^* are plotted as a function of B_z . Horizontal dashed lines indicate the centre-to-centre distance at bead contact. In all cases, the equilibrium distances show a monotonic dependence on B_z . However, the data do not collapse onto the single black master curve as expected from the dimensionless potential u_{Mc} given by Eq. (3.2).

While the approach using monopolar capillary charge has been extensively used in the case of spherical particles, here we face the limit of the superposition principle [14]. This can be understood in the sketch of Figure 3.1(b,d). The contact lines pinned on the particles, which are horizontal when far from each other, start to tilt more and more when particles come closer [22, 47]. This effect is more present for asymmetric cases, i.e., when different particle sizes are used, as sketched in Figure 3.1(d). Please note that the contact lines can only tilt when they are pinned on the spherical particles. Indeed, if the contact angle is fixed, the spheres would rotate to keep a horizontal contact line until they are very close, where the contact line would undulate [27]. Using identical spherical beads with inclined contact lines, Cooray et al. [92] numerically calculated an additional attraction of up to 30% when the beads are brought close together.

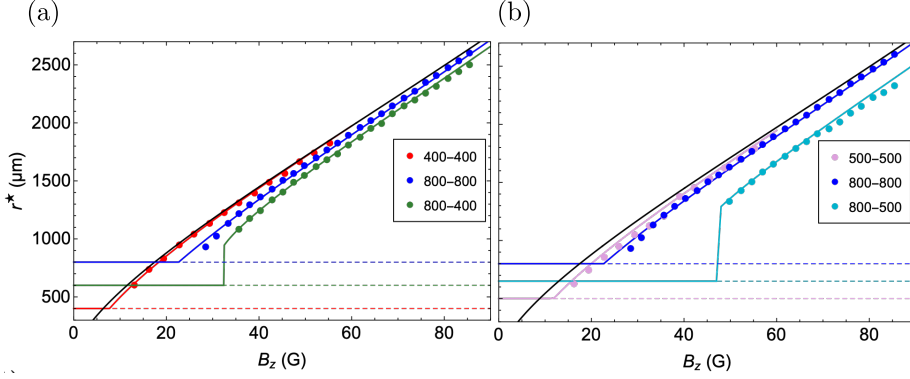


Figure 3.3: Equilibrium situation. Experimental equilibrium distances r^* as a function of B_z for (a) pairs of $d = 400 \mu\text{m}$, $d = 800 \mu\text{m}$, and the asymmetrical case $d_1 = 400 \mu\text{m}$ and $d_2 = 800 \mu\text{m}$, and (b) pairs of $d = 500 \mu\text{m}$, $d = 800 \mu\text{m}$, and the asymmetrical case $d_1 = 500 \mu\text{m}$ and $d_2 = 800 \mu\text{m}$. In most cases, the error bars are smaller than the symbol size. At low field values, near particle contact, the error bars are three times the symbol size. The black upper curve is the equilibrium distance of the monopolar potential u_{Mc} described in Eq. (3.2). Coloured curves are equilibrium distances predicted by the induced dipole model $u_{\text{Mc}+}$ described in Eq. (3.7).

For symmetric pairs, the experimental data show an increase of the capillary attraction, i.e., a slight decrease of r^* , with the size d of the spheres. For asymmetric pairs, the deviation from Eq. (3.2) is even more pronounced. In both cases, the experimental equilibrium distance r^* is always smaller than the one predicted by the monopolar model. Two physical effects contribute to this deviation: (i) an additional capillary attraction due to tilted contact lines, sketched in Figure 3.1(b,d), and (ii) a small reduction of magnetic repulsion in asymmetric systems due to a depth difference Δz between particle centres, also sketched in Figure 3.1(d). The increase in capillary attraction combined with the reduction in magnetic repulsion explains why the observed r^* is systematically lower than the monopole prediction.

3.4 Induced capillary dipole model

When two particles come together, the contact line of diameter $2a$ around each particle becomes tilted. As discussed in Chapter 1, this tilt corresponds to the appearance of a dipolar contribution to the interface deformation. This additional distortion induces extra attraction between particles.

To model this effect within the discrete-charge framework, we propose to add a positive and a negative charge $\pm q$ around each particle, as shown in Figure 3.1(b,d). The total capillary charge Q of each particle remains unchanged, but a capillary dipole of size $2a$ is added. More precisely, the dipolar charges $\pm q_j$ induced on particle j are generated by the slope $\partial z/\partial r$ due to the meniscus shape of particle i , which is given by the Bessel decay in Eq. (1.29). Taking the derivative of Eq. (1.29), this induced charge is given by

$$q_j = \frac{a_j Q_i}{\lambda} K_1 \left(\frac{r_{ij}}{\lambda} \right). \quad (3.4)$$

The additional charges $\pm q_j$ are placed along the line joining the two particle centres, at distances $r_{ij} \pm a_j$ from particle i . A similar capillary dipole is induced on particle i by particle j .

In order to evaluate the total interaction potential between particles i and j in our discrete-charge formalism introduced in Chapter 2, one has to consider the interactions between all capillary charges of particle i , $\{Q_i, +q_i, -q_i\}$, and of particle j , $\{Q_j, +q_j, -q_j\}$ and compute the total interaction using Eq. (2.3).

The capillary charge-dipole interaction U_{Qd} considers the interaction between a charge Q and the induced dipolar charges $\pm q$ of the opposite particle. Each case has attractive and repulsive components:

$$\begin{aligned} U_{Qd} = & - 2\pi\gamma Q_i q_j K_0 \left(\frac{r_{ij} - a_j}{\lambda} \right) \\ & + 2\pi\gamma Q_i q_j K_0 \left(\frac{r_{ij} + a_j}{\lambda} \right) \\ & - 2\pi\gamma Q_j q_i K_0 \left(\frac{r_{ij} - a_i}{\lambda} \right) \\ & + 2\pi\gamma Q_j q_i K_0 \left(\frac{r_{ij} + a_i}{\lambda} \right). \end{aligned} \quad (3.5)$$

Using Eq. (3.4) and expanding the Bessel functions K_0 around r for $a \ll r$, one obtains the leading term

$$U_{Qd} = -4\pi\gamma \left[Q_i^2 \frac{a_j^2}{\lambda^2} + Q_j^2 \frac{a_i^2}{\lambda^2} \right] K_1^2 \left(\frac{r_{ij}}{\lambda} \right), \quad (3.6)$$

which is always attractive.

Using the same process, we find that the interaction between the capillary dipoles, denoted U_{dd} , scales as $(1/r)K_1^3(r/\lambda)$. This term is negligible

compared to U_{QQ} and U_{Qd} when $r \lesssim \lambda$ and can be disregarded, together with higher-order multipoles. Hence, the total capillary interaction potential is well approximated by $U_{QQ} + U_{Qd}$. Dividing by $2\pi\gamma Q_i Q_j$, which represents the characteristic capillary energy scale in the system, one obtains the corresponding dimensionless form.

Finally, the dimensionless magnetocapillary interaction potential of Eq. (3.2) becomes

$$u_{\text{Mc}^+} = - \left[K_0(x_{ij}) + 2 \left(\frac{Q_i^2 a_j^2 + Q_j^2 a_i^2}{\lambda^2 Q_i Q_j} \right) K_1^2(x_{ij}) \right] + \frac{\text{Mc}}{x_{ij}^3} \left[1 - 3 \left(\frac{\Delta z}{\lambda x_{ij}} \right)^2 \right], \quad (3.7)$$

where only leading terms are retained. The capillary attraction, given in the first large brackets, is modified by the K_1^2 term, which becomes comparable to K_0 for $r \sim \lambda$. When the ratio a/λ tends to zero, one recovers the pure monopolar attraction of Eq. (3.2). The factor $(Q_i^2 a_j^2 + Q_j^2 a_i^2)/(\lambda^2 Q_i Q_j)$ in the charge-dipole term is highly non-linear and increases rapidly with the asymmetry of the system.

In asymmetric cases only, the depth difference Δz between particle centres also affects the magnetic repulsion. The last term of Eq. (3.7) shows that the magnetic potential is reduced by a simple factor $[1 - 3(\Delta z/\lambda x_{ij})^2]$. For symmetric pairs, $\Delta z = 0$ and one recovers the dimensionless magnetic potential of Eq. (3.2).

In Figure 3.3, the equilibrium distances predicted by our induced dipole model u_{Mc^+} are plotted for beads with identical diameters (red, violet, and blue curves), showing good agreement with the experimental observations. The difference between these curves is solely due to the induced dipoles, whose strength grows with particle size.

The fits of the asymmetric 800-400 and 800-500 pairs (green and turquoise curves, respectively) are obtained using Δz as the only fitting parameter. Due to geometrical considerations, Δz is constrained between $0 \mu\text{m}$ and $330 \mu\text{m}$, the height between the centre of an $800 \mu\text{m}$ bead and its contact line. We obtain $\Delta z = 270 \mu\text{m}$ for the 800-400 pair and $\Delta z = 300 \mu\text{m}$ for the 800-500 pair. For distances above $1000 \mu\text{m}$ between the beads, the magnetic reduction factor $[1 - 3(\Delta z/\lambda x_{ij})^2] > 0.7$, so that the deviations from the monopole model in Figure 3.3 are mostly due to induced capillary dipoles and the non-linear term in Eq. (3.7). For asymmetric cases, it is worth noting that the fits using Eq. (3.7) correctly capture the threshold below which beads come into contact, thus providing the precise field B_z at which capillary attraction overcomes magnetic repulsion.

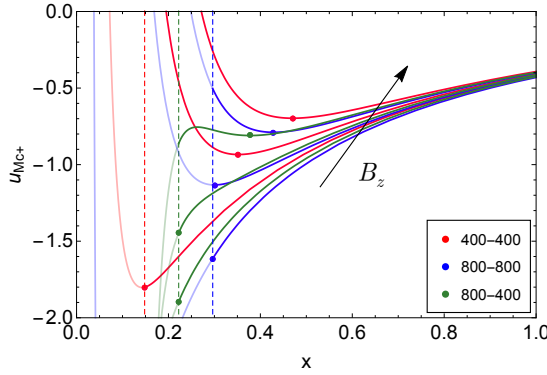


Figure 3.4: Magnetocapillary potential with induced dipoles. Dimensionless magnetocapillary interaction potential u_{Mc+} as a function of normalized interdistance $x = r/\lambda$ for three different B_z values increasing along the black arrow. Dots indicate the minimum of each potential, corresponding to the equilibrium distance reported in Figure 3.3(a). Vertical dashed lines indicate bead contact.

We conclude that all data are well described by the induced capillary dipole model.

3.5 Extra capillary force

Furthermore, as stated in Chapter 1 on the research context, our magnetocapillary pair provides a direct way to estimate the lateral capillary force F_c between particles by measuring the magnetic force that counterbalances it at equilibrium.

Experimental measurements of the dimensionless capillary force for all pairs of particles are presented in Figure 3.5. When the beads are far from each other, the contact lines are horizontal, $U_{Qd} = 0$, such that the capillary force is only given by $F_c = -\partial(U_{QQ})/\partial r$. For the symmetrical pairs 400-400, 500-500, and 800-800, we can therefore define a subset of the data with large values of r^* , where the measurement of the force directly provides access to the capillary charges by their product. We obtain capillary charges of $-5 \mu\text{m}$, $-11 \mu\text{m}$, and $-42 \mu\text{m}$ for the 400 μm , 500 μm , and 800 μm beads, respectively, which align with the expected values from Eq. (1.25) with a contact angle $\theta \approx 75^\circ$. The coloured curves in Figure 3.5 represent the dimensionless capillary forces predicted by our model $F_c = -\partial(U_{QQ} + U_{Qd})/\partial r$, while the black curve does not consider the tilt of the contact line. Once again, we observe a good agreement between the experimental data and our induced capillary dipole model.

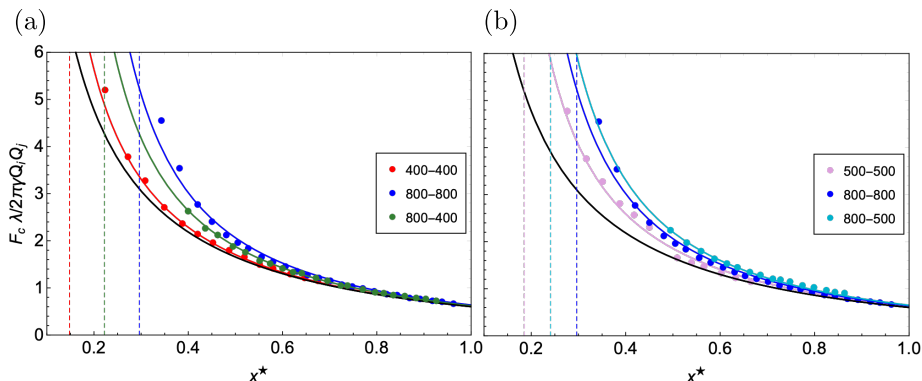


Figure 3.5: Capillary force. Experimental data of the dimensionless capillary force as a function of the normalised interdistance r/λ for (a): pairs of $d = 400 \mu\text{m}$, $d = 800 \mu\text{m}$, and the asymmetrical case $d_1 = 400 \mu\text{m}$ and $d_2 = 800 \mu\text{m}$ and (b): pairs of $d = 500 \mu\text{m}$, $d = 800 \mu\text{m}$, and the asymmetrical case $d_1 = 500 \mu\text{m}$ and $d_2 = 800 \mu\text{m}$. Coloured curves are capillary forces derived from the potential $U_{QQ} + U_{Qd}$. The black curve is the capillary force derived from the potential U_{QQ} from Eq. (1.35) only. Vertical dashed lines indicate contact-bead situations.

At $r^*/\lambda = 0.45$, we observe an extra attraction of 4% for the 400-400 pair, 19% for the 500-500 pair, and 30% for the 800-800 pair. For these identical pairs, such increases are consistent with the numerical observations of Cooray et al. [92]. The asymmetrical 800-400 pair exhibits 16% of extra attraction, which is less than the 800-800 pair. However, when the $400 \mu\text{m}$ bead is replaced with a $500 \mu\text{m}$ bead, forming an 800-500 pair, an additional attraction of 41% is observed. Interestingly, in the case of the asymmetrical pair 800-500, we observe a further increase in attraction compared to the 800-800 pair, despite a smaller product of charges in the U_{QQ} potential. This behaviour can be explained by induced dipoles and the resulting nonlinearity of the model described in Eq. (3.7).

3.6 Implications for self-assembly

The next relevant question is: can we visualise the effects of capillary dipoles on floating particle assemblies? The answer is affirmative. Figure 3.6 shows various pictures of self-assemblies.

The first picture (a) shows an assembly of $N = 9$ equivalent beads (diameter $400 \mu\text{m}$), which is compared to (b) a similar assembly in which a small bead is replaced by a much larger one (diameter $800 \mu\text{m}$). The

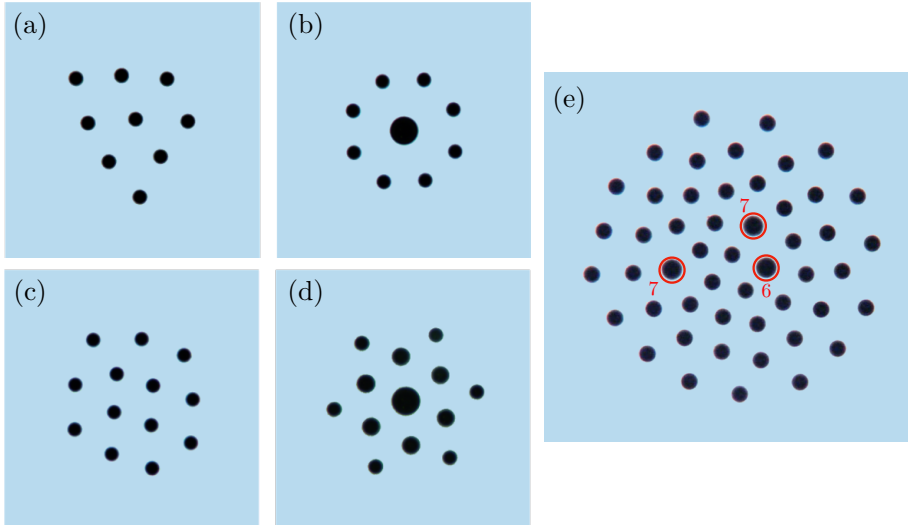


Figure 3.6: Effect of asymmetry on self-assemblies. Various typical pictures of magnetocapillary self-assemblies. (a) Floating crystal of $N = 9$ small beads ($400\ \mu\text{m}$ in diameter). (b) A similar system, having one bead replaced by a large one ($800\ \mu\text{m}$ in diameter): the crystal now has an octagonal symmetry. (c) Floating crystal of $N = 13$ beads. (d) Seven small beads are replaced by one large bead and six medium beads, resulting in a flower-like self-assembly with clear six-fold crystalline order. (e) Large binary self-assembly of $400\ \mu\text{m}$ and $500\ \mu\text{m}$ floating particles. The $500\ \mu\text{m}$ beads (in red) have 6 or 7 neighbours.

monodisperse assembly is a tiny floating crystal with six-fold symmetry as expected from an isotropic interaction. Please note that five-fold defects could be observed in larger assemblies, but these rely on local curvature effects [93]. However, when a large bead is present, one first observes that the surrounding beads are arranged to maximise asymmetrical binding, which has lower potential energy, as shown in Figure 3.4. Here, the large central bead can have up to 8 neighbours.

From what we discussed above, this octagonal symmetry is quite surprising because the asymmetrical binding is shorter than the symmetrical bonds. In fact, the central bead is not polarised because all dipoles are cancelling. However, strongly induced dipoles on peripheral beads are all pointing to the central bead. One understands that in that case, the neighbouring dipoles are forming angles around 45° , a configuration that provides a strong extra attraction in between peripheral beads, allowing for eight beads to surround the heavy central one.

A similar situation is shown in Figure 3.6(c,d) for the $N = 13$ bead system.

For that specific number, identical beads always form a tiny floating assembly with few symmetrical features: a rhombus of 4 beads surrounded by nine beads. However, by changing a small bead to a large one ($800\ \mu\text{m}$) and six small beads to medium ones ($500\ \mu\text{m}$), a flower is formed. Again, large beads tend to be surrounded by a shell of medium ones, themselves surrounded by small ones. This trick can be used to form highly ordered floating crystals at liquid interfaces. In much larger floating crystals of identical particles, the induced dipoles in various directions may cancel. In that case, six-fold symmetry is expected, and some five-fold defects may appear depending on the curvature of the interface [93].

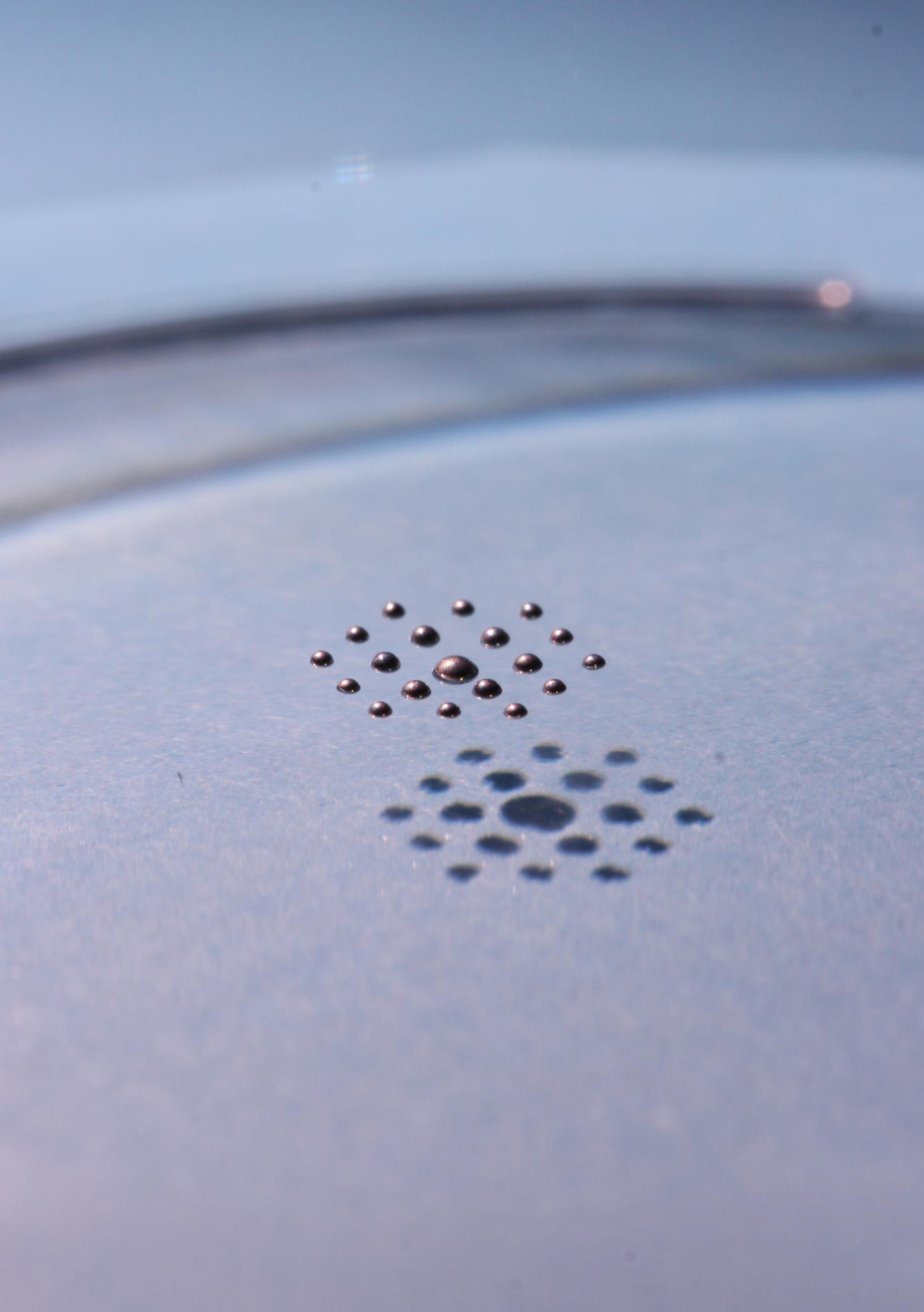
No seven-fold defect has ever been observed for identical particles. When some particles are replaced by larger ones, as shown in Figure 3.6(e), one observes seven-fold defects induced by the larger particles. Binary floating systems may therefore reach a higher degree of complexity. These observations show that induced dipoles not only affect isolated pairs but also reorganise the local neighbourhood within larger aggregates.

3.7 Summary

In summary, we have shown that an extra attraction is observed between close floating objects due to the tilt of their contact lines. Within the capillary-charge framework introduced in Chapter 1, this effect can be captured by the appearance of induced capillary dipoles. The resulting extended potential quantitatively fits our experimental data for both symmetric and asymmetric bead pairs. We found that asymmetrical situations enhance this phenomenon through the non-linear charge-dipole term, and we illustrated how these effects manifest in real self-assemblies. Since capillary-driven self-assembly is encountered in many contexts, from model systems to applications, our findings provide a simple and physically transparent way to enrich the interaction rules at the mesoscale. In the next chapter, we will exploit this idea further by encoding capillary information into elementary building blocks to create self-folding chains and more elaborate programmable structures, including functional assemblies achieving locomotion [78, 79].

Magnetocapillary self-assembly made of 19 beads. The central beads are $800\ \mu\text{m}$ in diameter, and the peripheral ones are $500\ \mu\text{m}$ or $400\ \mu\text{m}$ in diameter.
Credits: Ylona Collard.





It is a capital mistake to theorise before one has data.

-Arthur Conan Doyle,
through Sherlock Holmes

4

Quadrupolar capillary interactions

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In this chapter, we focus on elongated saddle-shaped objects whose interface deformation is well described by the superposition of a central monopolar contribution and a quadrupolar component. By tuning the relative strength of monopolar and quadrupolar contributions through particle geometry, we establish a design rule that dictates whether particles self-assemble preferentially in end-to-end or side-by-side configurations.

The results presented in this chapter are partially published as

M. Delens and N. Vandewalle, *Encoding Quadrupolar Capillary Information into Saddle-Shaped Objects for Self-Assembly*, Physical Review Fluids **10**, 104003 (2025).

4.1 Motivations

In Chapters 1 and 2, we have shown that capillary multipoles provide a convenient framework to describe selective bonding at liquid interfaces and to program self-assembly through the shape and wettability of floating objects. In particular, capillary quadrupoles naturally arise when the contact line is elongated or undulated, and they enable directional interactions beyond the purely attractive or repulsive monopolar Cheerios effect.

In this chapter, we focus on how such capillary information can be encoded directly in the geometry of mesoscale particles. More specifically, we consider elongated saddle-shaped objects whose interface deformation is well captured by the superposition of a central monopole, arising from gravity, and a single quadrupole represented by four discrete charges. Our aim is to determine how the relative strength and polarity of these monopolar and quadrupolar contributions can be tuned so that the particles self-assemble either in an end-to-end configuration or in a side-by-side configuration on an otherwise flat interface.

On the theoretical side, we build on the discrete-charge formalism introduced in Chapter 2 and reuse the asymptotic expansion strategy developed in Chapter 3 for induced capillary dipoles, namely an expansion of the total interaction potential in powers of the reduced separation between charges and as a function of the relative orientation between the objects. By comparing the orientational contribution to the interaction potential, we derive a simple geometrical condition under which side-by-side attraction is favoured at long range. On the experimental side, we design and 3D-print curved ellipses whose saddle-like curvature and thickness can be tuned so as to satisfy or not this design condition through the quadrupole-to-monopole ratio.

To better illustrate the scope of this chapter, Figure 4.1 summarises the two key ingredients of our approach:

- The saddle-like meniscus created by a single elongated object (a);
- The resulting programmability of pairwise and collective assemblies. In particular, the same “versatile” design can yield either end-to-end or side-by-side bonding depending only on the polarity of the quadrupole (b-e).

The 3D files of the saddle-shaped objects, as well as the raw experimental data, are made available via a [Zenodo](#) repository [97]. For ease of access,

a QR code linking to this resource is provided at the end of the chapter.

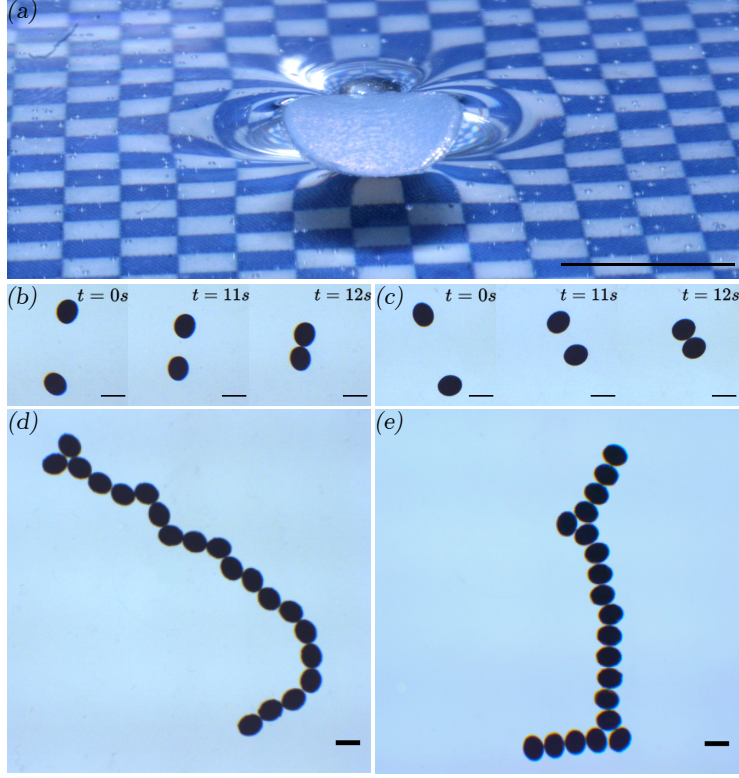


Figure 4.1: Pringles and their self-assemblies. (a) Typical 3D-printed elongated saddle-shaped objects used in this work. When floating on the water, four lobes of deformation appear following the curvature of the object, as revealed by the refraction of a checkerboard pattern placed below. (b) Experimental aggregation in the end-to-end configuration of two elongated Pringles with special parameters that we call versatile Pringles. (c) Side-by-side aggregation with the same objects as picture (b) but flipped. (d) End-to-end chaining of 20 versatile Pringles. (e) Side-by-side chaining of the same 20 versatile Pringles as in the picture (c), but flipped. Scale bars: 5 mm.

4.2 The Pringles effect

Following the discrete-charge formalism introduced in Chapter 2 and applied in Chapter 3 to induced dipolar interactions, we now consider a qualitatively different source of anisotropy. In the present chapter, we extend this approach to elongated objects whose interface deformation is instead dominated by an intrinsic quadrupolar contribution, in addition

to a central negative monopolar capillary charge Q_c due to gravity. The quadrupole is modelled as four equal discrete charges Q with alternating polarity. Based on the general form of the interface elevation given by Eq. (2.1), the liquid profile around a particle i is given by

$$z_i = Q_c K_0 \left(\frac{|\vec{r}|}{\lambda} \right) - Q K_0 \left(\frac{|\vec{r} \pm \vec{\delta}_i|}{\lambda} \right) + Q K_0 \left(\frac{|\vec{r} \pm \vec{\zeta}_i|}{\lambda} \right), \quad (4.1)$$

where $\vec{\delta}_i$ and $\vec{\zeta}_i$ are vectors from the centre of the object to the positions of the positive and negative quadrupolar charges, respectively. Their magnitudes are a or b , corresponding to the semi-major and semi-minor axes of the object, depending on which axis carries the positive or negative charges.

Two typical elongated quadrupolar objects separated by $\vec{r}$ are illustrated in the sketch of Figure 4.2. Following this schematic, one must consider

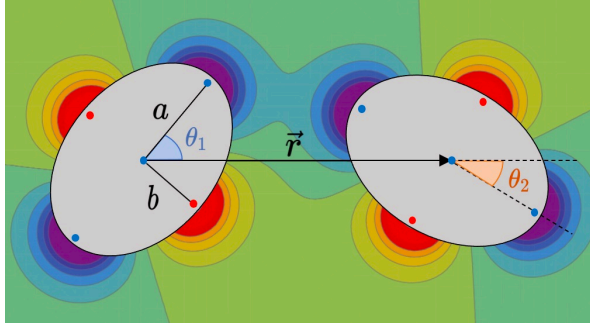


Figure 4.2: Schematic liquid landscape between two Pringles. Two identical elliptic quadrupolar objects at a distance r and theoretical elevation of the liquid profile around them, following Eq. (4.1). The coloured dots inside the particles indicate negative (blue) and positive charges (red), accounting for the central monopolar charge and the four charges that comprise the quadrupole. Relative angles θ_1 and θ_2 are defined.

25 terms to calculate the interaction potential of Eq. (2.3), the discrete-charge interaction potential introduced in Chapter 2. The potential is therefore described by

$$U = U_{cc} + U_{cq} + U_{qq} \quad (4.2)$$

where U_{cc} is the interaction potential between the two central charges, U_{cq} , the potential between a central charge and a quadrupole, and U_{qq} , the potential between the quadrupolar components. Following the method

introduced in Chapter 3, where capillary interactions between induced dipoles were developed within the same discrete-charge framework, we expand the Bessel functions K_0 about the centre-to-centre distance r in the far-field limit $r \gg a$. As in the dipolar case, the interaction is expressed as a sum over pairwise charge contributions, while orientational effects arise naturally through small geometric parameters encoding the relative offsets of the discrete charges. We first focus on the interaction potential between two quadrupoles, denoted U_{qq} . One has

$$\begin{aligned}
U_{qq} = & -2\pi\gamma Q^2 \sum_{\pm\pm} K_0 \left(\frac{|\vec{r} \pm \vec{\delta}_1 \pm \vec{\delta}_2|}{\lambda} \right) \\
& -2\pi\gamma Q^2 \sum_{\pm\pm} K_0 \left(\frac{|\vec{r} \pm \vec{\zeta}_1 \pm \vec{\zeta}_2|}{\lambda} \right) \\
& +2\pi\gamma Q^2 \sum_{\pm\pm} K_0 \left(\frac{|\vec{r} \pm \vec{\delta}_1 \pm \vec{\zeta}_2|}{\lambda} \right) \\
& +2\pi\gamma Q^2 \sum_{\pm\pm} K_0 \left(\frac{|\vec{r} \pm \vec{\zeta}_1 \pm \vec{\delta}_2|}{\lambda} \right).
\end{aligned} \tag{4.3}$$

The notation $\sum_{\pm\pm}$ denotes the sum over all four combinations of signs. The first two sums correspond to the eight attractive interactions between two vertices of the same charge, and the last terms correspond to the repulsive interactions between opposite charges. One should remark that each Bessel function in the previous equation is of the form

$$K_0 \left(\frac{|\vec{r} \pm \vec{\delta}_1 \pm \vec{\delta}_2|}{\lambda} \right) = K_0 \left(\frac{r}{\lambda} \sqrt{1 + 2\alpha x + 2\beta x^2} \right) \tag{4.4}$$

where the reduced variable is $x = a/r$, or $x = b/r$ depending on the displacement vector. The remaining parameters α and β differ for each term and depend on the object's size and orientation. Noting $K_0 = K_0(\frac{r}{\lambda})$ and $K_1 = K_1(\frac{r}{\lambda})$, the leading orders of the Taylor expansion of Eq. (4.4) when

$r \gg a$ gives

$$\begin{aligned}
K_0 \left(\frac{r}{\lambda} \sqrt{1 + 2\alpha x + 2\beta x^2} \right) \simeq & + K_0 \\
& - \frac{\alpha r x}{\lambda} K_1 \\
& + \frac{r x^2}{2\lambda^2} \left[2\lambda(\alpha^2 - \beta) K_1 + \alpha^2 r K_0 \right] \\
& - \frac{\alpha r x^3}{6\lambda^3} \left[K_1 (4\lambda^2(2\alpha^2 - 3\beta) + \alpha^2 r^2) \right. \\
& \quad \left. + 2\lambda r(2\alpha^2 - 3\beta) K_0 \right] \\
& + \frac{r x^4}{24\lambda^4} \left[r K_0 (12\lambda^2(2\alpha^4 - 4\alpha^2\beta + \beta^2) + \alpha^4 r^2) \right. \\
& \quad + 4\lambda K_1 (6\lambda^2(2\alpha^4 - 4\alpha^2\beta + \beta^2) \\
& \quad \left. + r^2(2\alpha^4 - 3\alpha^2\beta)) \right] \\
& + O(x^5).
\end{aligned} \tag{4.5}$$

Considering these terms in Eq. (4.3), the zero-order term becomes null since the sum of all capillary charges Q is zero. The first three orders are also zero from symmetry arguments because the sum of the four α 's and α^2 's is zero. One has to reach the fourth order to obtain a non-zero term in the series. The fourth non-vanishing term $\sim r^4 x^4$ in this Taylor expansion is given by

$$\frac{1}{24} \alpha^4 \left(\frac{r}{\lambda} \right)^4 K_0 \left(\frac{r}{\lambda} \right) x^4 \tag{4.6}$$

The sum of all different α^4 's gives the orientational term

$$\Gamma(\theta_1, \theta_2) = -6 \left((a^2 + b^2) \cos(2\theta_1) + a^2 - b^2 \right) \times \left((a^2 + b^2) \cos(2\theta_2) + a^2 - b^2 \right). \tag{4.7}$$

The interaction potential between one central monopole and one quadrupole, U_{cq} , can be obtained using the same expansion procedure, but differs qualitatively in that the leading non-vanishing contribution already appears at second order in x . It originates from the cross-terms between the central monopolar charge Q_c of one particle and the four discrete charges Q forming the quadrupole of the other particle. Within the discrete-charge formalism, this contribution reads

$$U_{cq} = -2\pi\gamma Q_c Q \sum_{i=1}^2 \sum_{\pm} \left[-K_0 \left(\frac{|\vec{r} \pm \vec{\delta}_i|}{\lambda} \right) + K_0 \left(\frac{|\vec{r} \pm \vec{\zeta}_i|}{\lambda} \right) \right]. \tag{4.8}$$

Here, $\sum_{\pm}$ denotes the sum over the two symmetric contributions corresponding to $\vec{r} + \vec{r}_i$ and $\vec{r} - \vec{r}_i$.

Each Bessel function appearing in Eq. (4.8) is of the form

$$K_0\left(\frac{|\vec{r} \pm \vec{r}_i|}{\lambda}\right) = K_0\left(\frac{r}{\lambda} \sqrt{1 + 2\alpha x + x^2}\right), \quad (4.9)$$

where $\alpha = \cos\varphi$ is the cosine of the angle between $\vec{r}$ and the displacement vector. Expanding this expression for $r \gg a$ and summing over the $\pm$ contributions eliminates the first-order term by symmetry. Keeping terms up to second order in x , one obtains

$$K_0\left(\frac{r}{\lambda} \sqrt{1 + 2\alpha x + x^2}\right) \simeq 2K_0 + \frac{rx^2}{\lambda^2} \left[\alpha^2 r K_0 + 2\lambda(\alpha^2 - \tfrac{1}{2}) K_1 \right]. \quad (4.10)$$

When inserted into Eq. (4.8), the expansion yields a non-vanishing contribution already at second order in x , from which only the term proportional to rK_0 is retained in the far-field limit. This yields

$$U_{cq} \simeq -2\pi\gamma Q_c Q K_0 \left(\frac{r}{\lambda}\right) \frac{1}{\lambda^2} \left[-a^2(\cos^2\theta_1 + \cos^2\theta_2) + b^2(\sin^2\theta_1 + \sin^2\theta_2) \right]. \quad (4.11)$$

Combining the monopolar, charge-quadrupole, and quadrupolar contributions, the interaction potential between two elongated particles can be expressed as

$$\begin{aligned} U &= -2\pi\gamma Q_c^2 K_0 \left(\frac{r}{\lambda}\right) \left[1 + \frac{Q}{Q_c} \frac{a^2}{\lambda^2} \Theta(\theta_1, \theta_2) + \frac{Q^2}{Q_c^2} \frac{a^4}{\lambda^4} \Gamma(\theta_1, \theta_2) \right] \\ &= -2\pi\gamma Q_c^2 K_0 \left(\frac{r}{\lambda}\right) \Phi(\theta_1, \theta_2), \end{aligned} \quad (4.12)$$

where only leading terms are retained. Angles θ_1 and θ_2 denote the orientations of the particles with respect to the centre-centre axis. The orientational factors, rewritten as functions of the eccentricity $e = \sqrt{1 - b^2/a^2}$, read

$$\Gamma(\theta_1, \theta_2) = 24 \left(\cos(2\theta_1) + e^2 \sin^2\theta_1 \right) \left(\cos(2\theta_2) + e^2 \sin^2\theta_2 \right), \quad (4.13)$$

and

$$\Theta(\theta_1, \theta_2) = \pm \left[2 + (e^2 - 2) (\sin^2\theta_1 + \sin^2\theta_2) \right], \quad (4.14)$$

while $\Phi(\theta_1, \theta_2)$ encodes the total orientational contribution to the interaction strength. The form of $\Phi(\theta_1, \theta_2)$ highlights the strengthening of

the attraction thanks to the quadrupolar component Q compared to the monopolar interaction only.

As a first analysis, it is instructive to consider the limit $e = 0$, corresponding to circular contact lines, and to compare the resulting orientational dependence with the polar multipole framework presented in Chapter 1. In the far-field multipolar expansion discussed in the state of the art, the quadrupole-quadrupole interaction depends only on the relative orientation and takes the form $\cos(2\theta_1 - 2\theta_2)$. In contrast, the present discrete-charge formulation yields an angular dependence $\cos(2\theta_1)\cos(2\theta_2)$, since the orientations are defined with respect to the centre-centre axis. Using the identity $\cos(2\theta_1)\cos(2\theta_2) = \frac{1}{2}[\cos(2\theta_1 - 2\theta_2) + \cos(2\theta_1 + 2\theta_2)]$, the relative-orientation term is recovered, while the additional contribution reflects the explicit role of the interaction axis in the discrete-charge description.

A similar interpretation applies to the monopole-quadrupole interaction. In the present formulation, the term is of the form $1 + \cos(2\theta)$. In the far-field multipolar expansion, the interaction reduces to $\cos(2\theta)$ dependence given in Eq. (1.37), thereby demonstrating consistency between the two approaches.

Let us now return to elongated particles and discuss the preferred orientations as functions of the ratio Q/Q_c , the particle size a , and the eccentricity e . The quadrupolar term $\Gamma(\theta_1, \theta_2)$ favours configurations in which both particles align along the centre-centre axis, i.e., the end-to-end configuration. The contribution of $\Theta(\theta_1, \theta_2)$ depends on the polarity of the quadrupole. When negative charges lie along the major axis, Θ is positive and reinforces this alignment, so that the total interaction potential is minimised in end-to-end configurations, independently of the geometrical parameters. The strength of this attraction increases with particle elongation.

When the polarity of the quadrupole is reversed, and positive charges lie along the major axis, the sign of Θ changes and this factor now favours side-by-side configurations. In this flipped configuration, long-range side-by-side attraction is now possible. Comparing $\Phi(\pi/2, \pi/2)$ and $\Phi(0, 0)$ shows that side-by-side attraction occurs if the conditions are such that

$$\frac{e^2 a^2}{\lambda^2} < \frac{Q_c}{12Q}, \quad (4.15)$$

which corresponds to a weak quadrupolar component compared to the central monopole and to particles with low eccentricity. This attraction

arises because the central monopole has the same polarity as the minor-axis charges of the quadrupole. Equation (4.15) serves as a design rule for the present chapter: it links geometry and meniscus anisotropy to the selected bonding configuration. This condition is summarised in the design map shown in Figure 4.3.

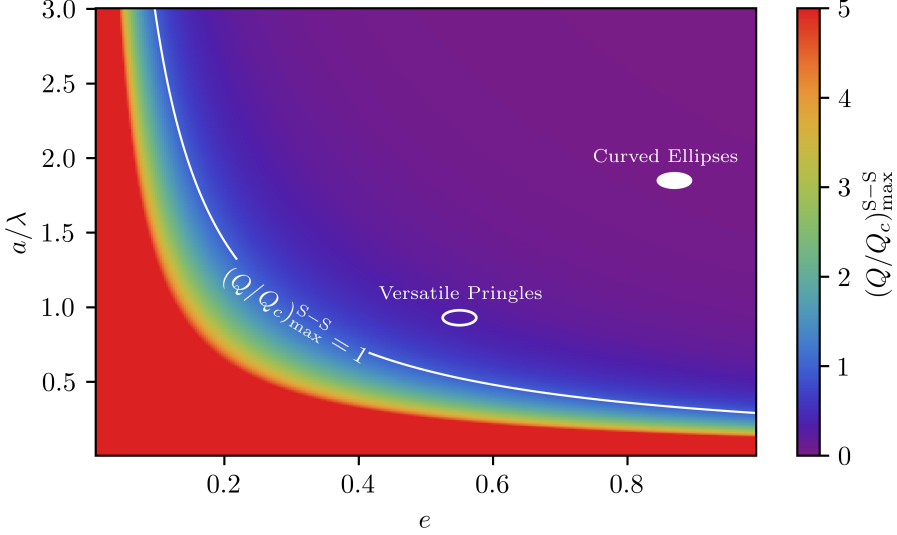


Figure 4.3: Design map associated with the side-by-side attraction condition given by Eq. (4.15). The colour scale represents the maximum admissible ratio $(Q/Q_c)_{\max}^{S-S}$ allowing side-by-side attraction as a function of the particle eccentricity e and the size ratio a/λ . The white contour corresponds to $(Q/Q_c)_{\max}^{S-S} = 1$, which delimits the regime where the quadrupolar contribution remains sufficiently weak compared to the central monopole. White markers indicate the geometrical parameters of the curved ellipses and versatile Pringles used in experiments.

The Figures 4.4(a) and 4.4(b) show the contour-plot diagram of the opposite of the orientation term $\Phi(\theta_1, \theta_2)$ between (a) two particles with major axis carrying negative charges and for which the favoured configuration is end-to-end, and (b) two particles with major axis carrying the positive charges and whose geometrical parameters respect the conditions of Eq. (4.15). One can observe that in this latter case, the side-by-side is favoured. Another remark concerns the appearance of the quadrupole's dimensions in the orientation term. Indeed, the factors $(a/\lambda)^2$ and $(a/\lambda)^4$ in Eq. (4.12) demonstrate that the size a and b compared to the capillary length λ is highly relevant. Large objects tend to orient themselves more, while smaller objects are less sensitive to orientation effects when far from each other.

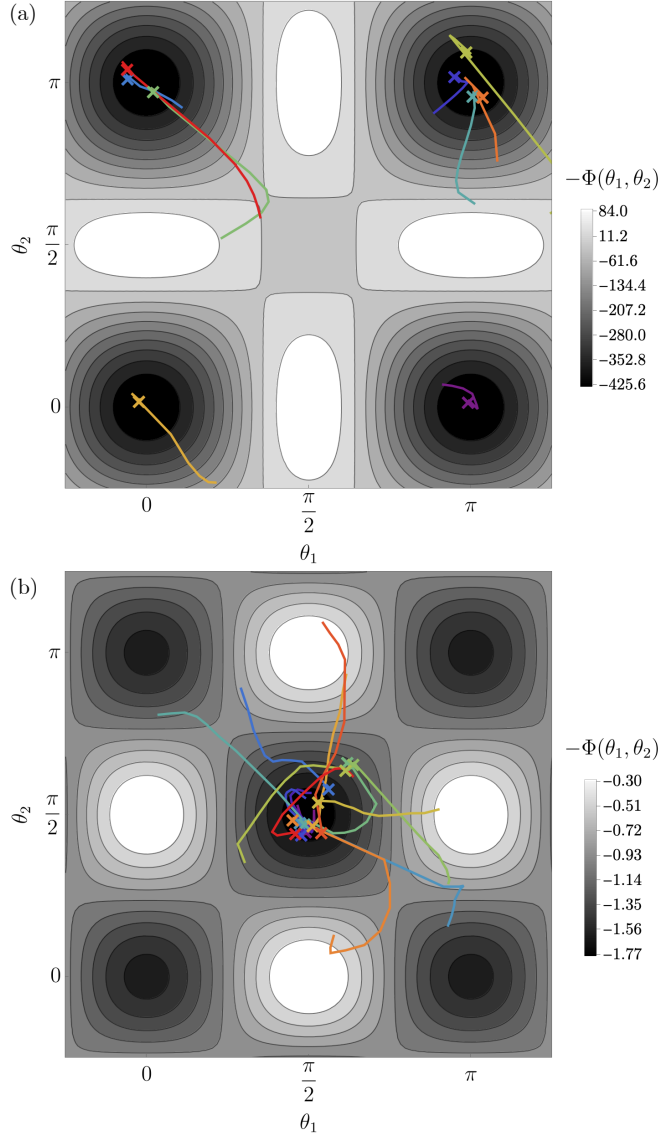


Figure 4.4: Evolution in the configuration space. (In gray-scale) Contour-plot diagram of the orientational term $-\Phi(\theta_1, \theta_2)$ of Eq. (4.12). The darkest areas correspond to the orientation (θ_1, θ_2) that minimises the interaction potential. (In colours) Experimental data of the evolution of a configuration (θ_1, θ_2) of two similar objects approaching each other until contact in the configuration space θ_1, θ_2 . Each colour represents a different experiment. Final orientations (θ_1, θ_2) are represented by a cross $\times$. (a) Relative orientations favoured for curved ellipses with $e = 0.87$. The four dark areas correspond to the end-to-end configuration. (b) Relative orientations favoured for versatile Pringles ($e = 0.55$) with positive major axis. The central darkest area at $(\pi/2, \pi/2)$ corresponds to the side-by-side configuration.

At long distances, the eccentricity e , size, and ratio Q/Q_c are the key ingredients to control the dynamics and reorientation of interaction between two multipolar objects. The potential of Eq. (4.12) can be derived to provide radial force and torques on the objects to deduce the dynamic behaviour for a pair of particles. Since the Reynolds number $\text{Re} = \frac{\rho_l}{\eta} \frac{dr}{dt} a \simeq 1$ is low when particles are far from each other, inertial forces can be neglected in front of dissipative forces on most parts of the trajectories of the particles. Thus, the equations of motion are:

$$\begin{aligned} -\frac{\partial U}{\partial r} + c\eta a \frac{dr}{dt} &= 0 \\ -\frac{\partial U}{\partial \theta_1} + c'\eta (ab)^{3/2} \frac{d\theta_1}{dt} &= 0 \\ -\frac{\partial U}{\partial \theta_2} + c'\eta (ab)^{3/2} \frac{d\theta_2}{dt} &= 0 \end{aligned} \tag{4.16}$$

with η , the dynamic viscosity; and c and c' , the resistance coefficients for translation and rotation, respectively, both depending on the shape and immersion ratio.

4.3 Experimental realisation

Elongated millimetre-scale quadrupolar objects have been designed to test our model. Using a Mathematica script, we created curved ellipses whose surface follows a hyperbolic paraboloid, like the famous Pringles crisps, and exported them as an STL file. We 3D printed the multipolar objects using a PolyJet 3D printer (Stratasys J35 Pro). This 3D-printing method boasts high precision with an announced precision of 16 μm . It prints a shell of support resin around the object that dissolves in water, ensuring the saddle curvature is precisely followed. This eliminates support structures and contact points that can alter the surface and increase roughness. Consequently, a smooth contact line is achieved, avoiding an additional capillary multipolar effect. We used a resin similar to ABS plastic (Vero Blue) with a polymerised density of $\rho_p = 1180 \text{ kg/m}^3$. This material is mildly hydrophilic, with a static water contact angle of approximately 50°- 60°. The positive and negative curvatures of the saddle are aligned with the minor and major axes, respectively, producing equal upward and downward deviations of the particle edges. The sharp top rim of the object promotes strong contact-line pinning, allowing us to create the desired menisci with large contact angle hysteresis [27]. Thus,

the particle's deformation corresponds to the four charges that make up the quadrupole. One should note that by flipping the object upside down, the polarity of the quadrupole is therefore switched.

The previous section highlighted that three parameters are of great importance for the capillary interaction: e , a , and Q/Q_c . When designing our objects, each of these anisotropic aspects can be varied. The eccentricity e and the size are directly linked to the major and minor axes. The object's thickness controls the central monopole, while the quadrupolar component depends only on the parameters of the hyperbolic paraboloid. In this work, slight variations in thickness and curvature were introduced intentionally to tune the relative magnitude of the central monopolar charge Q_c with respect to the quadrupolar charges Q . This approach strengthens the central attraction and is essential for designing versatile objects capable of assembling either in end-to-end or in side-by-side configuration. These charges are, therefore, entirely editable when creating our multipoles, and we can measure the ratio Q/Q_c thanks to profilometry methods. The resulting sets of geometrical and capillary parameters were chosen with respect to the design rule given by Eq. (4.15). Typically, by carefully tuning these anisotropic parameters, we have created and named three types of particles:

- Flat disks: Monopolar circular objects,
- Curved ellipses: Quadrupolar heavy objects that won't respect the conditions of Eq. (4.15) even if flipped,
- Versatile Pringles: Specially designed quadrupolar objects that respect the design rule given in Eq. (4.15) to favour the side-by-side configuration.

The three types of objects are represented in Figure 4.5(a,b,c). Their geometrical parameters are given in the Table 4.1.

Table 4.1: Geometrical and capillary properties of the three families of 3D-printed objects. Here a is the semi-major axis and e the eccentricity; the ratio Q/Q_c is obtained by fitting experimental profiles with Eq. (4.1).

Object type	Eccentricity e	a [mm]	Thickness T [mm]	Q/Q_c
Flat disk	0.00	5.0	0.4	0.00
Curved ellipse	0.87	5.0	0.4	1.22
Versatile Pringles	0.55	2.5	0.6	0.24

Defining the Bond number of Eq. (1.17) for our particles with thickness T , we found $\text{Bo} = \frac{(\rho_p - \rho_l)gaT}{\gamma} \sim 0.1 - 1$, meaning that the central

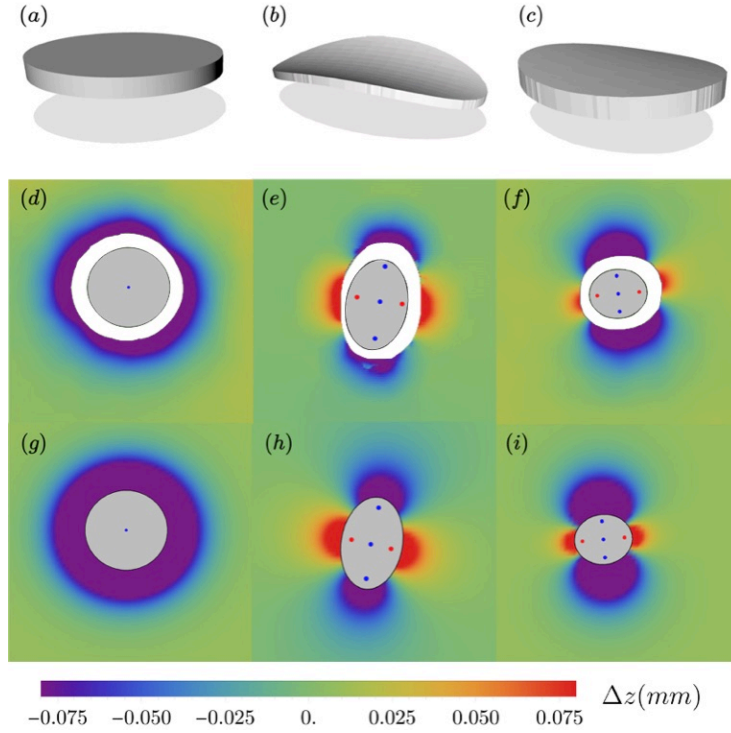


Figure 4.5: Types of objects and profilometry. (a,b,c) 3D view of a 3D-printed flat disk, a curved ellipse, and a versatile Pringles, respectively. The apparent differences in thickness and curvature between designs are intentional and are used to tune the ratio Q/Q_c (see Table 4.1). (d,e,f) Experimental profile $z(x,y)$ of the liquid surface around the above objects in a colour scale, as measured by a Schlieren method [35, 36] (g) Fitted profile of the interface for one central negative monopole Q_c represented by the blue dot (h, i) Fitted liquid interface for the linear combination of four discrete charges of magnitude Q placed inside the objects and a central negative monopole Q_c , following Eq. (4.1).

monopolar component Q_c should be taken into account. As summarised in Figure 4.3, the curved ellipses lie outside the region allowing long-range side-by-side attraction, whereas the versatile Pringles fall within the admissible domain. This intentional choice ensures that the two families of objects explore opposite sides of the design map, thereby enabling a direct experimental validation of the predicted selection between end-to-end and side-by-side bonding configurations.

The liquid interface deformation around a single floating particle is observed using an improved Schlieren method proposed by Metzmacher et al. [36], which is based on the work of Moisy et al. [35]. The experi-

mental liquid profile around the particle is displayed in a colour scale in Figure 4.5, where red represents positive elevation Δz and purple represents negative Δz . Around the objects, gradients become too strong, leading to some uncertainty regarding the liquid elevation. This zone is, therefore, not measured and corresponds to the white zone around objects on profilometry pictures.

In profilometry pictures, one can directly notice the difference between a flat monopolar object and a curved quadrupolar object. For the quadrupolar objects, positive and negative charges Q accounting for the four lobes were considered in addition to the negative central monopole Q_c . We approximated the experimental profile well using a linear combination of those charges. The fitted profiles around our multipolar objects are shown in Figure 4.5(g,h,i).

4.4 Attraction and reorientation

To validate our model, experiments were conducted using the 3D-printed multipolar objects presented in the previous section. Two identical objects were positioned at a distance $r_0 \gg a$ on a flat water–air interface using tweezers, the most reliable method we found to minimise disturbances. This method can occasionally impart a slight initial velocity to the particles and results in a small variability in r_0 (15–30 mm). While this affects the time to contact, it does not change the nature of the capillary interaction. In fact, the residual motion from manual placement is quickly damped by viscosity, after which the capillary interaction dominates and drives the reorientation and attraction, thereby highlighting the robustness of the experiments to the initial conditions. Reorientation and attraction between the floating objects were observed, and their trajectories and orientations were recorded. The spacing $r(t)$ and the objects' orientations over time $\theta_1(t)$ and $\theta_2(t)$ were then extracted from the sequence of images.

Experimental data of the spacing and the orientation over time of a pair of curved ellipses from one typical experiment are shown in Figure 4.6. We observe that the spacing $r(t)$ follows a logarithmic-like decay because, given the size of our objects, the $K_1(r/\lambda)$ factor in the capillary force exhibits an approximately exponential decay at large separation. This is observed for all object types, whether quadrupolar or not. However, the decay rate varies significantly with the quadrupolar components and the initial orientations. Looking at the orientations, we observe a reorienta-

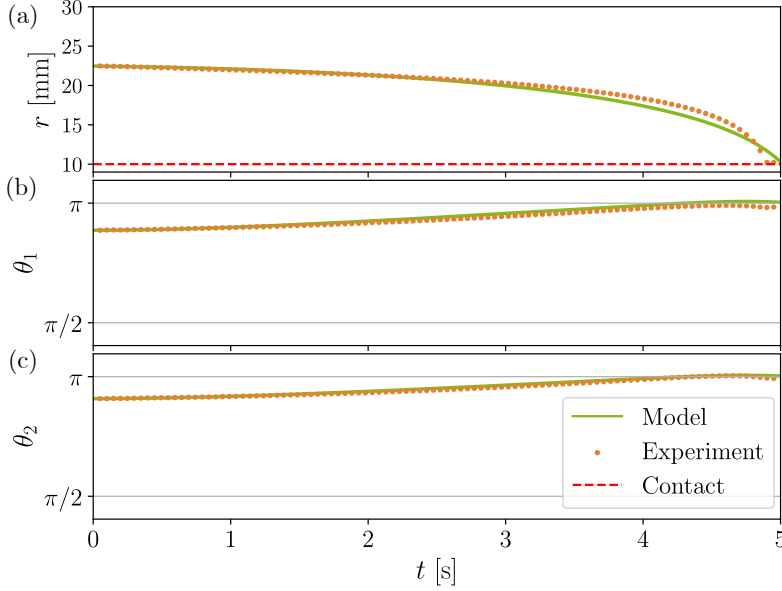


Figure 4.6: Experimental dynamics and overdamped solutions of the model.

Typical evolutions of (a) spacing $r(t)$ and orientations (b) $\theta_1(t)$ and (c) $\theta_2(t)$ between two curved ellipses before contact. Orange dots represent the experimental data, and green curves represent the numerical solutions of the coupled equations of motion given in Eq. (4.16). The red dotted line represents the distance at contact.

tion over time that leads to a final favoured configuration, the end-to-end orientation in the present case. No particular orientation is observed between non-curved disks. In order to give a better view of the orientation process, more experimental evolutions of configuration (θ_1, θ_2) between pairs of curved ellipses and versatile Pringles are shown in colours in Figure 4.4(a) and (b), respectively. The grey-scale background represents the contour plot diagram corresponding to the opposite of the orientational term $-\Phi(\theta_1, \theta_2)$ in the interaction potential. Figure 4.4(a) shows that curved ellipses reorient themselves in the end-to-end configuration. This effect has been observed in all experiments with curved ellipses. One can also see that corotation is observed since the evolution of the orientations follows the diagonals $|\theta_1| = |\theta_2|$ and $|\theta_1| = |\pi - \theta_2|$ of the diagram of Figure 4.4. This corotation has been reported by Stamou et al. for circular quadrupolar particles [27].

Figure 4.4(b) shows orientations between versatile Pringles, our specially designed objects that follow the condition of Eq. (4.15), and whose positive charges are on the major axis. As predicted by the energy landscape,

these objects can reorient themselves in the side-by-side configuration $\{\frac{\pi}{2}, \frac{\pi}{2}\}$. However, if we flip them, as the negative charges will now be on the major axis, the preferred orientation will therefore be end-to-end. The same objects can achieve two completely different configurations, which explains our choice to call them “versatile” Pringles. This versatility is shown in Figure 4.1(b-c) where an end-to-end configuration is observed for versatile Pringles with negative charges along the major axis (b) while flipping the particles results in a side-by-side configuration (c). The sharp orientation changes in some trajectories correspond to real transient motions occurring at the start of the experiment, caused by small residual velocities unintentionally imparted during manual placement. These motions are rapidly damped by viscous dissipation, after which capillary torque dominates and the orientation evolves smoothly.

To further characterise the dynamics and reveal the importance of both the initial orientations and the quadrupolar component through the ratio Q/Q_c in the self-assembly process, we can numerically solve the equations of motion given in Eq. (4.16). The numerical solutions are presented for the initial condition of the experimental data shown in Figure 4.6, and we observe good agreement between the model and the experiments.

The equations were numerically integrated using the Runge-Kutta method of order 5(4), also known as the Dormand-Prince method, which is implemented in the `solve_ivp` function from the SciPy library in Python. Resistance coefficients c and c' were calibrated on multiple experiments for each type of particle to fit their experimental attraction and reorientation rate. For each quadrupolar type of particle, both the experiments and the equations of motion reveal the coupling between the orientation and the attraction for these quadrupolar objects.

With the resistance coefficients calibrated on our experimental data for both the curved ellipse and the versatile Pringles type of objects, we were able to numerically acquire the dynamics of the self-assembly and the reorientation for all sets of initial interdistance r_0 and orientations $\{\theta_{1,0}, \theta_{2,0}\}$. Additionally, we can numerically compare the quadrupolar effect, which we call the “Pringles effect” and the monopolar-only effect, the Cheerios effect. Figure 4.7(a) and (b) illustrate, for curved ellipse and versatile Pringles respectively, the time ratio $\tau = t/t_{cc}$ between the attraction time until contact for two quadrupolar objects t and the attraction time for the same uncurved ($Q = 0$) objects t_{cc} from an initial distance $r_0 = 25$ mm for orientation $\theta_{1,0}$ and $\theta_{2,0}$ ranging from 0 to π . Red and purple regions indicate that the system reaches an end-to-end or side-by-

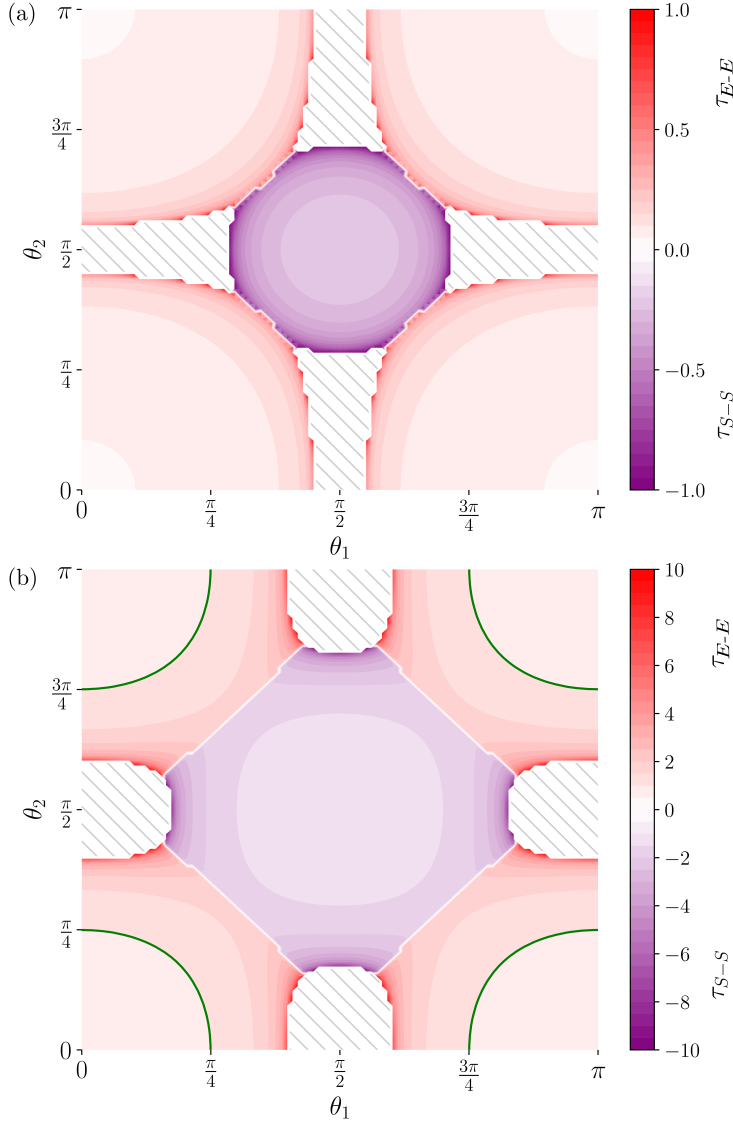


Figure 4.7: Time to contact in the configuration space. Time ratio $\tau = t/t_{cc}$ between the attraction time t for quadrupolar objects and the attraction time t_{cc} for their uncurved counterparts ($Q = 0$) as a function of their initial orientations. Contour plots depict the normalised attraction time τ for (a) curved ellipses and (b) versatile Pringles. The initial interdistance is fixed at $r_0 = 25$ mm, with initial orientations $\theta_{1,0}$ and $\theta_{2,0}$ varying from 0 to π . Red and purple regions indicate final end-to-end (τ_{E-E}) and side-by-side (τ_{S-S}) configurations, respectively, while hatched regions correspond to cases where contact was not reached within 10000 s. Green contours mark $\tau = 1$, where the attraction time equals that of uncurved objects.

side state, respectively. Hatched regions represent initial orientations for which contact was not reached after 10000 seconds of simulation. The versatile Pringles exhibit a stronger preference for side-by-side assembly over a broader range of initial orientations than the curved ellipses, a trend amplified by short-range interactions that are not taken into account in the present study. Differences between the curved ellipse and the versatile Pringles can also be seen in the time ratio τ . Indeed, while the quadrupolar component of the curved ellipse strongly strengthens the attraction whenever attraction is possible, it weakens the far-range attraction for the versatile Pringles except inside the green contours, representing a time ratio τ equal to 1. Figure 4.7 allows a straightforward comparison between the Pringles and the Cheerios Effect, highlighting the impact of the quadrupolar components on the self-assembly time and pattern.

4.5 Implications for quadrupolar self-assembly

While our theoretical study focuses on long- and near-field interactions between two bodies, Figure 4.1(d-e) reveals that by tailoring the quadrupolar and anisotropic properties of floating objects, we can also select final configurations between multiple bodies. When three or more particles are introduced to the interface, new configurations, metastable or stable, arise. For versatile Pringles with negative charges on the major axis, end-to-end chaining occurs as well as a “flower-like” structure where the tips of the ellipses touch in the centre of a triangle, as one can observe in Figure 4.1(d). These contact configurations have been observed in different studies with objects possessing similar quadrupolar shapes of the meniscus and can be attributed to multibody effects [4, 7, 31, 98, 99]. One can easily understand that these configurations are favoured because the central negative charge reinforces the negative tips of the ellipses. When we flip the particles, the negative charges are now on the minor axis, and we observe side-by-side chaining as well as a triangular structure where the ellipse tips touch at the corners of an equilateral triangle in Figure 4.1(e). Again, it is straightforward that these configurations are the way to make the sides of the ellipses closer. Although such assemblies, particularly the end-to-end chains, can be metastable, capillary bridges may appear due to the shape of the particles and stabilise the chains [52, 100]. We note that these multi-particle configurations were observed qualitatively and

are included here for illustration; a systematic study of their stability and assembly pathways lies beyond the scope of the present thesis and will be the subject of future investigations.

4.6 Summary

In this chapter, we extended the capillary interactions introduced in Chapter 1 using the discrete-charge formalism exposed in Chapter 2 to elongated quadrupolar particles at liquid interfaces. We showed that the meniscus around a saddle-shaped object can be accurately modelled as the superposition of a central monopolar charge and four discrete quadrupolar charges, and we derived an explicit interaction potential for a pair of such objects. The resulting energy landscape retains the $K_0(r/\lambda)$ decay of the Cheerios interaction with possible enhancement or reduction factors, but acquires a rich orientational dependence encapsulated in the factor $\Phi(\theta_1, \theta_2)$ of Eq. (4.12). On the experimental side, we implemented this theoretical strategy by designing and 3D-printing different saddle-shaped ellipses with controlled size, eccentricity, thickness and curvature. Profilometry measurements allowed us to fit the corresponding menisci with the discrete-charge model and to extract the ratio Q/Q_c , thereby providing a direct link between geometry and capillary charges. Using these calibrated objects, we validated the quadrupolar interaction potential by comparing overdamped numerical trajectories with experimentally measured attraction and reorientation dynamics for particle pairs. Finally, by tuning the quadrupole-to-monopole ratio to satisfy the design rule of Eq. (4.15), we engineered versatile Pringles that can be encoded to self-assemble either end-to-end or side-by-side on demand, simply by flipping the particles at the interface.

Supplementary resources

Access to the [Zenodo](#) repository containing raw data and the 3D files associated with this chapter:



If you know you are on the right track, if you have this inner knowledge, then nobody can turn you off... no matter what they say.

-Barbara McClintock

5

Higher-order capillary interactions

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In this chapter, we extend the shape-encoded capillary interactions introduced previously to flexible chains of connected elements. By combining discrete-charge modelling, numerical energy-landscape analysis, and experiments with 3D-printed curved branched components, we demonstrate how a one-dimensional capillary sequence governs both the final folded geometry and the complexity of the associated folding pathways. This establishes capillary self-folding chains as a minimal and controllable platform to investigate programmable many-body interactions at fluid interfaces.

The results presented in this chapter are partially included in:

M. Delens, A. Franckart, M. Poty, and N. Vandewalle, *Capillary self-folding chains*, in preparation (2026).

5.1 Motivations

In Chapter 4, we showed that particle geometry and contact-line anisotropy can encode directional capillary interactions at liquid interfaces. In particular, 3D-printed Pringles demonstrated how a well-defined multipolar meniscus leads to selective bonding and predictable pairwise configurations. Although collective effects already arise when several free particles interact at an interface, our analysis deliberately focused on simple interaction motifs to establish clear design rules.

In this chapter, we take a first step toward modelling many-body interactions by considering flexible chains of connected capillary elements. Unlike free-floating particles, the components of a chain cannot rearrange independently: their relative positions are constrained, and capillary interactions act cooperatively along the backbone. As a result, folding cannot be understood as a succession of independent pair interactions, but instead emerges from the collective competition between many interactions acting simultaneously. An example of a chain encoded to fold into a zigzag configuration is shown in Figure 5.1. In this configuration, the chain bends successively to opposite sides, forming a periodic sequence of up-down folds along the backbone.

Inspired by molecular folding, each chain element is designed to encode capillary information through its geometry. Each building block generates a controlled multipolar meniscus composed of a central monopolar contribution and two dipolar components, whose relative orientation and magnitude can be tuned. The sequence of these elements along the chain thus defines a one-dimensional capillary code.

Self-folding then results from minimising a high-dimensional energy landscape shaped by this code. By exploiting this collective behaviour, the present chapter extends shape-encoded capillary interactions beyond isolated objects and simple assemblies. It demonstrates how programmable chains can fold deterministically into target mesoscale structures.

Supplementary videos illustrating the experimental folding discussed in this chapter, as well as the 3D files for creating chain elements, are available via a Zenodo repository. For ease of access, a QR code linking to this resource is provided at the end of the present chapter.

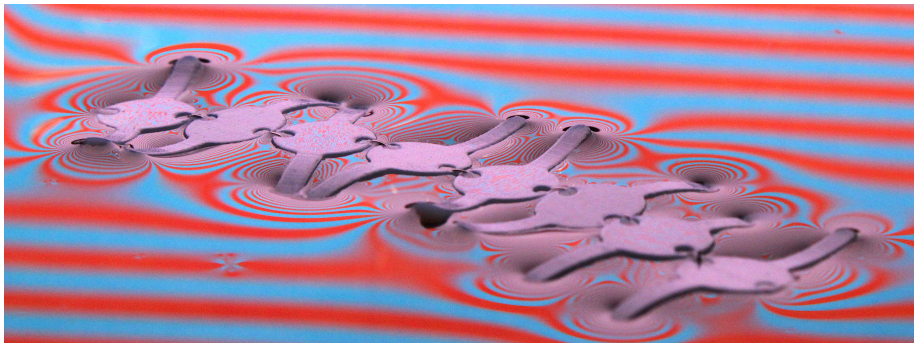


Figure 5.1: Picture of a flexible chain made of 8 components floating on a liquid-air interface. Each component has two opposite branches. By using the reflection of a striped pattern, the local deformations of the liquid interface are revealed. Both positive and negative deformations are observed, particularly near branch tips. The chain has been encoded to induce zigzag folding.

5.2 Capillary code in the monomer

The self-folding behaviour of the chains originates from the way capillary information is encoded at the level of a single floating element, the monomer. As shown in Chapter 4 with saddle-shaped objects, curvature combined with a pinned contact line provides a robust way to sculpt anisotropic menisci and encode directional capillary interactions. Here, we exploit this principle to design and 3D-print elementary building blocks that generate a two-sided capillary signature, suitable for chaining and folding.

Each element consists of a central circular disk (diameter $D = 8$ mm, thickness 1.75 mm) from which two opposing branches extend. The branches have length $L = 10$ mm, width $W = 2$ mm, and rounded tips of radius $\varepsilon = 1$ mm to avoid sharp contact-line variations. The two branches, indexed by $k \in \{1, 2\}$, can have either positive or negative curvature, which we encode through a curvature-sign variable $c_k \in \{+1, -1\}$. The flexion angle is set to 10° . The curvature of each branch directly sets the sign of the capillary charge generated at its tip, such that each monomer is characterised by one of the four possible logical capillary codes: $\{^+_+\}$, $\{^-_-\}$, $\{^+_-\}$, and $\{^-_+\}$. Objects are printed with the same PolyJet 3D printer as in Chapter 4. This printing method allows two different surface finishes, slightly rough or smooth, on the top and bottom faces of the element. The smooth finish is more wetting than the rough finish. In the present work, we exploit this feature: the face exposed to air is always

rough, preventing the liquid from climbing onto the upper surface, while the face in contact with the liquid is smooth, increasing wettability and promoting contact-line pinning. As a consequence, the mixed-curvature codes $\{\bar{+}\}$ and $\{+\}$ are physically identical up to a π rotation in the air-water plane, whereas the homogeneous codes $\{+\}$ and $\{-\}$ correspond to two distinct elements depending on which face is oriented toward the liquid. In practice, this results in three distinct physical building blocks implementing four logical capillary codes.

Using the same profilometry method as in Chapter 4, we then measure the liquid interface deformation generated by the curved branches. As shown in Figures 5.2(d–f), branches with positive curvature produce upward deformations of the interface near their tips, while negatively curved branches induce downward deformations. Profilometry further shows that the deformation induced by each branch tip is systematically accompanied by an opposite deformation near the branch base, close to the central disk. This compensation reflects the constraint that the total capillary deformation remains governed by the net weight of the element: while branch curvature redistributes capillary charges locally, any additional deformation must be balanced elsewhere on the object.

Within the discrete-charge formalism introduced in Chapter 2, these anisotropic menisci can be represented as a superposition of elementary monopolar contributions. Each curved branch is naturally described as a capillary dipole of strength Q_b , composed of two opposite charges located near the branch tip and near its base, respectively, at a distance ε from these geometric features. The curvature of the branches, indicated by the curvature sign c_k , sets the orientation of these dipoles. For elements with branches of opposite curvature, such as $\{\bar{+}\}$, the two dipoles are aligned in the same direction. Conversely, for elements with identical branch curvature, the dipoles are anti-parallel. In addition to these branch dipoles, a central monopolar charge Q_c accounts for the weight of the element. As a result, each building block can be reduced to a simple capillary representation composed of one central monopole and two parallel or anti-parallel dipoles. The liquid elevation generated by a single element can therefore be written as

$$z_i(\vec{r}) = Q_c K_0 \left(\frac{|\vec{r} - \vec{r}_i|}{\lambda} \right) + \sum_{k=1}^2 c_k Q_b \left[K_0 \left(\frac{|\vec{r} - \vec{r}_{\text{tip}}^{(k)}|}{\lambda} \right) - K_0 \left(\frac{|\vec{r} - \vec{r}_{\text{base}}^{(k)}|}{\lambda} \right) \right], \quad (5.1)$$

with branch charge positions defined by

$$\vec{r}_{\text{tip}}^{(k)} = \vec{r}_i + (L - \varepsilon) \hat{\mathbf{t}}_k, \quad \vec{r}_{\text{base}}^{(k)} = \vec{r}_i + \left(\frac{D}{2} + \varepsilon \right) \hat{\mathbf{t}}_k, \quad (5.2)$$

where $\hat{\mathbf{t}}_k$ is a unit vector pointing from the centre of the element toward the tip of branch k .

As a first step to obtain the complete set of capillary charges, the magnitude of the branch charges Q_b is determined experimentally by fitting the liquid profile near branch tips using only the monopolar description given in Eq. (1.20), as shown in Figure 5.2(j). Except for their sign, the positive and negative branches exhibit identical deformations, yielding $|Q_b| = 0.2$ mm. Using these values, the whole meniscus around each element is fitted with Eq. (5.1), leaving Q_c as the only free parameter. For all element types, we find $Q_c = -Q_b/4$, and the resulting simulated profiles, presented in Figures 5.2(g-i), are in excellent agreement with experiments.

When several such elements are connected to form a flexible chain, capillary charges appear along both sides of the backbone, forming a sequence of dipolar contributions. The specific arrangement of branch curvatures along the chain, therefore, encodes a capillary interaction pattern that governs how local menisci combine. This capillary code provides the physical basis for the self-folding behaviour of the chains, which we analyse in the following sections.

5.3 Pair interactions - Dimer

Before addressing the folding of an extended polymer, we first analyse the interactions within a single dimer. A dimer consists of two components linked by a rigid connector and free to rotate with respect to one another. This minimal system defines the local interaction rule from which collective folding emerges.

For a typical spacing $d \simeq 1$ mm between connected components, geometry constrains the relative angle θ between them. The maximal angle is given by

$$\theta_{\text{max}} = 2 \arcsin \left(\frac{(D - W + d)/2}{L - \varepsilon} \right), \quad (5.3)$$

which yields $\theta_{\text{max}} = \pi/4$ for the component dimensions and geometry used here.

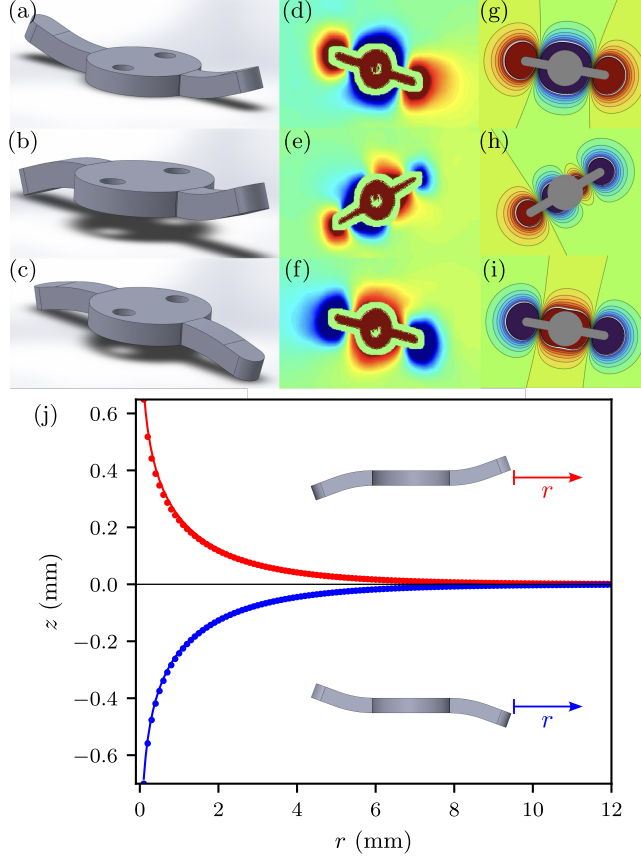


Figure 5.2: Capillary coding of a single chain element. (a-c) Three elementary building blocks with different combinations of branch curvature. (d-f) Corresponding liquid interface deformations measured by profilometry, showing upward (red) and downward (blue) menisci relative to the undisturbed surface (green). (g-i) Simulated interface profiles obtained from the discrete-charge model of Eq. (5.1), using one central charge and two branch dipoles per element. (j) Experimental liquid profiles measured along a branch axis for a $\{+\}$ element; fits near the branch tips using the monopolar expression yield capillary charges $\pm Q_b$ of equal magnitude and opposite sign.

Each component carries two branch charges of sign $c_k = \pm 1$, leading to $\mathcal{N} = 4^2 = 16$ possible capillary codes for the dimer. Despite this apparent diversity, capillary interactions restrict the system to only $\Omega = 3$ distinct final configurations: parallel components ($\theta = 0$), or touching components at $\theta = \pm\theta_{\max}$. These configurations are conveniently described by a discrete state variable

$$s = \theta/\theta_{\max} \in \{-1, 0, +1\}. \quad (5.4)$$

Figure 5.3(a) summarises the mapping between the 16 capillary codes and the three accessible states. Codes dominated by repulsive interactions on both sides lead to the parallel state ($s = 0$). A strong attraction on only one side produces asymmetric folded configurations ($s = -1$ or $s = +1$), whereas codes with attraction on both sides are bistable and allow either folded state ($s = \pm 1$). In the bistable case, an important distinction must be made between symmetric and asymmetric bistability. When the capillary code is asymmetric with respect to the horizontal axis of the dimer, bistability is biased toward one state: the global energy minimum corresponds to the configuration in which branch tips carrying positive capillary charge come into contact. This asymmetry arises because positive tip charges induce negative deformations near the central floater on the same branch side, which are reinforced by the negative central charge Q_c . As already discussed in Chapter 4, Q_c therefore breaks the symmetry and enriches the interaction behaviour.

Naturally, several capillary codes are related by simple symmetry operations. A vertical reflection, corresponding to the exchange of the top and bottom branch sequences, leaves the interaction energy invariant and therefore leads to degeneracies in the two-element coding. By contrast, a horizontal reflection exchanges the left and right branches and maps one folded configuration onto its mirror counterpart, resulting in symmetric energy landscapes with respect to the parallel state.

For dimers, these symmetries imply that the capillary codes considered different in Figure 5.3(a) may be energetically equivalent. However, when multiple elements are connected into a chain, such up-down and left-right symmetries are no longer interchangeable. This emerging chirality becomes a key ingredient for generating complexity, as it allows otherwise equivalent local codes to produce distinct global folding pathways.

These interaction classes and their subsequent degeneracies can be made explicit by examining the corresponding pair energy landscapes shown in Figures 5.3(b) and 5.3 (c).

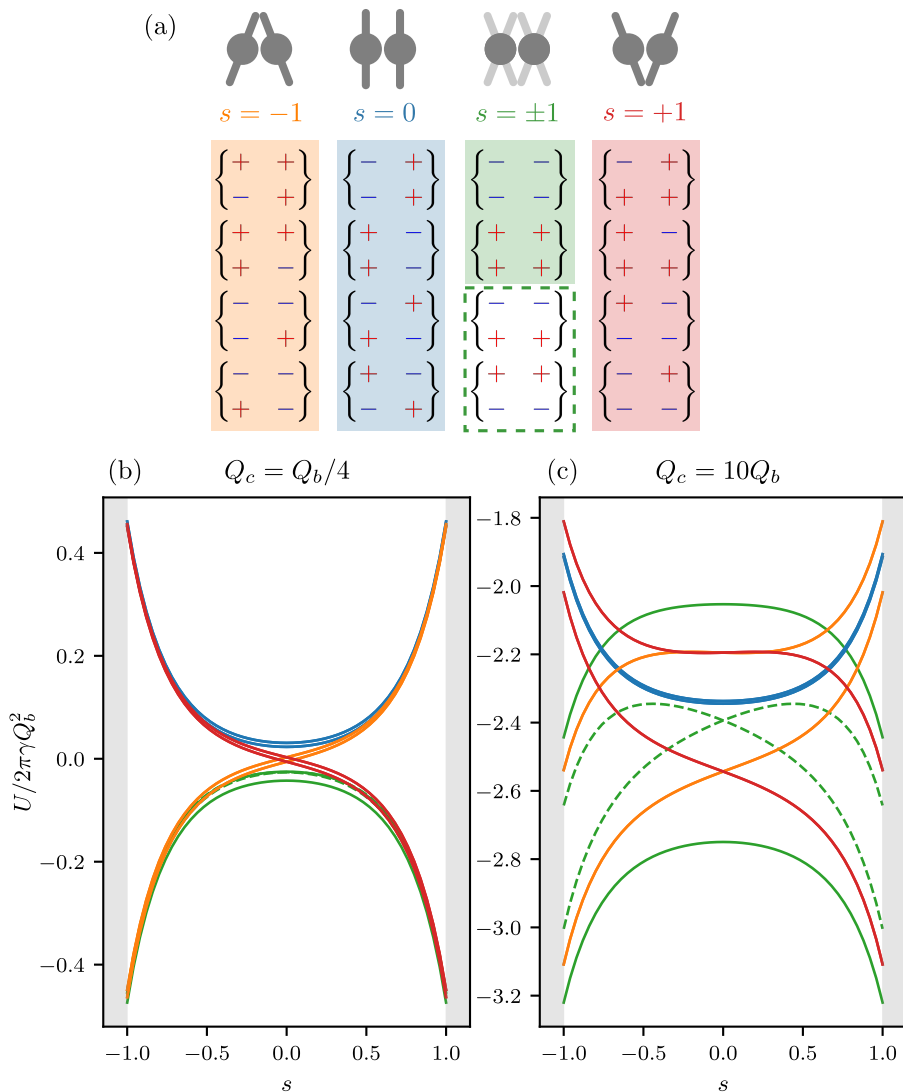


Figure 5.3: (a) The 16 possible capillary codes for dimer, colour-coded in function of the corresponding final states $s \in \{-1, 0, +1\}$. Symmetric and asymmetric bistability are separated, the latter being outlined in dashed green. (b) Normalised capillary energy landscapes $U(s)$ computed from the discrete-charge interaction potential using experimental parameters. (c) Same landscapes computed with an enhanced central charge ($Q_c = 10Q_b$) to highlight its effects, particularly the symmetry breaking in the asymmetric bistable cases (dashed green). Colours correspond to (a) and indicate the different interaction classes. The grey areas represent forbidden regions due to steric contacts.

The corresponding energy landscapes $U(s)$ are obtained by evaluating the discrete-charge interaction potential of Eq. (2.3) for the full five-charge representation of each element, i.e., the central charge and the two branch dipoles. Figure 5.3(b) shows the resulting energy landscapes as a function of the reduced state variable $s = \theta/\theta_{\max}$, normalised by the characteristic interaction scale $2\pi\gamma Q_b^2$. In all cases, stable configurations correspond to minima of the capillary energy $U(s)$. The folded states $s = \pm 1$ define the characteristic bonding energy of the system and are further stabilised by the formation of capillary bridges between tips, which effectively lock the components together. In practice, significant mechanical agitation is required to break these bonds.

The central charge amplitude Q_c both rescales and reshapes the interaction potential, as illustrated in Figure 5.3(c), where an exaggerated value of Q_c is used to highlight its effect. While the accessible folding behaviours remain organised into the same families of states $s \in \{-1, 0, +1\}$, the detailed shape of the energy landscape depends on the distribution and net balance of branch-tip charges within a given capillary code, whether positive, negative, or neutral. In particular, this exaggerated view highlights the two competing minima of unequal depth for the asymmetric bistable states.

As in the previous Chapter 4, the robustness of the selected state depends on the relative scale of the component dimensions compared to the capillary length. The millimetric size chosen here, comparable to λ , yields well-defined energy minima. Changing the system scale reshapes the energy landscape: increasing the object size shifts the effective positions of the capillary charges apart and flattens $U(s)$, reducing state selectivity. In contrast, decreasing the scale may introduce screening effects that compromise the reliability of the encoded outcome.

5.4 Folding of programmed polymers

When $N > 2$ elementary units are connected by wires and allowed to rotate freely, they form a flexible self-folding capillary chain. Along the backbone, branch tips generate alternating positive and negative capillary charges on both sides of the chain. As a result, the chain can be described by two parallel sequences of capillary charges. The fundamental question is, therefore, how a given capillary sequence translates into folding pathways and final configurations. As we demonstrate below, first theoretically and numerically, then experimentally, the system be-

haves as a programmable material, in which both random and designed sequences give rise to distinct self-folding behaviours.

5.4.1 Theoretical and numerical analysis

Each joint between adjacent elements can only adopt three local angular states $s \in \{-1, 0, +1\}$. Each chain configuration can thus be represented by a discrete state vector $\mathbf{s} = (s_1, \dots, s_{N-1})$. From a purely geometric perspective, this would suggest that the total number of accessible chain configurations scales as 3^{N-1} . Geometric constraints further restrict this space. With a maximal angular deflection $\theta_{\max} = \pi/4$, self-intersection is avoided only up to $N = 8$ elements ($2\pi = 8\theta_{\max}$). For longer chains ($N > 8$), self-overlapping configurations must be excluded. For instance, for $N = 16$, about 93% of the 3^{15} discrete configurations are geometrically valid. However, most of these configurations are not mechanically stable: they correspond to transient states along folding pathways rather than to stable folded structures. From an energetic perspective, only a much smaller subset of configurations corresponds to local minima of the capillary energy landscape. We denote by $\mathcal{M}$ the set of metastable microstates, defined as local minima of the energy landscape in joint space $\mathbf{s} = s_1, \dots, s_{N-1}$. A first natural measure of the system's complexity is the number of such minima, $|\mathcal{M}|$, which quantifies the number of metastable configurations accessible in the joint space.

However, distinct microstates in $\mathcal{M}$ may correspond to geometrically identical folded structures. Such degeneracies arise from symmetries of the system (e.g., equivalent foldings obtained by different joint sequences) and lead to identical energies and final shapes. Although these configurations are distinct microstates in configuration space, they correspond to the same physical folded object.

It is therefore useful to distinguish between metastable microstates and metastable macrostates. We define a macrostate as a distinct folded geometry, free of degeneracy, and denote by $\mathcal{G}$ the set of such geometrical macrostates. Macrostates provide a more physically relevant measure of the diversity of achievable self-assembled structures.

In practice, the energy landscape for a given polymer sequence is explored numerically over the non-self-overlapping admissible discrete configurations. For each valid state vector $\mathbf{s}$, the total capillary energy is computed from Eq. (2.3), which accounts for all pairwise interactions between discrete charges. Local minima are identified by comparing the energy of

a configuration to that of its neighbouring states obtained by a single-joint variation $s_i \rightarrow s'_i$. A configuration is considered as metastable when its energy is lower than that of all such adjacent configurations. The corresponding folded geometries are then reconstructed from $\mathbf{s}$, allowing geometrically identical minima to be grouped into a single macrostate.

Figure 5.4(a) shows the evolution of the number of metastable microstates $|\mathcal{M}|$ and macrostates $|\mathcal{G}|$, averaged over 1000 randomly generated capillary sequences as a function of N , the chain size. In addition to random sequences, two representative deterministic chains are displayed. The first consists of elements that are attractive on one side of the backbone and repulsive on the other. This coding promotes maximal curvature and will be referred to as the fold-biased chain. The second, termed the straight-biased chain, is composed of elements that are repulsive on both sides of the backbone, thereby stabilising straight or weakly folded configurations.

Figure 5.4(b) shows the corresponding probability density functions for random chains at $N = 4, 8$, and 15 , highlighting the evolution of the distribution of metastable macrostates. For short chains ($N < 8$), both $|\mathcal{M}|$ and $|\mathcal{G}|$ remain small, typically of order unity. Only a small fraction of sequences exhibit more than one metastable state. For such sizes, the folded configuration is largely deterministic and primarily encoded by nearest-neighbour interactions, as discussed in Figure 5.3.

For longer chains ($N \geq 8$), the energy landscape becomes rapidly more complex. In this regime, both types of metastable states grow approximately exponentially with N . The confidence intervals in Figure 5.4(a) and the histograms in (b) show that this growth strongly depends on the chain sequence. As N increases, the distributions broaden and develop heavy tails, reflecting the increasing heterogeneity of folding landscapes across different codes.

The median number of metastable macrostates for random chains grows approximately as $\sim e^{0.43N}$. By comparison, the fold-biased chain exhibits a much faster growth, $\sim e^{1.02N}$. Its enforced curvature brings multiple capillary charges into close proximity, enhancing competition between interactions and generating a proliferation of local minima. It therefore gives the typical upper bound on landscape complexity. The straight-biased chain shows a slower growth, $\sim e^{0.57N}$. Although curvature is reduced, folding of straight bits and partial self-zipping can occur, producing additional local minima as N increases. Overall, this comparison demonstrates that the capillary code controls not only the final folded

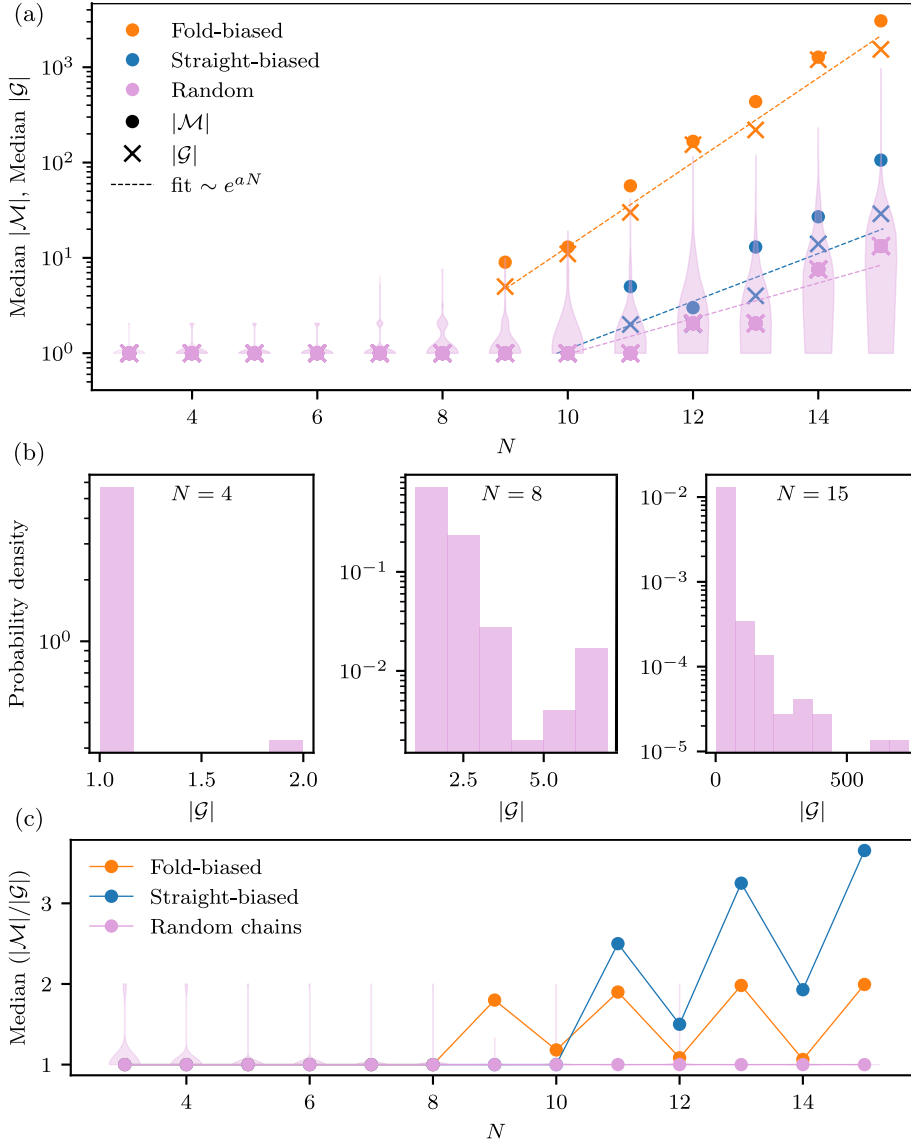


Figure 5.4: Metastable states as a function of the chain size N . (a) Semi-log plot of the number of metastable microstates $|\mathcal{M}|$ and macrostates $|\mathcal{G}|$ for fold-biased and straight-biased chains, together with the distribution over 1000 random sequences. For random chains, violin plots represent the full distribution at each N , and markers indicate the median. (b) Probability density functions of $|\mathcal{G}|$ for random chains at $N = 4, 8$, and 15 . (c) Degeneracy $|\mathcal{M}|/|\mathcal{G}|$ as a function of N . For random chains, violin plots show the distribution of per-sequence degeneracy and markers denote the median.

structure but also the complexity of the associated energy landscape. Figure 5.4(c) shows the median degeneracy, defined as the ratio $|\mathcal{M}|/|\mathcal{G}|$, which measures how many distinct configurations in joint space correspond, on average, to the same folded geometry. For random chains, the median degeneracy remains close to unity for all N . This indicates that, for a typical sequence, each folded geometry is selected by a single configuration in joint space. Degeneracy appears only for a small subset of highly symmetric sequences. In contrast, straight-biased chains exhibit a degeneracy that increases with N , together with a clear even-odd modulation. For odd N , the chain is globally symmetric, which preserves geometric equivalences between folded configurations and enhances degeneracy. For even N , the boundary elements differ, breaking this symmetry and reducing degeneracy. This symmetry effect is even more pronounced for fold-biased chains. Because their coding strictly alternates along the backbone, global symmetry is achieved only for odd N . For even N , the alternation produces inequivalent boundary elements, fully lifting the degeneracy and driving $|\mathcal{M}|/|\mathcal{G}|$ back to unity. Overall, degeneracy is not a generic consequence of landscape complexity. It primarily emerges from the symmetry of the capillary code.

Beyond chain length, the number of metastable states is also controlled by the relative strength of the central and branch charges, as already highlighted by their effect on pair interactions. Figure 5.5 shows the evolution of the number of metastable macrostates as a function of the ratio Q_c/Q_b for a fixed chain length $N = 10$. Again, three types of sequences are compared: fully random capillary codes (median over 1000 realizations), a fold-biased chain, and a straight-biased chain. We note that the randomly selected chains remain identical across variations in charge ratio.

As Q_c/Q_b increases, two concomitant effects shape the folding landscape. First, the energy landscape at the level of individual joints becomes increasingly structured as observed in Figure 5.3(b): the relative depth of local minima changes. More importantly, at the scale of the full chain, increasing Q_c/Q_b strengthens the attraction between the central disks. This monopolar contribution tends to promote aggregation of elements, leading to more compact, highly folded conformations. As discussed above, from a topological perspective, such compact folding configurations are associated with geometric frustration and self-avoidance constraints, which, in turn, lead to the proliferation of local energy minima. In this regime, the influence of the branch curvature pattern becomes

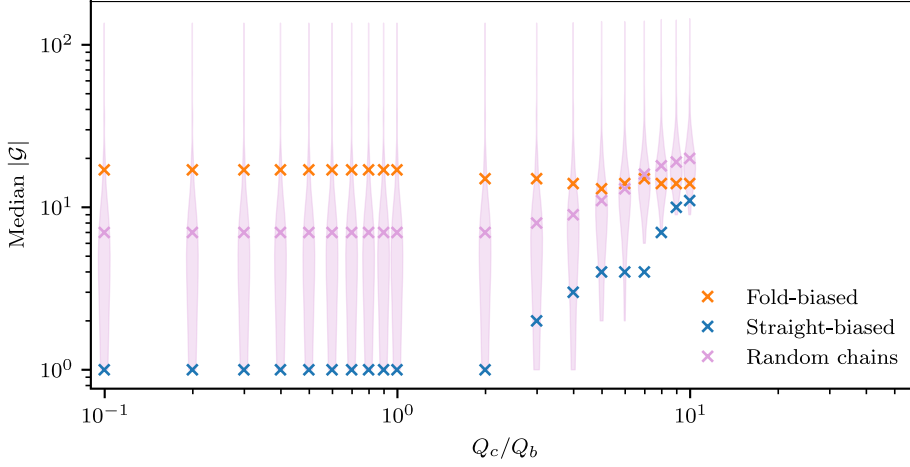


Figure 5.5: Metastable macrostates as a function of the charge ratio Q_c/Q_b for $N = 10$. Log-log representation of the number of metastable macrostates $|\mathcal{G}|$ for fully random chains (1000 realisations), a fold-biased chain, and a straight-biased chain as a function of Q_c/Q_b . For random chains, violin plots show the full distribution of $|\mathcal{G}|$ at each value of Q_c/Q_b , and markers denote the median.

progressively less dominant, as evidenced by the comparison of the three sequence types. The fold-biased and straight-biased chains, previously well separated in terms of metastable counts, become increasingly similar. Simultaneously, the dispersion across random sequences decreases, as reflected by the progressive narrowing of the distribution. In addition, the median number of macrostates increases, indicating that a larger set of compact geometries becomes accessible, independently of the specific chain sequence. The specific capillary sequence therefore becomes less predictive of the folding landscape, and the chain behaves more like a compact aggregate dominated by central-central attraction.

While the number of metastable states provides a first quantitative indication of the system's complexity, it does not capture how these states are connected mechanically and energetically. Folding pathways are governed by the energy barriers separating minima and by the organisation of their basins of attraction. For short chains ($N \leq 3$), the full energy landscape can still be visualised explicitly. Figure 5.6(a) shows an example for a $N = 3$ chain, where local and global minima are directly identifiable in the joint-state space (s_1, s_2) . The corresponding transition pathway and energy barrier are represented in Figure 5.6(b) in the form of a disconnectivity graph, which explicitly encodes both metastable

minima and the barriers separating them.

For longer chains ($N > 3$), the configuration space becomes intrinsically high-dimensional, which prevents any direct visualisation of the full energy landscape. In this regime, disconnectivity graphs are particularly relevant, as each leaf represents a local minimum and branches merge at the energy level of the lowest barrier connecting their basins of attraction. The vertical axis represents energy, and the resulting hierarchical structure encodes the accessibility of folding pathways.

The structural distance between two configurations $\mathbf{s}$ and $\mathbf{s}'$ is quantified by the Hamming distance, which counts the number of joints whose local state differs between the two configurations. It is defined as

$$d_H(\mathbf{s}, \mathbf{s}') = \sum_{i=1}^{N-1} (1 - \delta_{s_i, s'_i}), \quad (5.5)$$

where δ_{s_i, s'_i} is the Kronecker delta. As illustrated in Figure 5.6(c), this metric measures the minimal number of elementary folding or unfolding events required to transform one configuration into another.

Using the Hamming distance, metastable microstates can be grouped according to their structural similarity. Hierarchical clustering based on d_H yields a dendrogram that organises folded configurations into families. Figure 5.6(d) shows the resulting dendrogram together with the corresponding Hamming distance matrix for a $N = 12$ fold-biased chain, where block structures along the diagonal identify clusters of closely related folded states, while large off-diagonal distances signal structurally distant minima.

In practice, clusters are identified and coloured by applying a threshold on the Hamming distance, here set as $d_H \leq 3$, which groups configurations differing by at most three joint states. Microstates that do not belong to any cluster defined by this threshold appear as isolated leaves in the dendrogram and are referred to as singletons. Physically, singletons correspond to metastable configurations that are mechanically and structurally isolated, lacking nearby alternative folding pathways.

Unlike biological or chemical systems typically described within a thermodynamic equilibrium framework, the present system is dissipative and mechanically driven. As a result, energetic proximity alone does not fully characterise folding pathways. To make energetic and structural information directly comparable, we therefore order and colour the leaves of the disconnectivity graph according to the Hamming clustering, with sin-

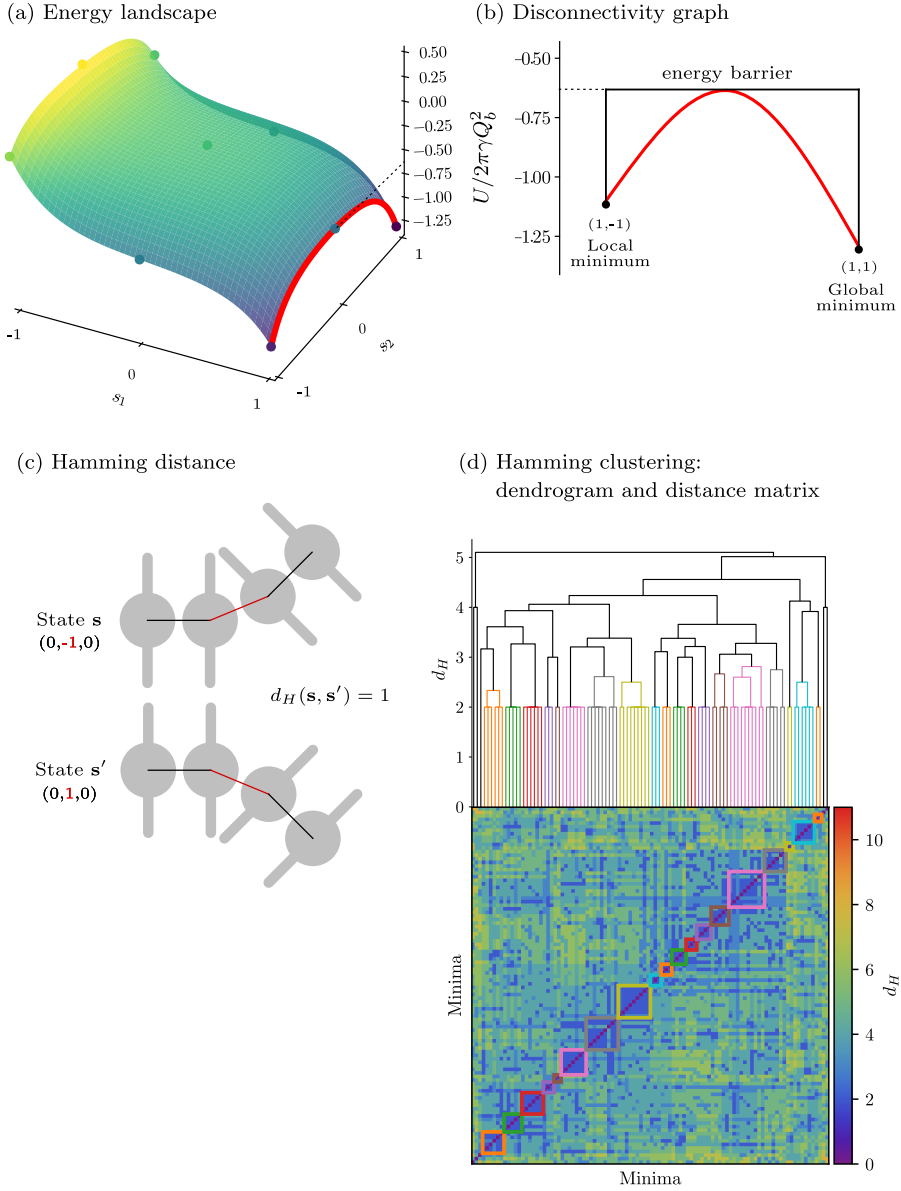


Figure 5.6: Analysis tools of folding landscapes. (a) Energy landscape of a $N = 3$ chain in the joint-state space (s_1, s_2) . (b) Corresponding disconnectivity graph, where each leaf represents a local minimum and branches merge at the energy level of the lowest barrier connecting their basins of attraction. (c) Illustration of the Hamming distance. (d) Hierarchical clustering of metastable states based on the Hamming distance for a $N = 12$ fold-biased chain. The dendrogram groups structurally similar folded configurations into families, while the associated Hamming distance matrix highlights clusters of closely related states using the same cluster colours as the dendrogram.

gletons shown in black. This representation enables a direct comparison between configurations that are close in configuration space and those connected by low-energy barriers. The combined use of disconnectivity graphs and Hamming-based analysis thus provides a complete framework to describe folding landscapes in programmed capillary chains.

We now illustrate how these analysis tools operate on a specific chain sequence: the fold-biased chain. For a moderate chain length $N = 10$, it provides a rich yet interpretable energy landscape.

Figure 5.7 shows the disconnectivity graph of such a fold-biased chain, together with the associated Hamming dendrogram and distance matrix. The disconnectivity graph reveals 13 metastable microstates, and the first five lowest-energy microstates are shown. Although several distinct microstates appear in the graph, they correspond to only a smaller number of macrostates that are energetically degenerate. This illustrates how the same folded object may emerge through multiple folding pathways, a feature that is not captured when only final geometries are considered. The Hamming-based analysis in Figure 5.7(b) provides a complementary view. Indeed, in the present case, no singleton is present, meaning that each minimum is mechanically close to another one. For our dissipative, mechanically driven system, this proximity suggests that, once the system is trapped within a given cluster, moderate agitation can facilitate transitions between microstates within the same cluster, whereas transitions between distant clusters require overcoming larger structural and energetic barriers.

Let us now probe the sensitivity of the folding landscape to local mutations by modifying a single element in the fold-biased chain. Figure 5.8 shows three representative cases, where the element at position 3 is changed while the rest of the sequence is kept unchanged.

In the first case (Figure 5.8(a)), the mutation induces opposite folding tendencies in the two adjacent joints. This local incompatibility suppresses alternative folding pathways, leaving a single metastable microstate, in contrast with the 13 microstates observed for the original chain. In the second case (Figure 5.8(b)), the mutation introduces bistability in the two adjacent joints. This results in the appearance of nine metastable microstates organised into small Hamming clusters, together with two isolated microstates that appear as singletons in the clustering. Finally, in the third case (Figure 5.8(c)), the mutation induces repulsion in both adjacent joints. Despite this local straightening tendency, the

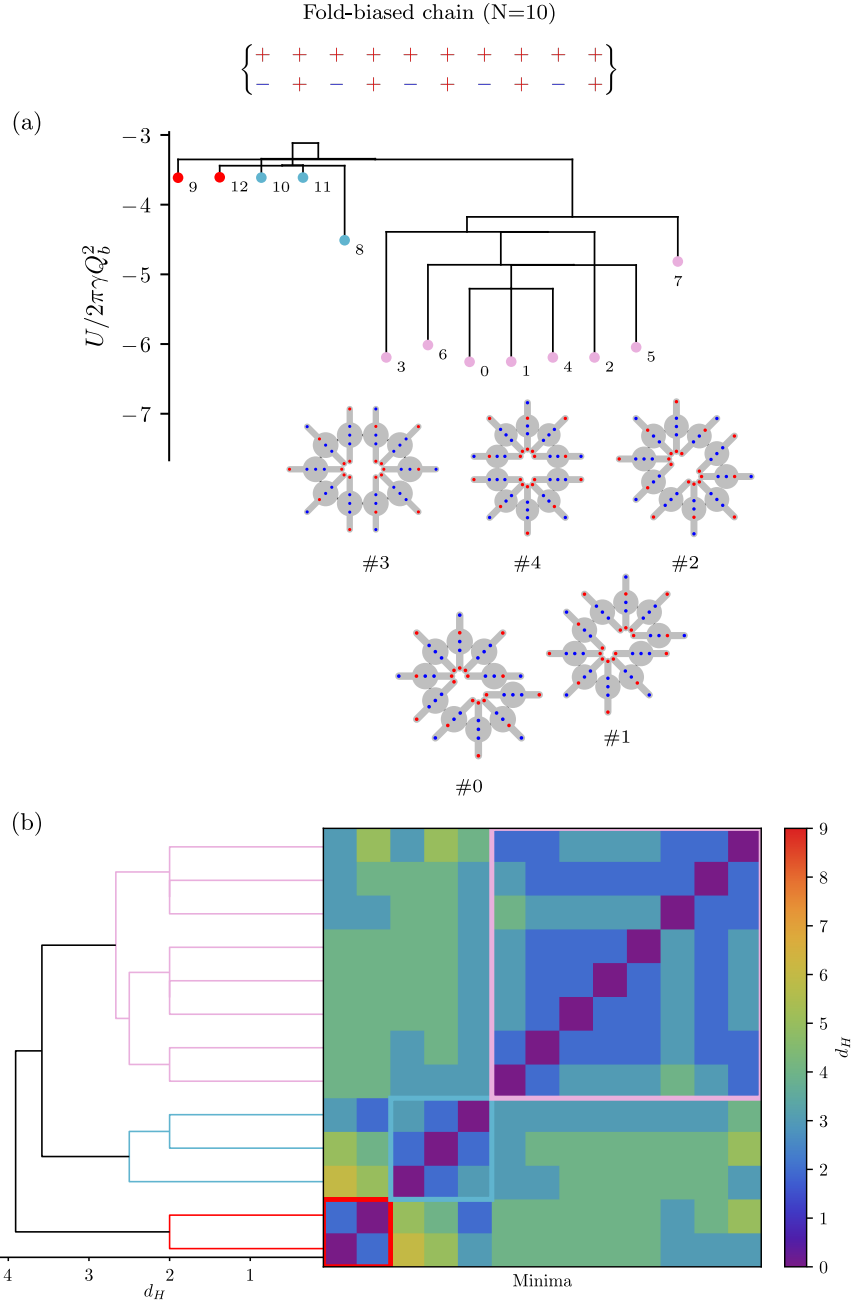


Figure 5.7: Fold-biased chain N=10. (a) Disconnectivity graph with minima ordered by Hamming distance and coloured by identical Hamming clusters. The first five minimal microstates are shown, although they correspond to only three macrostates. (b) Associated dendrogram and Hamming distance matrix based on the definition of Eq. (5.5).

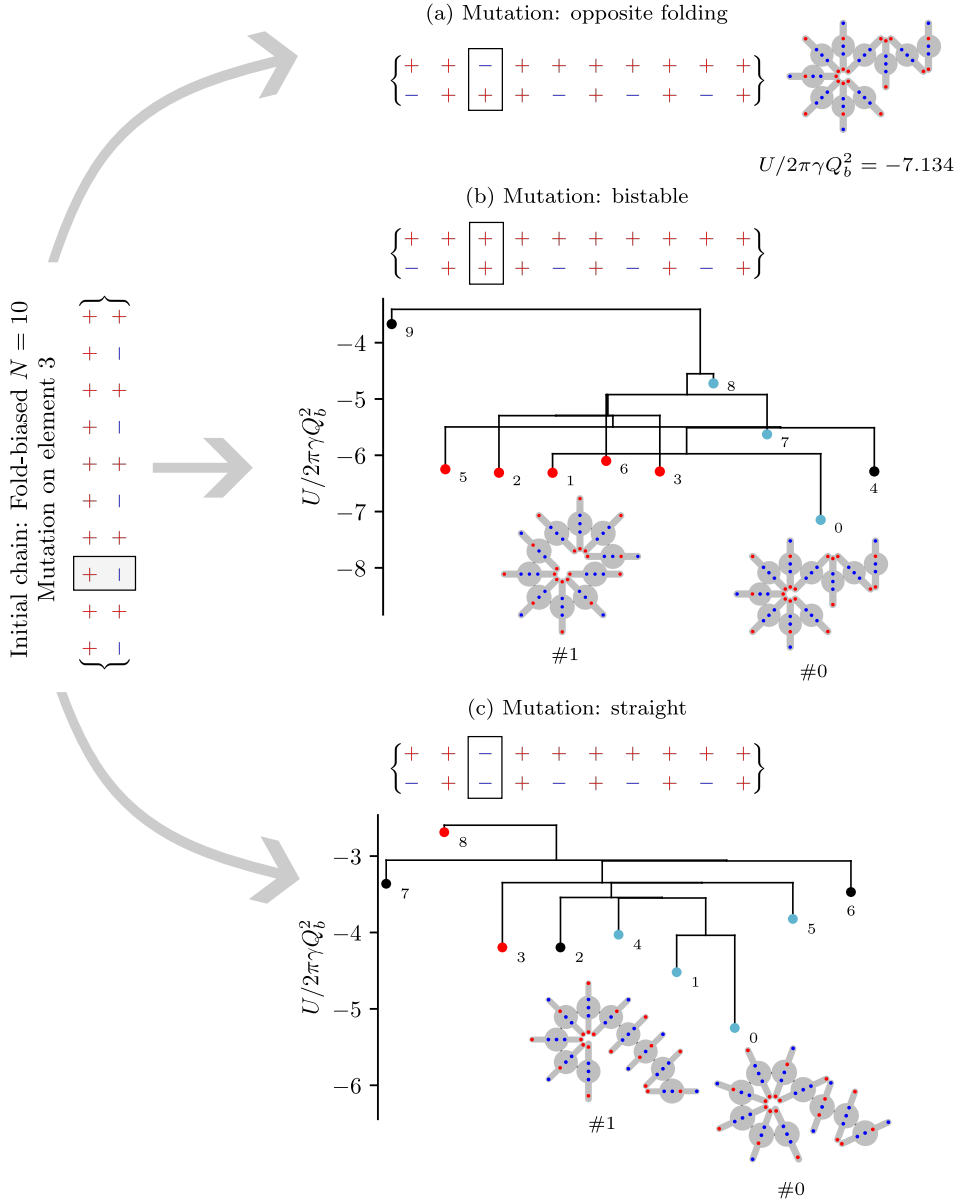


Figure 5.8: Mutation effect on fold-biased chain $N=10$. Disconnectivity graphs and associated first two minimal configurations for mutation on element 3. (a) Mutation inducing opposite foldings compared to the rest of the chain in the two adjacent joints of element 3. Only one minimal configuration exists. (b) Mutation inducing bistable foldings in the two adjacent joints of element 3. (c) Mutation inducing repulsion in the two adjacent joints of element 3. In this case, one should note that the overall curvature of the chain and the proximity of central charges still induce a folding in the ground state (#0).

overall curvature of the chain and the attraction between central disks still favour a folded joint in the ground state. The folding occurs at the joint closest to the most strongly curved region of the chain. Here again, the Hamming analysis reveals isolated microstates that appear as singletons, reflecting mechanically and structurally isolated configurations.

It is worth noting that both the bistable and opposite-folding mutations lead to the same ground-state configuration. More generally, several identical minimal macrostates occur across the different mutated chains, despite substantial differences in their local capillary codes. This situation is reminiscent of biological coding, in which distinct genetic sequences can give rise to similar structural motifs.

Taken together, these examples demonstrate that even a single local mutation can drastically reshape the folding landscape, altering both the number of metastable states and the organisation of folding pathways, while still preserving access to some identical minimal configurations.

The observation that distinct local mutations can preserve the same minimal macrostate naturally raises an inverse-design question: For a given chain length N and a target folded geometry $G^\star$, how many distinct capillary codes produce this same target?

Formally, if $g(C)$ denotes the ground macrostate obtained from a code $C = (c_1, \dots, c_N) \in \{1, \dots, 4\}^N$, we define the degeneracy

$$\Xi_N(G^\star) = \left| \left\{ C \in \{1, \dots, 4\}^N : g(C) = G^\star \right\} \right|, \quad (5.6)$$

which counts the number of sequences whose folding landscape selects $G^\star$ as its minimal geometry. This quantity directly measures the redundancy of the capillary encoding and therefore the programmability of the target structure.

To characterise how a given target $G^\star$ is organised locally in sequence space, we introduce a mutation radius around a reference code C_0 . The mutation radius r simply corresponds to allowing up to r element substitutions along the chain. In other words, we consider all sequences that differ from C_0 in at most r positions. The size of this set of sequences $\mathcal{B}_r$ is given by

$$|\mathcal{B}_r| = \sum_{k=0}^r \frac{N!}{k!(N-k)!} 3^k, \quad (5.7)$$

since each mutated element can take three alternative types. For a given reference sequence C_0 with ground-state macrostructure $G^\star = g(C_0)$, we

define

$$f_{\text{keep}}(r) = \frac{\text{number of sequences in } \mathcal{B}_r \text{ that keep } G^*}{|\mathcal{B}_r|}, \quad (5.8)$$

which measures the fraction of sequences within mutation radius r that preserve the same minimal macrostate as the reference chain. By contrast, the global probability $p(G^*)$ measures the fraction of all possible sequences in $1, \dots, 4^N$ that produce G^* as their ground state.

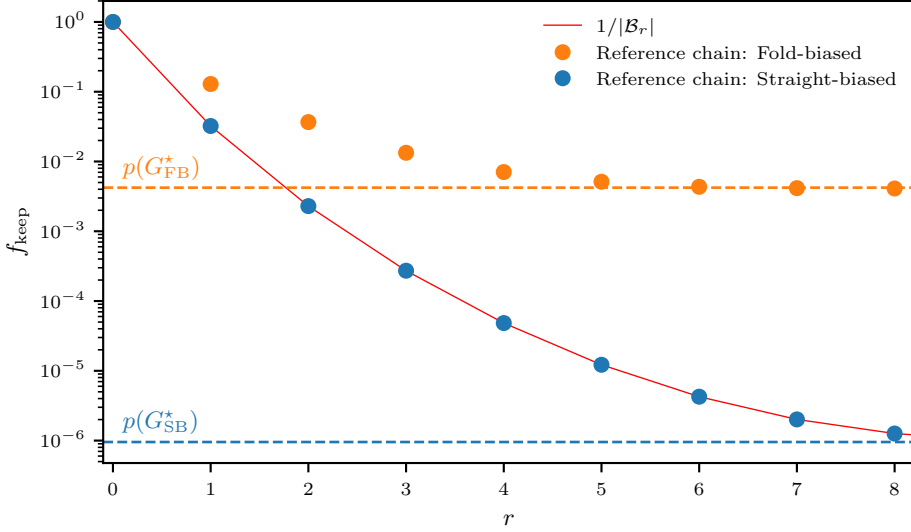


Figure 5.9: Mutational robustness and global degeneracy for $N = 10$. Fraction $f_{\text{keep}}(r)$ of sequences within mutational distance $\leq r$ from a reference code that produce the same ground-state macrostructure (G_{FB}^* for the fold-biased chain reference, G_{SB}^* for the straight-biased chain reference). Dashed horizontal lines indicate the corresponding global probabilities $p(G_{\text{FB}}^*)$ and $p(G_{\text{SB}}^*)$ estimated from Monte Carlo sampling over 10^5 random sequences. The red curve shows the lower combinatorial limit $1/|\mathcal{B}_r|$, corresponding to the situation where only the original sequence yields its target macrostate.

Figure 5.9 shows $f_{\text{keep}}(r)$ for, again, our two extreme reference sequences of length $N = 10$, the fold-biased chain and the straight-biased chain, associated respectively with their macrostate G_{FB}^* and G_{SB}^* . In both cases, the fraction decreases as the mutation radius increases, reflecting the progressive loss of structural stability as more elements are modified. However, the decay strongly depends on the nature of the reference code and the associated target macrostate.

The fold-biased chain exhibits a gradual decay: even for several simultaneous mutations, i.e. $r \geq 2$, a finite fraction of sequences still fold into

G_{FB}^* , meaning that this fully folded macrostate is not a rare configuration. Again, the fold-biased chain benefits from collective aggregation of central disks that reinforces curvature and partially compensates local perturbations. In contrast, the straight-biased chain displays a much sharper decay of $f_{\text{keep}}^{\text{SB}}(r)$. It follows closely the lower bound $1/|\mathcal{B}r|$, which corresponds to the limiting case where only the original sequence retains $G^*\text{SB}$. This behaviour indicates that the straight configuration is highly sensitive to mutations. Indeed, the ground state is in this case determined by local nearest-neighbour repulsion on both sides of each joint. Once these local constraints are perturbed, no collective mechanism stabilises the straight geometry, and the target macrostate G_{SB}^* is immediately lost.

The dashed horizontal lines in Figure 5.9 indicate the global probabilities $p(G_{\text{FB}}^*)$ and $p(G_{\text{SB}}^*)$ obtained from Monte Carlo sampling over 10^5 random sequences. Using $\Xi_N(G^*) \simeq 4^N p(G^*)$, this provides an estimate of the total degeneracy of each target structure across the full sequence space. While $f_{\text{keep}}(r)$ quantifies the local mutational robustness around a specific reference code, $p(G^*)$ measures the global prevalence of the corresponding macrostructure across the entire sequence space. As the mutation radius r increases and approaches the full chain length N , $\mathcal{B}r$ spans all possible sequences. In this limit, the local fraction $f_{\text{keep}}(r)$ necessarily converges to the corresponding global probability $p(G^*)$.

The numerical analysis above establishes how the capillary sequence, through its encoding, its size N and the charge ratio Q_c/Q_b , controls both the number of metastable states and the organisation of folding pathways. We now examine how these theoretical predictions manifest experimentally.

5.4.2 Experimental realisation

To experimentally illustrate the programmability of folded configurations through sequence encoding, we first consider short chains with $N = 8$ elements. For such a chain length, the theoretical landscape predicts a limited number of accessible configurations and well-defined ground states primarily governed by nearest-neighbour interactions, as illustrated in Figure 5.3. This is a natural starting point for experimental validation. Figure 5.10 presents three representative configurations obtained experimentally: a straight chain, a zigzag chain, and a closed-loop configuration.

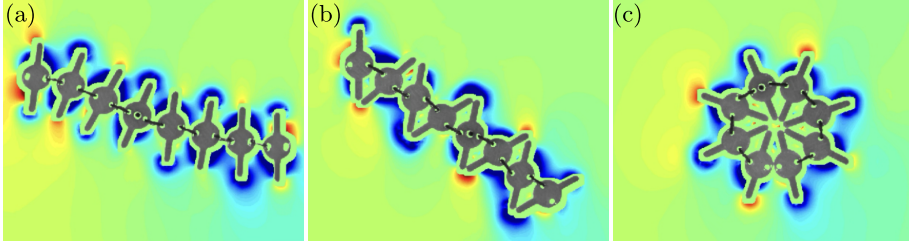


Figure 5.10: Deterministic configurations $N = 8$. Liquid profiles around self-folding chains $N = 8$ in colour scale: red for upward and blue for downward deformations. Three examples are shown. (a) The linear structure obtained with a straight-biased chain. (b) Zigzag line when pairs of successive tips attract each other. (c) A loop is formed with a fold-biased chain.

The straight configuration, shown in Figure 5.10(a), is realised using the straight-biased encoding introduced in the theoretical section. The straight configuration is stabilised by persistent repulsion and constitutes the only mechanically stable configuration identified in the exploration of discrete configurations performed in the previous subsection. As confirmed in Supplementary Movie S1, moderate perturbations do not destabilise the structure, which relaxes back to the linear configuration.

To further probe the robustness of this state and to allow the chains to explore their configuration space, experiments are performed in a vertically vibrated bath of pure water, 6 mm deep, in a rounded rectangular container of 13×17 cm, mounted on an electromagnetic shaker. The bath is driven sinusoidally at fixed frequency $f = 30$ Hz with a controlled acceleration $\Gamma = a/g = 1.2$, i.e. slightly above the Faraday instability threshold of order unity for our system, so that irregular Faraday waves develop. These chaotic surface waves provide mechanical agitation without directly imposing any specific folding mode, allowing the chain to explore its configuration space while remaining confined to the interface. Similar approaches have been used in the broader context of non-equilibrium capillary self-assembly [101].

The response of the straight configuration is also shown in Supplementary Movie S1. One can see that, although the final configuration remains predominantly straight, some joints are slightly folded, i.e., the angle differs from 0° but is not $\pm 45^\circ$, which would correspond to tip contact. Two initial hypotheses can be considered. First, the contact line may become pinned at a different location due to agitation, slightly modifying the effective capillary charge distribution. Second, our theoretical analysis considered only the discrete joint configurations $-45^\circ, 0^\circ, +45^\circ$, whereas

the experimental system spans a continuous range of angles. As a result, intermediate configurations may appear, corresponding to compromise states between repulsive tip interactions and the chain’s tendency to curve due to attractive central disks.

When the capillary sequence is designed to favour alternating local curvature, successive joints preferentially fold in opposite directions, leading to a zigzag configuration, shown in Figure 5.10(b) and Figure 5.1.

A loop configuration, presented in Figure 5.10(c), corresponds to the fold-biased chain discussed in the theoretical section. For $N = 8$, this coding yields a closed loop in agreement with the predicted ground state.

We now turn to longer chains with $N = 10$, for which the theoretical analysis predicts a richer folding landscape with multiple metastable configurations. Since the fold-biased chain was investigated in detail numerically, we focus our experimental investigation on this sequence. Under the chaotic Faraday waves, the chain explores different regions of configuration space and transitions between metastable states. Supplementary Movie S2 presents sequences of folding and unfolding events that progressively lead to increasingly folded structures. Selected snapshots are shown in Figure 5.11, highlighting distinct metastable configurations observed experimentally. In the first two configurations (a,b), one can see that some tips carrying opposite charges have attached to each other, thereby creating a capillary bridge that can only be broken by mechanical agitation. The final configuration in (f) is very close to the five lowest-energy minima identified theoretically in the discrete configuration space for the same chain and shown in Figure 5.7. These observations confirm that the experimental chains can reach the predicted ground state while also transiently occupying multiple metastable configurations, consistent with the computed energy landscape.

At this stage, the system constitutes a proof-of-concept realisation of programmable capillary self-folding. The present components are millimetric, ensuring robustness and visual accessibility. However, reducing the size of the elements would increase the relative strength of capillary interactions, thereby sharpening the selectivity of folded states. In parallel, fabrication strategies could be refined to better control contact-line pinning and minimise variability in effective capillary charges.

Finally, the mechanical energy injected by the Faraday waves acts as an external source of agitation, allowing the chain to overcome energy barriers between metastable states. A quantitative comparison between the

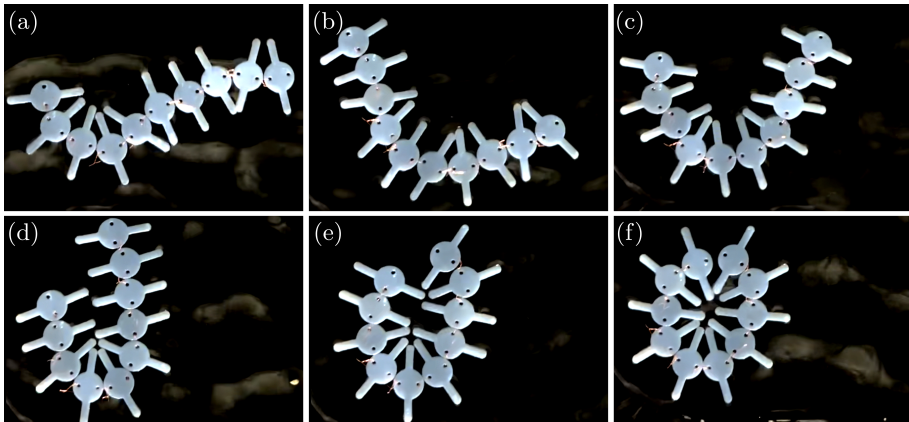


Figure 5.11: Experimental exploration of the folding landscape for a fold-biased chain with $N = 10$. (a-f) Snapshots extracted from the supplementary video showing distinct metastable configurations visited under vertical vibration. (f) Corresponds to the experimental ground macrostate.

energy injected by the waves and the computed energy barriers would help establish a link between mechanical forcing and the exploration of metastable configurations, and could eventually enable controlled activation of specific folding pathways in a similar approach as Thomson *et al.* [101].

5.5 Summary

We have shown that capillary chains constitute a mesoscale analogue of molecular folding. The discrete capillary code, implemented by one central monopolar charge and two branch dipoles per element, controls both the final folded geometry and the complexity of the associated energy landscape. At the pair level, the interaction map reduces the folding outcomes to three joint states $s \in \{-1, 0, +1\}$, providing the local rule underlying collective folding. At the scale of the full chain, these local rules combine cooperatively, generating a high-dimensional energy landscape whose structure depends on chain length and sequence. By tuning chain length, charge ratio Q_c/Q_b , and sequence design, it is possible to program not only target structures but also the number, degeneracy, and organisation of metastable states.

Experimental observations for $N = 8$ confirm deterministic folding governed by nearest-neighbour interactions. For longer chains such as $N =$

10, the landscape becomes significantly richer, with multiple competing folded configurations separated by finite barriers. Under controlled vertical agitation, the chain transitions between these metastable states, demonstrating real-time exploration of the predicted folding landscape.

Supplementary resources

Access to the supplementary videos and 3D files associated with this chapter:



Folded configuration created by a $\{\bar{-} \bar{-}\}$ pair.
 Local deformations of the liquid interface are revealed using the reflection of a striped pattern on the surface.
 Credits: Axel Franckart.





II

Manipulation

This second part focuses on an alternative and complementary strategy, in which the liquid interface itself is programmed to manipulate floating objects. Instead of encoding information in the particles, controlled deformations of the interface are imposed using fixed structures or actively actuated capillary elements. These prescribed liquid landscapes create effective potential fields that guide, trap, transport, or sort floating objects based on their capillary properties.

This discovery, indeed, is almost of that kind which I call Serendipity, a very expressive word, which, as I have nothing better to tell you, I shall endeavor to explain to you... I once read a silly fairy tale, called “The Three Princes of Serendip”: as their Highnesses travelled, they were always making discoveries, by accidents and sagacity, of things which they were not in quest of... now do you understand Serendipity?

-Horace Walpole

6

Programmable liquid interfaces

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In this chapter, we show that arrays of spines can be combined to generate programmable liquid landscapes whose characteristic size exceeds the capillary length. We demonstrate how these engineered interfaces can be exploited for controlled manipulation of floating particles, thereby introducing static interface programming as the first manipulation strategy of Part II.

The results presented in this chapter are partially published as

M. Delens, A. Franckart, D.M. Harris, and N. Vandewalle, *3D-printed spines for programmable liquid topographies and micromanipulation*, Nature Communications **16**, 4348 (2025).
Editors’ highlights: Applied physics and mathematics.

6.1 Motivations

This chapter marks the transition from capillary-driven self-assembly to interface-based manipulation, where floating objects are guided by prescribed liquid landscapes rather than by mutual interactions.

As discussed in Chapter 1, the horizontal extent of capillary deformations generated by isolated objects is intrinsically limited by the capillary length λ , which constrains their ability to guide particle motion over large distances. In contrast to the interaction-driven approaches developed in Part I, the strategy explored here relies on externally imposed liquid landscapes that act as prescribed energy fields.

In this chapter, we show that this limitation can be overcome by geometry alone, without relying on external actuation or particle-specific properties. Our objective is to create extended, programmable liquid topographies by combining simple conical spines arranged on regular or custom lattices. By controlling only the geometry of the spines and their spatial organisation, we demonstrate that a wide variety of functional and even artistic liquid landscapes can be generated, on which floating objects can subsequently be manipulated.

On the theoretical side, we build on the Linear Superposition Approximation introduced in Chapter 1 to describe collective interface deformations, complemented by a simple force-balance model. Experiments with 3D-printed arrays of conical spines and numerical simulations are used to assess the validity of these approaches.

Supplementary videos illustrating the experimental dynamics discussed in this chapter, as well as the code to create artistic devices, and the 3D files are made accessible through the [supplementary information](#) of the associated article and the lab's [GitHub](#). For ease of access, QR codes linking to these resources are provided at the end of the chapter.

6.2 Single spine

We consider a single conical spine piercing the water-air interface. Figure 6.1(a) defines the geometrical parameters of the spine: the base radius R and the height H , which together set the half-opening angle $\alpha = \arctan(R/H)$. When the spine intersects the interface, an axisymmetric meniscus forms around it, with the contact line located at a height $h + h_0$ above the base, where h_0 denotes the height of the undisturbed

liquid surface. A typical experimental meniscus obtained around a 3D-printed spine with $\alpha = 3^\circ$ is shown in Figure 6.1(b).

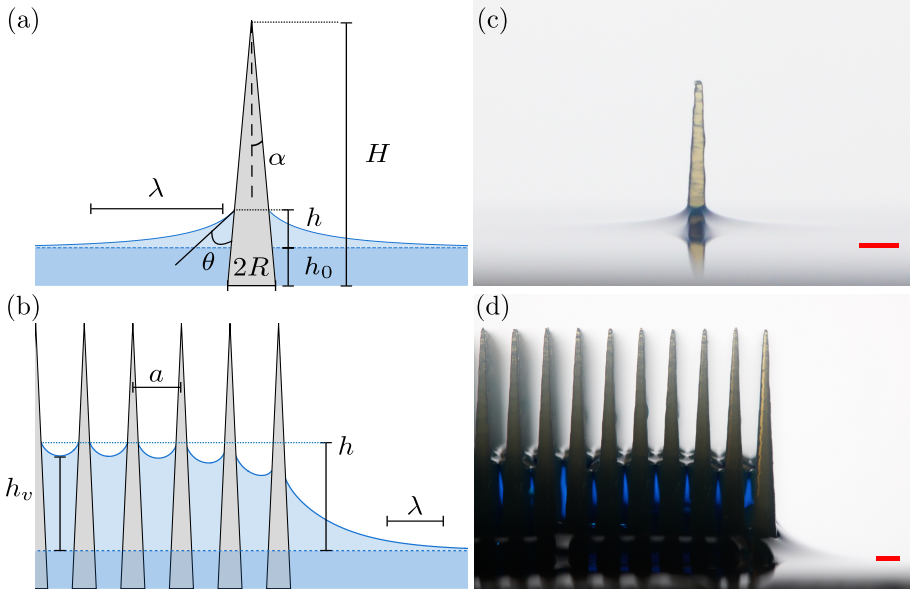


Figure 6.1: Superposition of menisci. (a) Sketch of a single conical spine crossing the liquid-air interface. The geometrical characteristics of the spine H and R and the associated meniscus height h are emphasised. The dashed horizontal line denotes the undisturbed interface $z = 0$ at height h_0 from the spine's base. (b) Sketch of the edge of a square array of spines separated by a . The water profile highlights the slight undulation of the interface between the spines from a maximal height h to a lower liquid height h_v between spines. (c) Picture of a 3D-printed conical spine crossing blue-coloured water and illustrating the meniscus formation. (d) A close-up of the liquid menisci at the edge of a square lattice. The liquid interface inside the lattice is 3.5 mm above the undisturbed interface. Scale bars: 1 mm.

As recalled in Chapter 1, the meniscus generated by an isolated axisymmetric object is described, in the small-slope limit, by a modified Bessel function $K_0(r/\lambda)$, with an amplitude set by the capillary charge as given in Eq. (1.20). We refer the reader to Chapter 1 for the general derivation and focus here on how the geometry of a conical spine sets the effective capillary charge.

For a vertical cylinder of radius $R \ll \lambda$, the capillary charge Q can be determined using Archimedes' principle, stating that, at equilibrium, the weight of the liquid lifted in the meniscus must equal the capillary force acting on the contact line, leading to $Q_{\text{cyl}} = R \cos \theta$ [102], where θ is the

equilibrium contact angle defined in the sketch of Figure 6.1. In the case of a conical spine, the same force-balance argument applies, but the radius of the contact line now depends on the vertical position of the interface along the cone.

Assuming that the contact line remains circular and axisymmetric, we approximate the effective capillary charge of the spine as

$$Q = (R - (h + h_0) \tan \alpha) \cos(\theta + \alpha), \quad (6.1)$$

where the factor $\cos(\theta + \alpha)$ accounts for the local inclination of the solid surface at the contact line. This expression reduces to the cylindrical result in the limit $\alpha \rightarrow 0$ and provides a simple geometrical estimate of the meniscus amplitude generated by a single spine.

6.3 Regularly arranged spines

A primary motivation of the present chapter is to overcome the capillary length limitation by creating giant menisci with a horizontal extension much larger than λ . In other words, we aim to achieve a steady situation in which the interface is tilted across the entire container. To reach this challenging situation, we consider an array of identical conical spines. Each spine crossing the interface is the origin of a meniscus, described by Eq. (1.20). When they are close to each other, i.e., when the lattice spacing $a \approx \lambda$, the menisci created on neighbouring spines superimpose. Regular microstructures are also notably used to mimic the wetting of specific surfaces [103, 104], like porous materials [105, 106] or super-hydrophobic surfaces [107]. Figure 6.1(c,d) shows a sketch and a picture of the edge of a square lattice of spines. The liquid rises above the undisturbed interface within the lattice, demonstrating that the effect is significant. On average, the interface on the whole lattice is nearly flat. Nevertheless, small valleys are seen in between neighbouring spines. In these valleys, the interface height h_v is slightly smaller than h .

Experimental measurements of the interface position were performed using optical means. All devices were designed using a Mathematica script that generates arrays of conical spines with prescribed geometry and lattice spacing, which were then exported as STL files and 3D-printed using a PolyJet printer. This fabrication method provides sufficient resolution to reliably produce the targeted spine geometries over a wide range of lattice spacings.

The printed lattices were placed at the centre of a Petri dish, and the liquid level was adjusted to define the reference height $z = 0$ and the bath level h_0 . Side-view imaging was used to measure the elevation of the interface at the contact line (h) and in the valleys between neighbouring spines (h_v). Top-view imaging and particle tracking were employed for micromanipulation experiments. The contact angle between water and the printed material was measured independently and remained constant across all devices. For the air-water interface, we measured a contact angle of $\theta = 53^\circ$ on our spines.

Figure 6.2(a) plots the heights h in orange and h_v in purple dots as a function of the unit cell area A for 12 square lattices. All lattices are 3D printed with fixed spine shapes ($R = 0.2$ mm and $\alpha = 1.15^\circ$) and varying lattice spacing a . The accessible range of lattice spacings a and spine radii R is constrained by fabrication limits, with reliable printing achieved down to inter-spine distances of approximately 0.3 mm. If this distance is reduced further, the gap between the spines becomes too small, causing complications during 3D printing and potentially resulting in the individual spines sticking together. Consequently, the chosen lattice spacing a and base radius R are determined by the limitations of our methodology.

For small lattice spacing a , h and h_v are quite similar, while the difference between those couples of points seems to increase with the unit cell area A . High water elevations h up to 5-6 mm are reached with small lattice spacing. This order of magnitude is comparable to the capillary rise in a millimetre tube as given by Jurin's law [108].

Following Chapter 1, we describe the interface using the Linear Superposition Approximation (LSA), which remains valid provided local slopes remain small. Based on previous studies on interacting cylindrical menisci [39], we assume this approximation to hold when the effective the spine spacing satisfies $a > 4(R - (h + h_0)\tan\alpha)$. Under this framework, the liquid elevation at a position $\vec{r} = (x, y)$ inside the lattice is given by:

$$z(x, y) = Q \sum_{k, \ell} K_0 \left(\frac{|\vec{r} - \vec{r}_{k, \ell}|}{\lambda} \right) = Q\sigma(x, y) \quad (6.2)$$

where k and ℓ are lattice indices running over the entire structure, with $\vec{r}_{k, \ell} = (ka, \ell a)$ for the square lattice. Looking around the central spine, i.e. when $k = \ell = 0$, and substituting Q using Eq.(6.1), one finds the

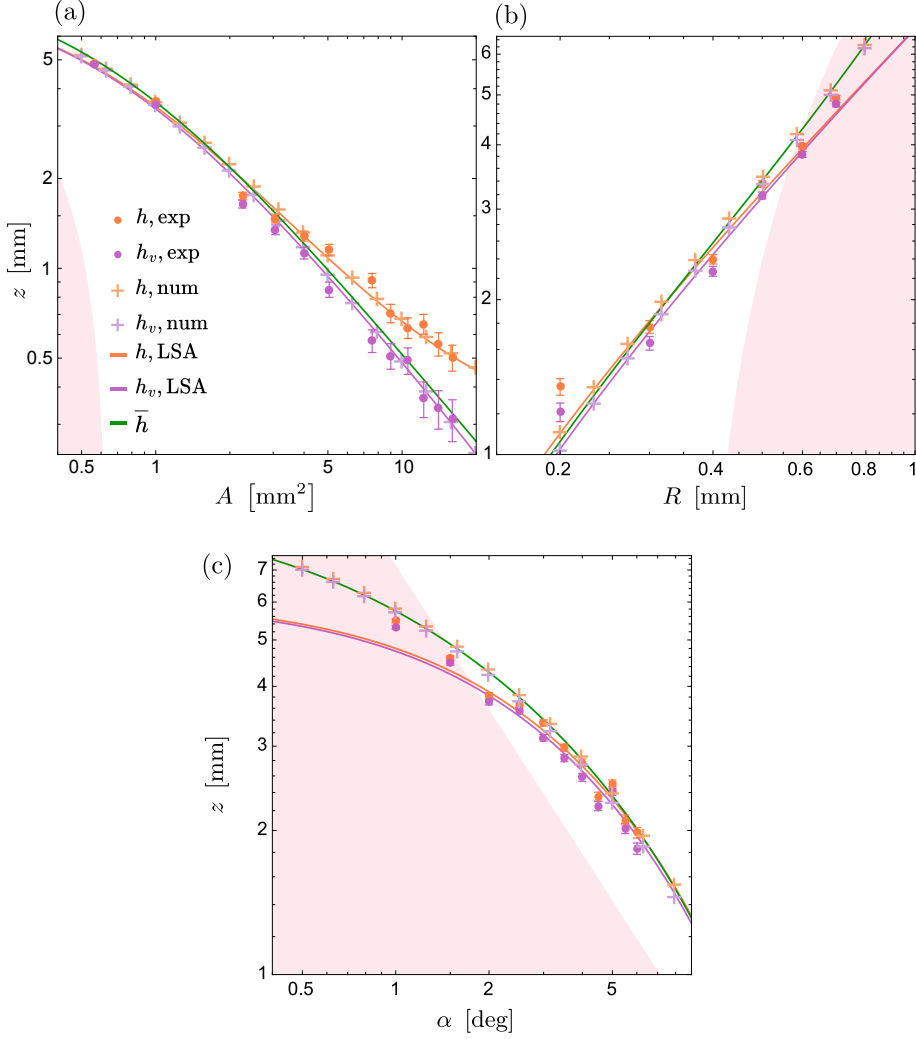


Figure 6.2: Experiments, numerics and models for liquid elevation inside regularly arranged spines. (a) Measured height at meniscus h and between spines h_v of water in square lattice as a function of the unit area A . Experimental and numerical results are presented. Spines' characteristics are $R = 0.2$ mm and $\alpha = 1.15^\circ$, and the bath level is $h_0 = 0$ mm. The orange and purple curves are predictions of Eqs. (6.3) and (6.4), respectively. The red region is where the superposition approximation is no longer valid. The green curve represents $\bar{h}$, the solution from Eq. (6.6), the force balance model. (b) Elevations h and h_v of the interface in a square lattice as a function of the spine radius R when $\alpha = 3^\circ$, $A = 2.25$ mm² and $h_0 = 1$ mm. (c) Height h and h_v as a function of the angle α for spines of radius $R = 0.5$ mm, lattice spacing $A = 2.25$ mm², and bath level $h_0 = 1$ mm.

expression of the liquid elevation h at the contact line:

$$\begin{aligned}
h &= z(R - (h + h_0) \tan \alpha, 0) \\
&= (R - h_0 \tan \alpha) \\
&\quad \times \left(\frac{1}{\cos(\theta + \alpha) \sigma(R - (h + h_0) \tan \alpha, 0)} + \tan(\alpha) \right)^{-1},
\end{aligned} \tag{6.3}$$

and the liquid elevation of the valley in between neighbouring spines:

$$\begin{aligned}
h_v &= z(a/2, 0) \\
&= (R - (h + h_0) \tan \alpha) \cos(\theta + \alpha) \sigma(a/2, 0).
\end{aligned} \tag{6.4}$$

Figure 6.2(a) compares the LSA predictions for h and h_v with experimental data. The agreement is excellent across all tested lattice spacings. Additionally, numerical solutions of the nonlinear Young–Laplace equation are presented and confirm the accuracy and validity range of the LSA across all experimental configurations.

While we concentrated on the central spine to experimentally measure and calculate liquid elevation throughout the entire lattice, it is worth noting that the menisci at the lattice edges are distorted differently due to the absence of neighbouring spines, which can be observed in Figure 6.1(c) and (d).

Figure 6.2 (b) presents graphs of the experimental and numerical results for the liquid heights h and h_v in a square grid when the radius of the spine R increases, with the $A = 2.25 \text{ mm}^2$ and $\alpha = 3^\circ$ fixed. Figure 6.2(c) presents similar measurements for square arrays as a function of α and with other parameters fixed ($R = 0.5 \text{ mm}$ and $A = 2.25 \text{ mm}^2$). As expected, when the superposition approximation breaks down, it underestimates the liquid elevation, consistent with earlier observations [39]. For sufficiently small lattice spacings, the interface between neighbouring spines becomes nearly flat. In this regime, the mean elevation can be estimated from a force balance between capillary forces at the contact lines and the weight of the displaced liquid within the unit-cell area A . Assuming a flat interface at elevation $\bar{h}$, the force balance is expressed as:

$$\begin{aligned}
&2\pi\gamma \cos(\theta + \alpha) \left(R - (\bar{h} + h_0) \tan \alpha \right) \\
&= \rho g \left(A - \pi(R - (\bar{h} + h_0) \tan \alpha)^2 \right) \bar{h}.
\end{aligned} \tag{6.5}$$

This results in a cubic equation for $\bar{h}$:

$$\begin{aligned} & \pi \tan^2 \alpha \bar{h}^3 - 2\pi(R - h_0 \tan \alpha) \tan \alpha \bar{h}^2 \\ & + \left(\pi(R - h_0 \tan \alpha)^2 - 2\pi\lambda^2 \cos(\theta + \alpha) \tan \alpha - A \right) \bar{h} \\ & + 2\pi\lambda^2 \cos(\theta + \alpha)(R - h_0 \tan \alpha) = 0 \end{aligned} \quad (6.6)$$

The solution to this equation yields the average liquid height $\bar{h}$, capturing the behaviour of the liquid interface under conditions in which the LSA model fails as shown in Figure 6.2. For a cylindrical pillar, $\alpha = 0^\circ$ and Eq.(6.6) simplifies nicely to

$$\bar{h} = \frac{2\pi R \lambda^2 \cos(\theta)}{A - \pi R^2}. \quad (6.7)$$

While the LSA resolves both local valleys and edge distortions, the force-balance model captures only the mean elevation and therefore cannot account for spatial features essential to manipulation.

6.4 Specific liquid topography

The above results show that liquid height is controlled by the geometric characteristics A , R , and α of an array of conical spines. Thus, the geometry of each spine or the lattice spacing can be adjusted to pin the interface at different heights within a unique array. Having effectively captured the impact of these parameters on the liquid elevation, we can employ this method to program unique liquid topography.

The examples proposed in Figure 6.3 illustrate how simple spatial variations of the spine height H or lattice spacing a enable the design of a wide range of liquid landscapes, including inclined, sinusoidal, and radially symmetric profiles, as well as more complex topographies involving changes in gradient direction. The resulting interfaces are fully determined by geometry and demonstrate the versatility of fixed structures for static interface programming.

To program arbitrary and complex liquid topographies, we solve the inverse problem of Eq. (6.3): starting from the desired liquid height, we numerically calculate the corresponding spines and lattice parameters. This allows us to create any liquid landscape from a given target shape, as exemplified in Figure 6.4. From the grayscale image of the *Atomium*, the famous Belgian monument, shown in Figure 6.4 (a), we designed a lattice of truncated conical spines where each spine represents a pixel of

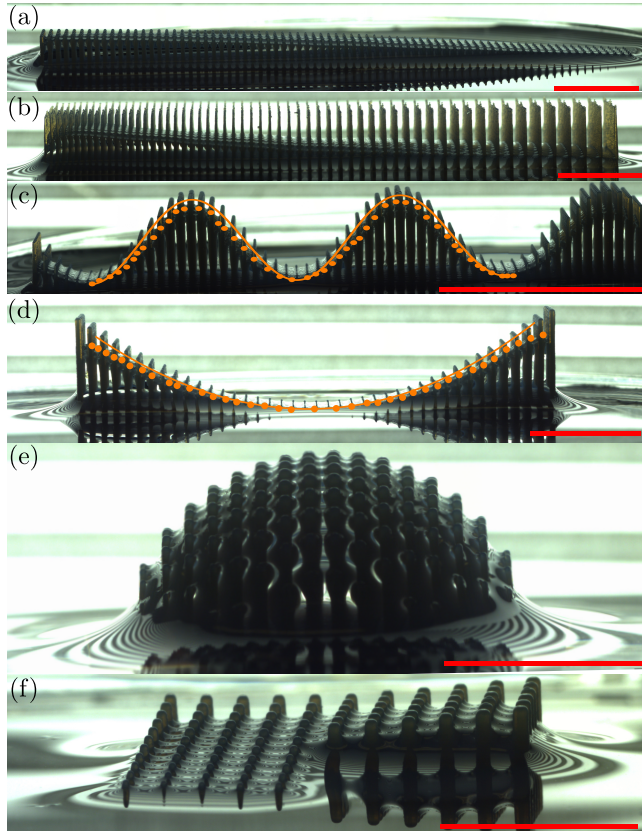


Figure 6.3: Examples of elementary topographies. (a) A liquid incline providing a tilted giant meniscus at equilibrium. The total height H of the spines gradually decreases along the lattice from left to right while the radius $R = 0.2$ mm is constant. (b) The same incline created by another lattice where the lattice spacing a gradually increases from left to right. (c) A sine wave topography created by sinusoidally varying the total height H of the spines of radius $R = 0.2$ mm. (d) A quadratic well created by varying quadratically the height H of spines of radius $R = 0.3$ mm. The experimental measurements and the predicted liquid elevation by Eq.(6.3) in devices c and d are plotted in the subfigures using dots and curves, respectively. (e) A hemisphere created by radially decreasing the total height H of spines of the same radius $R = 0.3$ mm. (f) Two adjacent inclines with perpendicular slopes, therefore, creating a 90° turn in the height gradient. The inclines are created by varying the height H of spines of radius $R = 0.5$ mm. Scale bars: 10 mm.

different total height H . The Atomium celebrates science and represents an enlarged body-centred cubic unit cell of iron. The values of H were determined based on the desired liquid elevation h , which is linked to each pixel value ranging from 0 to 255. As the liquid invades the lattice, it rises to different heights, resulting in a three-dimensional representation of the *Atomium*, as shown in Figure 6.4(b), which offers a perspective view of the experiment. Our method of designing the device that creates artistic liquid landscapes from any 2D images or 3D coordinates has been implemented in a Mathematica code available on our [GitHub](#) [109].

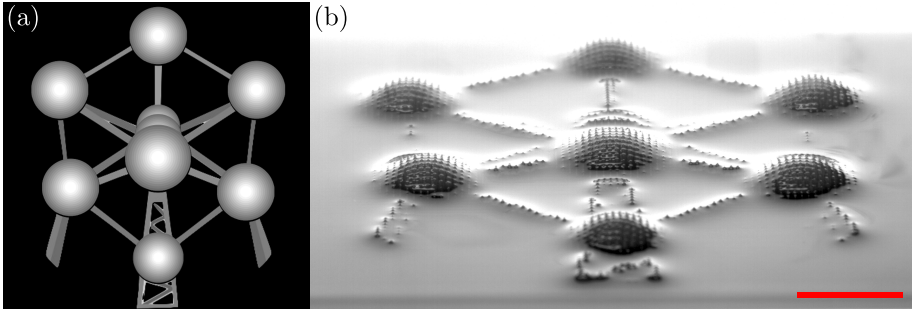


Figure 6.4: Artistic topography: The Atomium. From this simplified 2D-image of the *Atomium* monument in grey levels (a), a lattice of truncated conical spines has been designed and 3D-printed (b). As the liquid invades the device, it rises to reproduce the *Atomium*. Scale bar: 10 mm.

6.5 Meniscus-induced micromanipulation

Having established how arrays of spines can be used to generate extended and programmable liquid landscapes, we now turn to the consequences of such landscapes on the motion of floating objects. Here, particle motion is governed by the prescribed height field imposed by the spine array, rather than by the pairwise capillary interactions discussed in Part I.

In 2022, Peng *et al.* have notably achieved directional bubble transport on a few slippery oil-infused pillars with height-gradient [89]. Recognising that complex three-dimensional capillary transport can be achieved only by complexifying the liquid topography, we herein use specific arrays of spines as an effective strategy for particle transport at liquid interfaces. To test our strategy, we conducted transport experiments of a heavy submillimeter bead floating on desired liquid topographies. As a first experiment, we successfully achieved unidirectional micromanipulation using the array shown in Figure 6.3(a), forming a giant slope along the

interface. Figure 6.5(a) presents a 3D plot illustrating the $z(x,y)$ profile of the meniscus, calculated using Eq.(6.2), superimposed on the 3D STL file of the device. This plot effectively illustrates a liquid slope of 4° . The greyscale image within the same figure provides a top-down view of the device, with trajectories of $400\text{ }\mu\text{m}$ diameter beads colour-coded according to their instantaneous speed. Refer to the Supplementary Video S1 for the motion.

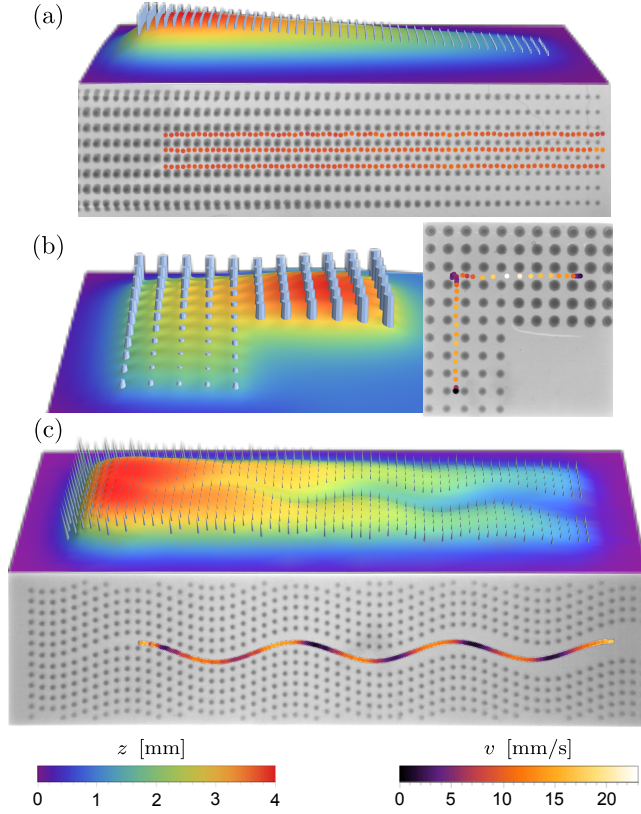


Figure 6.5: Micromanipulation over programmed liquid valleys. The 3D plots, calculated using Eq.(6.2), display the liquid landscape created by an arrangement of spines piercing the liquid. The plot is rainbow-coloured according to the liquid elevation, and the spines are light blue. In each subfigure, experimental trajectories of heavy submillimeter beads within the same arrangement are shown and colour-coded by speed, ranging from purple to yellow. Real-time movies are available at the end of the chapter and are labelled Supplementary Videos S1, S2, and S3 for figures (a), (b), and (c), respectively.

Similar motions are observed in each row, following the slope of the tilted interface. By varying the particle size, the steepness of the slope, or the lattice spacing, we observed similar behaviours but at different speeds. For instance, under the same incline, a $500\text{ }\mu\text{m}$ bead is faster than an $800\text{ }\mu\text{m}$ bead, which is also faster than a $400\text{ }\mu\text{m}$ bead. When testing slopes varying from 1° to 5° in increments of 0.5° , we observe a maximal speed for the slope of 3° for all bead sizes. The observed dynamics result from a balance between capillary driving forces and interfacial drag, which depends on particle size, immersion depth, and interface shape. Furthermore, the liquid interface is not only tilted but also slightly undulated between the heights h and h_v , following the periodic structure of the array, which significantly complicates the bead's dynamics. A detailed analysis of these effects lies beyond the scope of this chapter. However, it should be noted that because particles reach different speeds depending on their size as they exit the device, they come to rest at distinct positions. This observation opens up exciting possibilities for sorting particles based on size or wettability.

More strikingly, the multi-directional transport of particles can also be performed by other liquid topographies. Two examples are shown in Figure 6.5(b) and (c). Figure 6.5(b) presents the calculated liquid profile of the array displayed in Figure 6.3(f) and the trajectory of an $800\text{ }\mu\text{m}$ bead descending the slope. The bead first falls down the slope along the x-direction. When the height gradient in the x-direction vanishes, the bead briefly stops and then continues its descent along the y-direction gradient. The $800\text{ }\mu\text{m}$ stops permanently inside the device when the height gradient and the bead's inertia can no longer overcome the drag force and the slight undulation of the interface. The motion is shown in Supplementary Video S2. We note that smaller beads ($400\text{ }\mu\text{m}$ and $500\text{ }\mu\text{m}$) came to rest outside this device. Once again, different particles are sorted, and the array controls the final positions. In Figure 6.5(c), we display a particular lattice forming a sinusoidal valley with a slight slope, allowing the bead to make a series of turns while descending the hill. See Supplementary Video S3 at the end of the chapter for the real-time motion inside the sinusoidal valley. Unlike the constant speed measured on the liquid slope of Figure 6.5(a), one can observe from the color-coded trajectory of a $500\text{ }\mu\text{m}$ bead that it is always decelerated in the turns, i.e., when the direction of motion changes, just as in the 90° turn of Figure 6.5(b).

As an initial demonstration of actuation within this framework, we draw

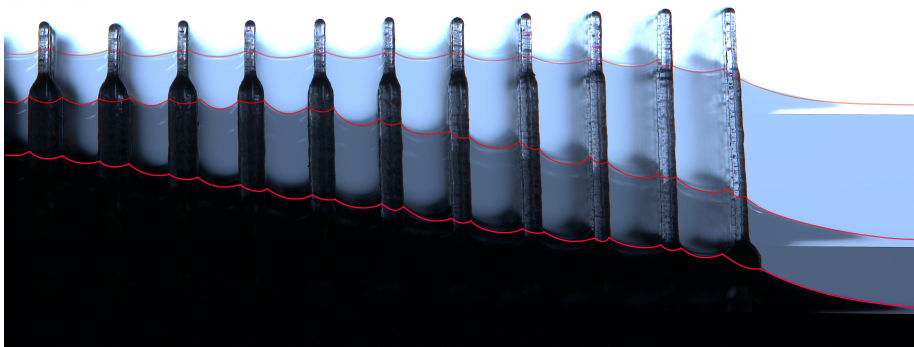


Figure 6.6: Time-dependent menisci on substructured spines. Experimental water profiles within an array of spines with substructures are presented for three different levels of bath liquid. Initially, the liquid interface is pinned to cylinders of identical radius. As the bath level descends, the liquid interface is pinned to cylinders of decreasing radius, and the liquid slope appears. The liquid interfaces are highlighted in red.

inspiration from the work of Zeng et al. [90], in which they manipulated floating objects by adjusting the liquid elevation within a vertical channel that has vertical variations in wettability. For our lattice, considering the simple case of cylinders ($\alpha = 0^\circ$), we have designed structural spines with substructures onto which the interface will be pinned as the liquid level falls. The upper part of the lattice consists of cylinders with small yet identical radii, creating a horizontal interface that traps particles. The lower part, uncovered as the liquid descends, consists of cylinders with decreasing radii to form a liquid slope and thus manipulate the floating particles. The menisci are, therefore, time-dependent. Figure 6.6 illustrates the upgraded device and demonstrates how the interface is pinned to the substructures as the liquid descends. Supplementary Video S4 showcases the manipulation of a $500\ \mu\text{m}$ bead by a combination of these devices, enabling the bead to make a complete 360° turn.

These illustrating examples offer promising prospects for precise object transport, such as positioning objects beneath a microscope lens, the utilisation of liquid curvature as a “capillary tweezer” [34, 110], or favoring specific structures on capillary self-assemblies, such as the side-by-side assembly of cylindrical particles on a curved interface [86, 87, 111, 112]. It is worth noting that this manipulation method works for objects of any nature, solid or liquid, as long as they are attached to the liquid interface. Furthermore, as long as the distance between the spines is on the order

of the capillary length, even microscopic objects can be controlled [90]. As the total size of the device is only limited by the fabrication process, one major and crucial application of our method could be the cleaning of interfaces from specific oil microdroplets and microscopic objects.

6.6 Summary

In this chapter, we demonstrated that arrays of conical spines provide a route to program static liquid interfaces over length scales exceeding the capillary length. By combining individual menisci through superposition, a wide variety of controlled liquid landscapes can be designed and realised experimentally. Beyond their static geometry, the spines also possess intrinsic subfeatures that enable limited reconfiguration of the liquid landscape through global control parameters. In particular, adjusting the bath level modifies the position of the contact line along each spine, thereby tuning the effective capillary charge and the resulting interface shape. This mechanism provides a first, quasi-static form of actuation that allows the liquid landscape to be smoothly reshaped without altering the underlying structure. Together, these results establish static interface programming as a robust and scalable foundation for capillary-based micromanipulation, while naturally motivating the actively reconfigurable and locally controlled strategies.

Supplementary resources

Access to the supplementary videos associated with this chapter:



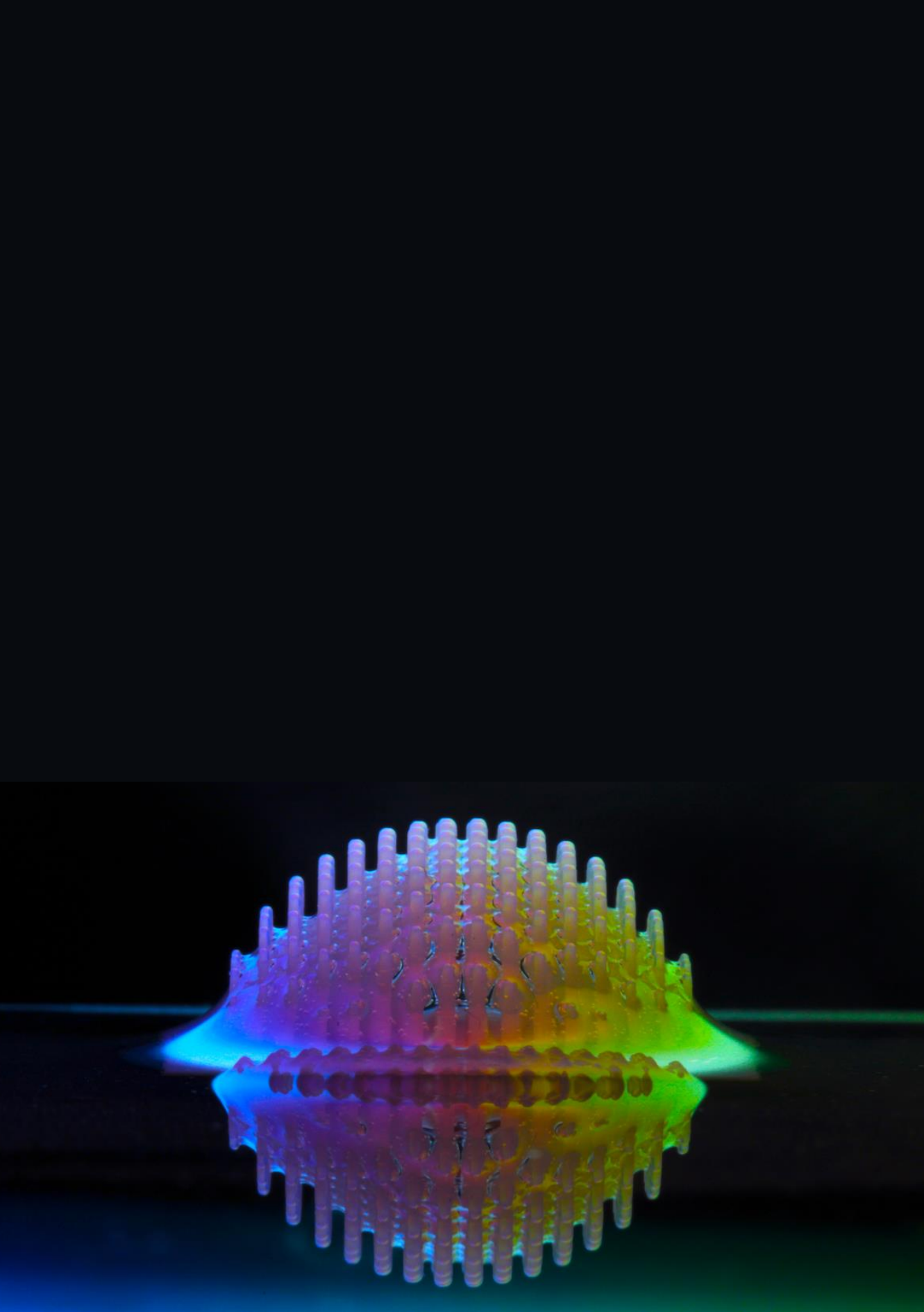
Access to the [GitHub](#) repository [109] containing the 3D files used in each experiment and the code used to generate the artistic devices:



Spines with radially decreasing height pierce the interface, producing a hemispherical meniscus. Controlled lighting and a Hue color circle are used to emphasize the surface curvature.

Credits: Axel Franckart and Megan Delens.





A scientist in his laboratory is not a mere technician: he is also a child confronting natural phenomena that impress him as though they were fairy tales.

-Marie Skłodowska-Curie

7

Actuated liquid landscapes

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In this chapter, we introduce Dipolar Capillary Actuators as elementary building blocks for dynamically programmable liquid landscapes. By actively controlling dipolar deformations of the interface, we demonstrate trapping, controlled displacement, and directional transport of floating particles, thereby extending the static interface programming strategies introduced in the previous chapter.

The results presented in this chapter are partially published as

J. Metzmacher, M. Delens, and N. Vandewalle, *Ring of capillary actuators as trap, tweezers and ratchet for floating particles*, Scientific Reports **15**, 20617 (2025).

7.1 Motivations

In the previous chapter, we demonstrated how fixed solid structures can be used to prescribe static liquid landscapes that transport floating objects along programmable paths. While powerful, this approach does not enable real-time reconfiguration of the interface, except by controlling the water level.

Here, we introduce a complementary strategy based on active control: liquid landscapes that can be dynamically reshaped in time. This is achieved by exploiting actuated capillary dipoles that continuously deform the interface under external control.

We introduce the Dipolar Capillary Actuator (DCA), a floating structure that tilts at the interface under an external magnetic field. This controlled tilt generates a capillary dipole, characterised by a positive slope on one side and a negative slope on the other, which selectively attracts or repels neighbouring particles. By arranging several DCAs into collective architectures, we demonstrate how such dipolar deformations can be combined to create functional liquid landscapes that act as capillary traps, tweezers, or ratchets. In particular, asymmetric arrangements of actuators generate non-reciprocal energy landscapes that induce directed motion, enabling one-way transport and rotation of floating particles [113].

Supplementary videos illustrating the experimental dynamics discussed in this chapter, as well as the 3D files for creating the DCA, are available in the supplementary information of the associated article. For ease of access, a QR code linking to this resource is provided at the end of the chapter.

7.2 Dipolar Capillary Actuator

As illustrated in Figure 7.1(a), the DCA comprises three components: a floater, a support, and a coil. The floater consists of a 4.5 mm diameter disk with two edge notches and a central protrusion holding a 1 mm thick magnet aligned parallel to the disk. The support maintains the floater in a fixed position and consists of two pillars that pass through the floater's notches. The coil surrounds the floater's protrusion and the pillars.

When the DCA is placed in a liquid, the floater naturally assumes a horizontal position at the surface, as shown in Figure 7.1(b). The contact line

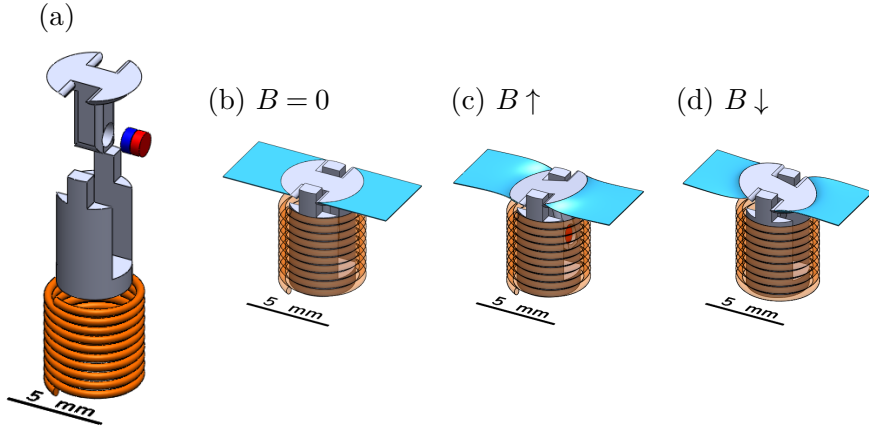


Figure 7.1: Dipolar Capillary Actuator (DCA). (a) Exploded view showing the floater, support, and surrounding coil. (b) Floater at rest on a flat liquid interface. (c,d) Interface deformation induced by the tilting of the floater under an applied vertical magnetic field, for opposite field orientations.

is pinned around the DCA perimeter. When current flows through the coil, a vertical magnetic field is generated around the floater's magnet, which, therefore, experiences a magnetic torque that attempts to align the magnetic moment with the field. However, surface tension forces and gravity oppose this torque. The balance between these opposing forces establishes a tilt angle α , causing the interface to deform, forming two lobes of opposite curvature, as one can observe on Figures 7.1(c,d). Reversing the field changes the floater's orientation, inverting the curvature.

As established in Chapter 1, the interface deformation generated by a pinned contact line can be expanded in capillary multipoles. Owing to the small thickness, near-neutral buoyancy, and circular geometry of the DCA floater, the monopolar contribution is negligible and the deformation is dominantly dipolar, i.e., $m = 1$ in Eq. (1.32).

We measured this deformation using the Schlieren method already introduced in Chapter 4 and used again in Chapter 5 [35, 36, 114], and fitted the dipolar expression of Eq. (1.32). As shown in Figures 7.2(a,b), our data are in good agreement with the theoretical profile. The dipolar capillary charge generated on the DCA is controlled by the magnetic field produced by the coil, which is proportional to the injected current. To determine how the surface deformation can be tuned with the DCA, we measured the dipolar charge $\pm Q_1$ as a function of the current. The

charge was obtained by fitting Eq. (1.32) to the liquid elevation, as in Figure 7.2(b). The evolution of the measured capillary charge Q_1 as a function of the current I injected into the DCA is shown in Figure 7.2(c). As expected, the capillary dipolar component increases with I since the contact line is pinned on the DCA's floater perimeter, which tilts more as I increases. Saturation is, however, observed because the surface and gravitational energies resisting the magnetic energy evolve more rapidly than the latter with the tilt angle α as shown in Figure 7.3.

The free energy difference of the floater between its flat equilibrium configuration and its tilted orientation can be written as

$$\Delta E = \gamma \Delta A + \rho \Delta V g \frac{H}{2} - \mu B \sin \alpha \quad (7.1)$$

where, in order, the differences in surface energy, gravitational energy, and magnetic energy are considered. The increased air-water interface area ΔA is given by [27, 115]

$$\begin{aligned} \Delta A &= \frac{1}{2} \int_0^{2\pi} \int_{R \cos \alpha}^{\infty} (\nabla h)^2 r \, dr d\theta \\ &= \frac{Q_1^2}{2} \int_0^{2\pi} \int_{R \cos \alpha}^{\infty} r \left(\frac{(-K_0(\frac{r}{\lambda}) - K_2(\frac{r}{\lambda}))^2 \cos^2 \theta}{4\lambda^2} + \frac{K_1(\frac{r}{\lambda})^2 \sin^2(\theta)}{r^2} \right) dr d\theta, \end{aligned} \quad (7.2)$$

where we also assume a small slope. The volume ΔV displaced by the meniscus is described by

$$\Delta V = 2 \int_{-\pi/2}^{\pi/2} \int_{R \cos \alpha}^{\infty} r Q_1 K_1 \left(\frac{r}{\lambda} \right) \cos \theta \, dr d\theta. \quad (7.3)$$

The maximal height/depth H of the meniscus is given by

$$H = Q_1 K_1 \left(\frac{R \cos \alpha}{\lambda} \right) = R \sin \alpha, \quad (7.4)$$

which finally relates the tilt angle α and the dipolar capillary charge Q_1 :

$$Q_1 = \frac{R \sin \alpha}{K_1 \left(\frac{R \cos \alpha}{\lambda} \right)}. \quad (7.5)$$

The product μB in the magnetic energy is the product of the magnetic moment μ of the embedded permanent magnet and the magnetic field B

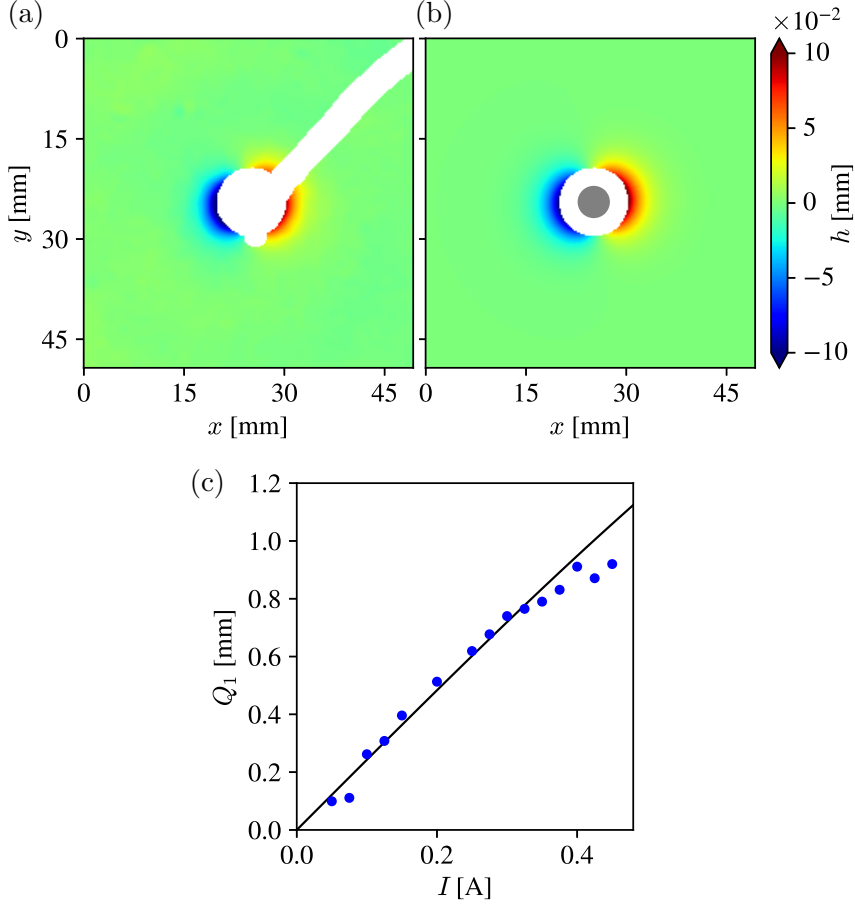


Figure 7.2: Deformation around the DCA. The resulting capillary multipole presents two lobes of opposite signs corresponding to a dipole. (a) Surface profile around a DCA measured by the Fast Checkerboard Demodulation method. A current of 0.275 A powers the DCA. The white line originating from the upper-right corner corresponds to the cable that powers the DCA. (b) Surface profile around a DCA as fitted with Eq. (1.32) with $m = 1$. (c) Measured capillary charge Q_1 of the DCA as a function of the current I injected into the coil. The curve represents the evolution of the charge Q_1 as a function of I as predicted by the numerical minimisation of Eq. (7.1).

7.3 Capillary trap

While a single DCA can successfully modulate the liquid surface, the extent of this deformation is limited. However, as shown in the previous chapter, with a combination of spines, combining multiple DCAs extends and complexifies the overall liquid landscape. As a first example, several DCAs can be arranged in a circular array to create a trap for floating particles. Within this array, the dipoles of the DCAs converge and combine to produce a global deformation of the liquid surface. By controlling the dipoles of the DCAs, the interface can be shaped to create an extremum where floating particles can be trapped. In all configurations presented below, particle motion directly follows the liquid landscape generated by the superposition of dipolar deformations.

Given that the capillary length λ is 2.7mm for pure water, the radius of the circular array should be on this order to achieve significant deformation at its centre. The inner radius of the trapping device is set to 4.75mm, slightly above the capillary length, allowing the displacement of sub-millimetre-sized particles over larger distances.

Six DCAs are symmetrically placed along the ring, which is the maximum number compatible with the chosen radius. Fewer DCAs can be used to build the trap, but using more DCAs allows for more elaborate interface shapes, as more local deformations combine to produce the overall deformation.

We captured various floating particles at its centre to demonstrate the trapping capability of the array. The device was placed in water with all DCAs oriented radially and set to the same current, resulting in the same liquid slope. This configuration deforms the interface by creating a valley or a hill, depending on the sign of the dipolar charge of the floaters. These profiles are computed from the theoretical expression of a dipolar meniscus using Eq. (1.32) with $m = 1$, and the LSA approximation used in all chapters stating that the total interface is simply the sum of all individual contributions. Figure 7.4(a) shows a simulated interface presenting a valley shape. The black triangle indicates the bottom of this valley, corresponding to the trap position.

We performed trapping experiments with two types of particles: a solid spherical bead and a droplet of mineral oil. The bead is a 1-millimetre-diameter glass sphere and floats thanks to partial wetting. Because it is denser than water, its capillary charge Q_p is negative. In the trapping configuration described above, the bead is consequently localised at the centre of the trap, as shown in Figure 7.4(b).

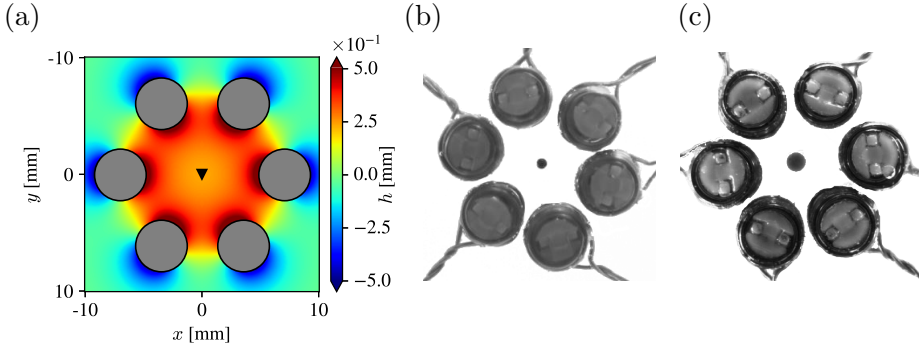


Figure 7.4: Capillary trap. Trap formed at the centre of a ring of six radially oriented DCAs with identical capillary charges. (a) Simulated surface topography showing a central minimum. (b,c) Trapping of a glass bead and a mineral oil droplet at the centre of the array.

We also investigated a small mineral oil droplet placed at the water-air interface. Although many oil droplets tend to spread on water surfaces, mineral oil forms a so-called floating "liquid lens" at equilibrium. This behaviour arises from the balance of interfacial tensions at the triple phase contact line: $\gamma \approx 72 \text{ mN/m}$ for the water-air interface, $\gamma_{wo} \approx 50 \text{ mN/m}$ for the water-oil interface and $\gamma_{oa} \approx 30 \text{ mN/m}$ for the oil-air interface. The equilibrium condition $\gamma < \gamma_{wo} + \gamma_{oa}$ is satisfied in our system. Although surfactants are often added to promote the formation of such liquid lenses with oil-water-based mixtures, we deliberately avoid them here, as they reduce the capillary length and affect the buoyancy of the DCA heads. Manipulating a floating mineral-oil droplet is delicate, as any contact with a solid surface may rupture the droplet or cause adhesion. Our system is particularly well-suited to trapping such liquid lenses without direct contact. At equilibrium, liquid lenses present a small negative curvature, i.e., a small negative Q_p , as demonstrated recently theoretically and experimentally by Ravazzoli *et al.* [116]. As a result, they are attracted by a trap with negative curvature, as illustrated in Figure 7.4(c).

7.4 Capillary tweezers

A natural extension of the static trap is to allow the controlled displacement of its minimum by varying the current of one or several DCAs. This enables the particle to be positioned at any location within the array, thereby transforming the trap into capillary tweezers. Each DCA's

dipole intensity can be independently controlled because the entire device is powered by six bi-directional current sources, individually driven by a microcontroller.

Figures 7.5(a-c) show simulated profiles of the liquid inside the array and the displacement of the trap when the capillary charges of some DCAs are increased. Simulations indicate that the minimum position moves when the charge capillary Q_1 of one or two DCAs is increased.

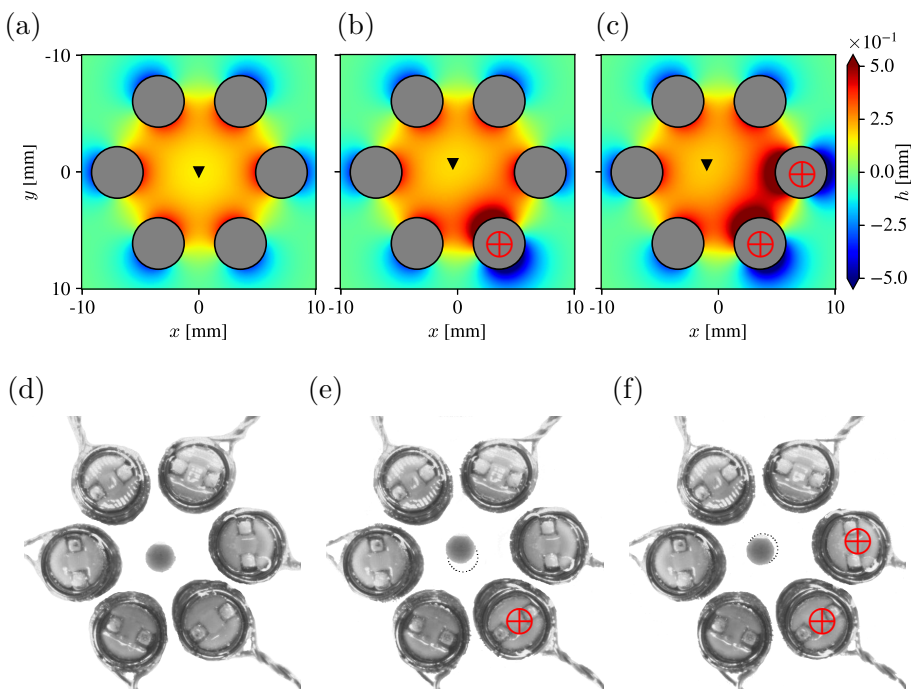


Figure 7.5: Capillary tweezers. (a–c) Simulated interface profiles showing displacement of the trap upon increasing the capillary charge of selected DCAs depicted by red $\oplus$ symbol. (d–f) Experimental manipulation of a mineral oil droplet following the same actuation protocol.

We conducted experiments to move various floating particles, such as beads and drops. Figures 7.5(d-f) show experimental images of the displacement of a mineral oil drop inside the capillary tweezers. The charges on some DCAs were modified as in the simulations in Figures 7.5(a-c), and a similar trajectory was observed. The real-time movie, labelled Supplementary Video S1, is available at the end of the chapter. This dynamic control enables real-time repositioning of particles without mechanical contact.

7.5 Capillary ratchet

The proposed capillary tweezers can also be converted into a ratchet, in which an asymmetric, time-dependent liquid landscape induces transport of floating particles in a single direction along the DCA ring, while preventing motion in the reverse direction.

To achieve rotation along the ring, adjacent DCAs should be set in phase opposition and actuated with sinusoidal currents. This configuration creates local minima and maxima in alternating fashion at the edges of the DCAs. After half a period of the current, each previous trap became repellent and vice versa. In the case where all DCAs are oriented radially, as in the previous trap and tweezers configurations, the manipulated particle will move equiprobably to either the left DCA or the right, resulting in no net motion after multiple periods.

Directional transport is obtained by breaking the radial symmetry of the energy landscape. This is achieved by tilting all DCAs by 45° with respect to the radial direction, an intermediate orientation between purely radial and tangential configurations. In this geometry, adjacent DCAs are actuated in phase opposition, such that the sequence of local minima is spatially biased along the ring.

Simulations of the resulting interface for the two extremal values of the magnetic field are shown in Figures 7.6(a,b). As a consequence of this asymmetric landscape, a floating glass bead is systematically transferred to the neighbouring DCA on its left after each half-period of the actuation, leading to a net clockwise motion, as observed experimentally in Figures 7.6(c,d) and in the real-time movie in Supplementary Video S2. This mechanism is robust and applies equally to single particles or assemblies, independently of their capillary nature.

Figure 7.7 shows the simultaneous directional transport of a single bead and a dimer composed of two beads. The associated real-time movie is given in Supplementary Video S3. The beads of the dimer stick together only by a capillary bridge. In a ring of six DCAs, any particle requires three time periods to complete a full rotation and return to its starting position. The speed of this motion can be adjusted by changing the frequency. However, efficient motion is possible only below a frequency threshold, which we can approximate using simple assumptions. Specifically, the displaced object must have enough time to enter the potential field of the adjacent DCA in approximately $T/4$, meaning that this frequency threshold highly depends on the shape, weight and nature of the displaced object. For the DCAs in a ratchet configuration with a current

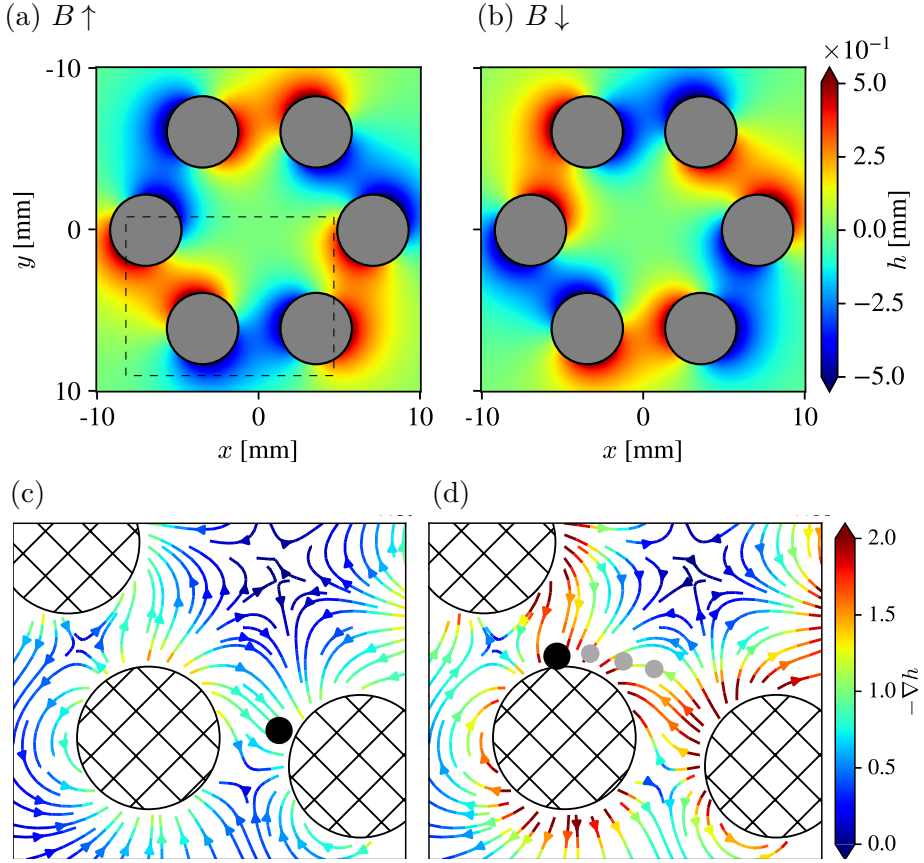


Figure 7.6: Capillary ratchet. Directional transport of a 1 mm floating glass bead inside a ring of six DCAs. (a,b) Simulated interface height for the two extremal values of the applied magnetic field, with adjacent DCAs in phase opposition and tilted by 45° from the radial direction. (c,d) Experimental trajectories corresponding to the configurations in (a,b); the current bead position is shown in black, and past positions are shown in grey. Streamlines indicate the opposite gradient of the simulated interface height. The hashed circles represent the DCAs.

of 0.2 A, a glass bead takes approximately 0.6 s to move from one DCA to the next. This means that it takes half of this time for the bead to exit the repulsive potential of one DCA and enter the attractive field of the next. Thus, for this setup, the minimum period and maximum frequency for effective movement are approximately $T_{\min} \approx 1.2$ s and $f_{\max} \approx 0.8$ Hz, providing an estimate of the magnitude order of the maximal frequency possible to observe ratcheting.

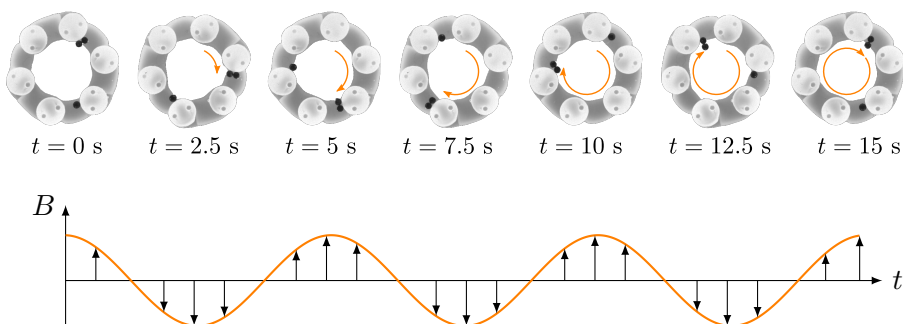


Figure 7.7: Transport of a single glass bead and a dimer inside the ratchet. The dimer is composed of two glass beads of 1mm that stick together only by a capillary bridge. A sinusoidal current is injected into the coils of the DCAs. They are tilted from the radial direction by an angle of 45° , and adjacent ones are 180° out of phase and therefore have opposite charges. The frequency of the electric current fixes the transport speed. This experiment sets the frequency to 0.2Hz. The time between successive step motions is therefore half the period, $T/2 = 2.5$ s.

7.6 Summary

In this chapter, we introduced Dipolar Capillary Actuators as building blocks for dynamically programmable liquid landscapes. By actively controlling dipolar deformations of the interface, we demonstrated trapping, controlled displacement, and directional transport of floating particles using reconfigurable liquid landscapes, extending the static strategies introduced in the previous chapter.

Beyond static guidance, the DCA-based approach enables real-time and reversible manipulation of particles through actively shaped energy landscapes. In particular, asymmetric actuation protocols give rise to capillary ratchets, allowing robust, non-reciprocal transport of single particles or assemblies. Together, these results establish actuated liquid landscapes as a versatile extension of capillary-based manipulation strategies.

Supplementary resources

Access to the supplementary videos associated with this chapter:



Access to the 3D files of the different DCA parts:



*Tout ce qu'un homme peut imaginer, d'autres
hommes peuvent le concrétiser.*

-Jules Verne



Conclusion and Perspectives

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8.1 Conclusion

The objective of this thesis was to encode multipolar capillary interactions solely through geometry, both within floating elements and across the liquid interface, to enable programmable self-assembly and controlled micromanipulation.

The results presented throughout this manuscript demonstrate that such programmable complexity can indeed be structured at fluid interfaces. By progressively enriching the description and control of capillary interactions, we have shown that liquid surfaces can be transformed into platforms in which geometry, interactions, and landscape combine to produce controlled behaviours: self-assembly, self-folding, trapping, and manipulation.

The first objective of this work was to establish a rigorous physical framework for capillary interactions upon which design rules could be constructed. Chapter 1 introduced the fundamental principles of surface tension and interface curvature, providing the theoretical basis for de-

scribing capillary forces. Chapter 2 extended this framework through a discrete-charge formalism capable of modelling anisotropic and multipolar deformations beyond simple monopolar approximations. Together, these chapters supplied the analytical and modelling tools required to encode complexity.

The first part of the thesis then focused on encoding interaction rules directly within floating elements to achieve controlled self-assembly.

In Chapter 3, we showed that the tilt of a pinned contact line induces dipolar capillary deformations that generate an additional short-range attraction between nearby floating spheres. Within the multipolar framework, this mechanism appears naturally as induced dipoles, enriching pairwise interaction rules and revealing the limits of linear superposition. Chapter 4 extended this encoding strategy to shape-defined quadrupolar particles. By modelling the meniscus as a combination of monopolar and quadrupolar charges and validating the resulting interaction landscapes experimentally, we established direct design rules linking geometry to orientation-dependent assembly. In Chapter 5, we further increased the level of complexity by considering flexible chains of connected elements. Through discrete-charge modelling and energy-landscape analysis, we demonstrated that a one-dimensional capillary sequence governs both folded geometries and the organisation of metastable states. These results establish capillary chains as a mesoscale analogue of molecular folding and demonstrate that programmable many-body behaviour can be implemented through minimal geometric encoding.

The second part of the thesis shifted the focus from particle-based encoding to interface-level programming, enabling controlled manipulation. Chapter 6 showed that arrays of conical spines can be combined to generate static liquid landscapes extending beyond the capillary length. Through controlled meniscus superposition and global tuning parameters, complex interface topographies were engineered and exploited for particle guidance and positioning. Chapter 7 introduced Dipolar Capillary Actuators as dynamically controlled building blocks for reconfigurable liquid landscapes. By actively shaping dipolar deformations, we demonstrated trapping, directed transport, and non-reciprocal motion through capillary ratchets, thereby achieving dynamic and adaptive manipulation.

Taken together, these results demonstrate that capillary interactions can be structured across multiple hierarchical levels: from induced pairwise corrections to orientation-selective binding, programmable folding landscapes, static interface topographies, and dynamically actuated energy fields. Multipolar capillary interactions thus provide a unifying frame-

work for introducing and controlling complexity at fluid interfaces. Beyond the specific systems studied here, the principles developed in this thesis open perspectives toward adaptive soft-matter devices, reconfigurable interfacial robotics, and programmable materials operating at liquid surfaces. More broadly, this work shows that simple physical ingredients can be organised into controllable, multi-level behaviours bridging natural capillary phenomena and engineered systems.

8.2 Perspectives

The richness of capillary-driven systems leaves considerable room for imagination. The designer is not constrained to a fixed interaction rule: by modifying shapes, wettability, or the surrounding landscape, entirely new interaction scenarios can be created. In this sense, capillary self-assembly constitutes not only a physical phenomenon but also an architectural playground for programmable matter.

Here are a few possible future horizons for the present work.

8.2.1 Capillary codons

In the same spirit as in Chapter 5, a natural direction is to continue drawing inspiration from biology by introducing capillary codons. The concept of capillary codons is inspired by nucleic acids. Each elementary block bears three curved branches distributed along its perimeter, generating menisci of equal magnitude and opposite sign. There are thus 2^3 possible building blocks. These objects are termed codons because their interactions are dictated by the ordered triplet of charges, in analogy with biological codons whose pairing is governed by complementary nucleobases. Each capillary codon is designed to preferentially pair with its corresponding anticodon, defined as the reversed sequence of the same charges, due to chirality. A perfect pairing between a codon and its anticodon ensures that three identical charges face each other simultaneously. To achieve selective pairing at the mesoscale, the global codon design must be carefully controlled. In particular, the distance between branches d_b is crucial. If the branches are too close, the capillary charges can partially screen one another, weakening the interaction and allowing mismatched pairing. If they are too far apart, the triplet no longer behaves as a coherent unit, and only partial pairing occurs. The spacing must therefore be tuned so that the three charges act collectively and

full pairing occurs only between a codon and its exact anticodon. This sensitivity to the branch spacing is illustrated in Figure 8.1. In Figure 8.1(a), two identical $+++$ codons created with $d_b = \lambda$ approach each other and achieve a full three-branch pairing, even when slightly off-centre. When the spacing is increased to $d_b = 1.5\lambda$, as shown in Figure 8.1(b), only two branches pair effectively, indicating that the triplet no longer behaves as a coherent interaction unit. In contrast, Figure 8.1(c) shows a full three-branch pairing between a $+-+$ codon and a $+++$ codon when $d_b = 0.5\lambda$, which corresponds to a mismatch. In this case, the middle charge is screened by its neighbours. Finally, for $d_b = \lambda$, Figure 8.1(d) shows that mismatched codons can attach only through a single compatible branch, resulting in a weak bond that can easily be broken by slight agitation.

The formation of ordered sequences is further illustrated in Figure 8.2, where several elements are arranged to spell the word *GRASP*. The different codons, created with the optimal spacing $d_b = \lambda$, form letters that were manually positioned to illustrate the targeted configuration. The codons corresponding to the letters G and P possess three neutral sides, while the other letters have two neutral sides. Each active side carries a specific triplet chosen to ensure the correct orientation and order of the letters. The objective is ultimately to apply controlled agitation so that each element can explore its local environment, allowing bonds to form, while providing only enough energy to break configurations involving one or two paired branches but not the perfect three-branch matching corresponding to the correct assembly.

One may further extend this approach by exploiting all sides of the building blocks. By assigning distinct triplets to different sides, self-assembly could create two-dimensional architectures governed by local compatibility conditions, reminiscent of crossword-like grids or domino-type tilings, where global order emerges from the satisfaction of multiple local matching rules.

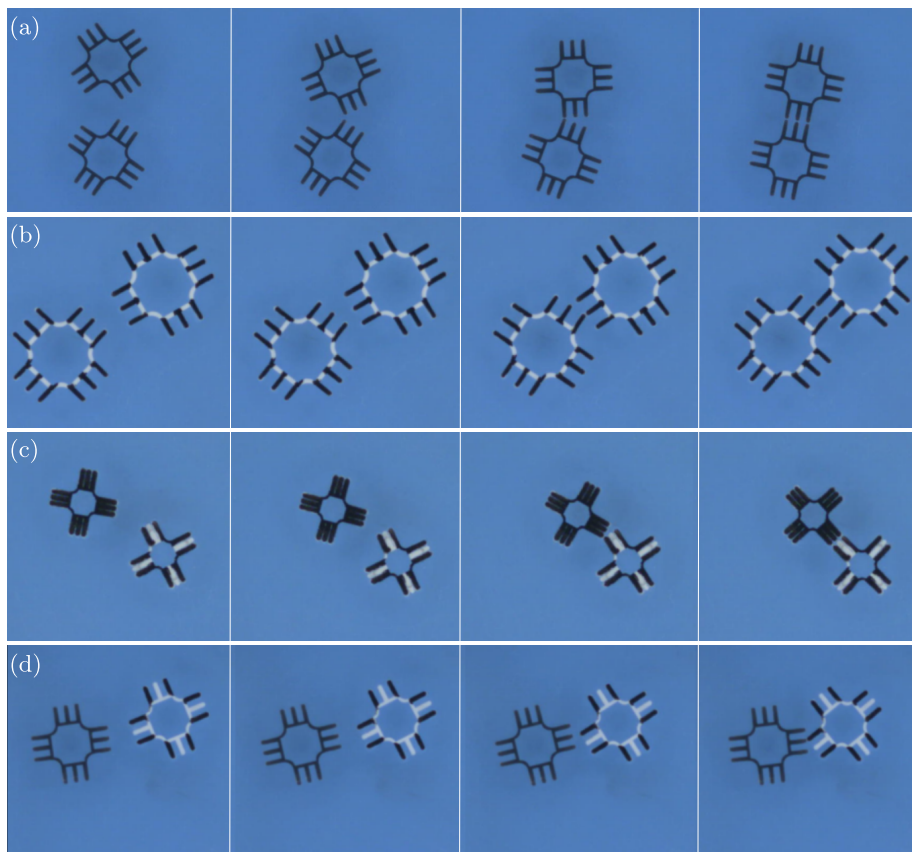


Figure 8.1: Pairing between codons. Each black branch represents a positive capillary charge, while each white branch represents a negative one. (a) Progressive pairing of two +++ codons with $d_b = \lambda$. (b) Progressive pairing of two +++ codons with $d_b = 1.5\lambda$. The codons pair only through two branches. (c) Mismatched pairing between a +-+ codon and a +++ codon with $d_b = 0.5\lambda$, due to screening of the central charge. (d) For $d_b = \lambda$, mismatched codons interact through a single compatible branch only, resulting in a weak and easily breakable attachment.



Figure 8.2: Goal assembly spelling *GRASP*.

A + - - codon with its triplet of curved branches distributed four times along the perimeter. Local deformations of the liquid interface are revealed using the reflection of a striped pattern on the surface.
Credits: Axel Franckart and Megan Delens.





8.2.2 Actuation of spines

In Chapter 6, structured landscapes were realised using static spines. A natural continuation is therefore to introduce dynamic actuation of the immersed platform, allowing the liquid surface curvature to be modified in real time.

Future developments could explore the integration of adaptive magnetic materials [117], magnetoelastic systems [118], bioinspired shape-shifting materials [104], or shape-memory polymers [69]. Such materials would enable controlled deformation of the supporting structures and, consequently, control the interfacial topography.

Mechanical actuation systems could also be implemented to locally adjust spine height or orientation. In particular, the MIT “TRANSFORM” table [119], presented in Figure 8.3, consists of an array of vertically actuated pins whose heights can be individually controlled to generate dynamic three-dimensional shapes. Translating this concept to an immersed platform would amount to controlling the elevation of a dense array of spines beneath the liquid interface, thereby prescribing the curvature field with both spatial and temporal resolution. Such a system would enable reconfiguration of the manipulation path on demand.

Beyond fundamental investigations of adaptive capillary systems, these developments would also constitute a concrete bridge between fundamental interfacial physics and industrial applications.

8.2.3 Self-assembly with programmable liquid landscapes

Beyond increasing the complexity of individual objects, another direction is to hybridise the strategies developed in this thesis. We can study the evolution of capillary or magnetocapillary self-assemblies when the surrounding interface is itself dynamically deformed.

A first example consists in coupling the magnetocapillary self-assemblies studied in Chapter 3 with the spines introduced in Chapter 6. The system consists of identical soft-ferromagnetic beads. On a flat interface, their organisation is governed by magnetic dipolar repulsion, leading to the formation of a hexagonal lattice.

When square-arranged spines progressively pierce the interface, the situation changes. Experimentally, this transition is achieved by lowering the liquid level, thereby uncovering the previously immersed spines. The interface is no longer flat but shaped by the valleys imposed by the square lattice of spines. The beads now experience an additional capillary repul-



Figure 8.3: The MIT TRANSFORM table The system consists of a dense array of vertically actuated pins whose heights can be individually controlled to render dynamic three-dimensional shapes in real time [119]. Adapting a similar concept to an immersed platform would enable programmable spatiotemporal control of the liquid interface curvature. © 2012 Tangible Media Group / MIT Media Lab.

sion induced by the spines. As a result, the magnetocapillary assembly reorganises and adopts the symmetry of the imposed square lattice. This structural transition can be quantified by the bond-orientational order parameters ψ_6 and ψ_4 , globally defined as

$$\psi_l = \left| \frac{1}{N} \sum_{j=1}^N \frac{1}{n_j} \sum_{k=1}^{n_j} e^{li\theta_{jk}} \right|, \quad (8.1)$$

where N is the total number of particles in the assembly, n_j is the number of nearest neighbours of particle j , and θ_{jk} is the angle between the bond connecting particle j to its neighbour k and a fixed reference axis. As illustrated in Figures 8.4(a,b), the assembly shifts from hexagonal order, characterised by $\psi_6 \approx 1$, to square order, characterised by $\psi_4 \approx 1$ and dictated by the programmable landscape.

This example illustrates how programmable liquid landscapes can redirect self-assembly pathways and impose symmetry transitions. More generally, coupling encoded particle interactions with dynamically tunable interfaces opens the possibility of externally steering collective organisa-

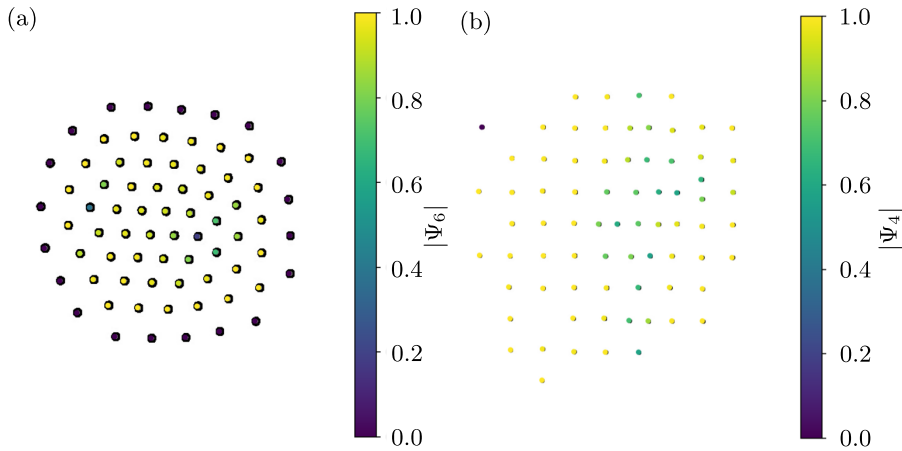


Figure 8.4: Magnetocapillary assembly coupled to a structured landscape. (a) Soft-ferromagnetic beads on a flat interface before the spines pierce the surface. The particles organise into a hexagonal lattice, coloured by the local bond-orientational order parameter ψ_6 . (b) After the spines arranged in a square lattice pierce the surface, the beads reorganise and adopt a square symmetry, coloured by the local bond-orientational order parameter ψ_4 .

tion, inducing controlled structural transitions, and designing adaptive self-assembled materials.

Liquid interfaces continue to reveal new mechanisms of organisation and manipulation. The present work contributes to this exploration by demonstrating how geometry encodes information and how deformable interfaces mediate programmable interactions. Yet this thesis likely represents only a fraction of the endless possibilities needed to be explored to entirely grasp the fascinating behaviour of multipolar capillary interactions.

Bibliography

- [1] P. Peruzzo, A. Defina, H. M. Nepf, and R. Stocker, *Capillary interception of floating particles by surface-piercing vegetation*, Phys. Rev. Lett. **111**, 164501 (2013).
- [2] P. A. Cox and R. B. Knox, *Two-dimensional pollination in hydrophilous plants: convergent evolution in the genera Halodule (Cymodoceaceae), Halophila (Hydrocharitaceae), Ruppia (Ruppiaceae), and Lepilaena (Zannichelliaceae)*. Am. J. Bot. **76**, 164–175 (1989).
- [3] P. Singh, D. D. Joseph, and N. Aubry, *Dispersion and attraction of particles floating on fluid–liquid surfaces*, Soft Matter **6**, 4310–4325 (2010).
- [4] J. Loudet and B. Pouligny, *How do mosquito eggs self-assemble on the water surface?* Eur. Phys. J. E **34**, 1–17 (2011).
- [5] K. Vulinec and M. Miller, *Aggregation and predator avoidance in whirligig beetles (Coleoptera: Gyrinidae)*, J. N.Y. Entomol. Soc., 438–447 (1989).
- [6] P. J. Watt and R. Chapman, *Whirligig beetle aggregations: what are the costs and the benefits?* Behav Ecol Sociobio **42**, 179–184 (1998).
- [7] J. Voise, M. Schindler, J. Casas, and E. Raphaël, *Capillary-based static self-assembly in higher organisms*, J. R. Soc. Interface **8**, 1357–1366 (2011).
- [8] D. L. Hu and J. W. Bush, *Meniscus-climbing insects*, Nature **437**, 733–736 (2005).
- [9] N. J. Mlot, C. A. Tovey, and D. L. Hu, *Fire ants self-assemble into waterproof rafts to survive floods*, Proc. Natl. Acad. Sci. U.S.A. **108**, 7669–7673 (2011).
- [10] J. W. Bush and D. L. Hu, *Walking on water: biolocomotion at the interface*, Annu. Rev. Fluid Mech. **38**, 339–369 (2006).

- [11] E. Y. Bormashenko, *Physics of wetting: phenomena and applications of fluids on surfaces* (Walter de Gruyter GmbH & Co KG, 2017).
- [12] L. D. Landau and E. M. Lifshitz, *Fluid mechanics: volume 6* (Elsevier, 1987).
- [13] P.-G. Gennes, F. Brochard-Wyart, D. Quéré, et al., *Capillarity and wetting phenomena: drops, bubbles, pearls, waves* (Springer, 2004).
- [14] M. M. Nicolson, *The interaction between floating particles*, Math. Proc. Cambridge Philos. Soc. **45**, 288–295 (1949).
- [15] P. Kralchevsky, V. Paunov, I. Ivanov, and K. Nagayama, *Capillary meniscus interaction between colloidal particles attached to a liquid—fluid interface*, J. Colloid Interface Sci. **151**, 79–94 (1992).
- [16] R. Finn, *Equilibrium capillary surfaces*, Vol. 284 (Springer Science & Business Media, 2012).
- [17] C. Pozrikidis, *Computation of three-dimensional hydrostatic menisci*, IMA J. Appl. Math. **75**, 418–438 (2010).
- [18] T. Young, *III. An essay on the cohesion of fluids*, Phil. Trans. R. Soc., 65–87 (1805).
- [19] J.-F. Joanny and P.-G. De Gennes, *A model for contact angle hysteresis*, J. Chem. Phys. **81**, 552–562 (1984).
- [20] R. Johnson and R. H. Dettre, *Wetting of low-energy surfaces*, Vol. 49 (Marcel Dekker, Inc.: New York, 1993).
- [21] D. Vella and L. Mahadevan, *The “Cheerios effect”*, Am. J. Phys. **73**, 817–825 (2005).
- [22] D. Vella, *Floating versus sinking*, Annu. Rev. Fluid Mech. **47**, 115–135 (2015).
- [23] P. A. Kralchevsky and K. Nagayama, *Capillary forces between colloidal particles*, Langmuir **10**, 23–36 (1994).
- [24] P. A. Kralchevsky and N. D. Denkov, *Capillary forces and structuring in layers of colloid particles*, Curr. Opin. Colloid Interface Sci. **6**, 383–401 (2001).
- [25] S. Protière, *Particle rafts and armored droplets*, Annu. Rev. Fluid Mech. **55**, 459–480 (2023).
- [26] D. Chan, J. Henry Jr, and L. White, *The interaction of colloidal particles collected at fluid interfaces*, J. Colloid Interface Sci. **79**, 410–418 (1981).

- [27] D. Stamou, C. Duschl, and D. Johannsmann, *Long-range attraction between colloidal spheres at the air-water interface: The consequence of an irregular meniscus*, Phys. Rev. E **62**, 5263 (2000).
- [28] F. Martínez-López, M. Cabrerizo-Vílchez, and R. Hidalgo-Alvarez, *Colloidal interaction at the air-liquid interface*, J. Colloid Interface Sci. **232**, 303–310 (2000).
- [29] K. D. Danov, P. A. Kralchevsky, B. N. Naydenov, and G. Brenn, *Interactions between particles with an undulated contact line at a fluid interface: Capillary multipoles of arbitrary order*, J. Colloid Interface Sci. **287**, 121–134 (2005).
- [30] P. A. Kralchevsky, N. D. Denkov, and K. D. Danov, *Particles with an undulated contact line at a fluid interface: interaction between capillary quadrupoles and rheology of particulate monolayers*, Langmuir **17**, 7694–7705 (2001).
- [31] A. Brown, C. Smith, and A. Rennie, *Fabricating colloidal particles with photolithography and their interactions at an air-water interface*, Phys. Rev. E **62**, 951 (2000).
- [32] M. Delens, Y. Collard, and N. Vandewalle, *Induced capillary dipoles in floating particle assemblies*, Phys. Rev. Fluids **8**, 074001 (2023).
- [33] G. B. Davies and L. Botto, *Dipolar capillary interactions between tilted ellipsoidal particles adsorbed at fluid-fluid interfaces*, Soft Matter **11**, 7969–7976 (2015).
- [34] J. Metzmacher, M. Delens, and N. Vandewalle, *Ring of capillary actuators as trap, tweezers and ratchet for floating particles*, Sci. Rep. **15**, 20617 (2025).
- [35] F. Moisy, M. Rabaud, and K. Salsac, *A synthetic Schlieren method for the measurement of the topography of a liquid interface*, Exp. Fluids **46**, 1021–1036 (2009).
- [36] J. Metzmacher, G. Lagubeau, M. Poty, and N. Vandewalle, *Double pattern improves the Schlieren methods for measuring liquid-air interface topography*, Exp. Fluids **63**, 120 (2022).
- [37] D. Chan, J. Henry Jr, and L. White, *The interaction of colloidal particles collected at fluid interfaces*, J. Colloid Interface Sci. **79**, 410–418 (1981).

- [38] C. Allain and M. Cloitre, *Interaction between particles trapped at fluid interfaces: I. exact and asymptotic solutions for the force between two horizontal cylinders*, J. Colloid Interface Sci. **157**, 261–268 (1993).
- [39] N. D. Vassileva, D. van den Ende, F. Mugele, and J. Mellema, *Capillary forces between spherical particles floating at a liquid-liquid interface*, Langmuir **21**, 11190–11200 (2005).
- [40] P. A. Kralchevsky and K. Nagayama, *Capillary interactions between particles bound to interfaces, liquid films and biomembranes*, Adv. Colloid Interface Sci. **85**, 145–192 (2000).
- [41] P. Kralchevsky and K. Nagayama, *Particles at fluid interfaces and membranes: attachment of colloid particles and proteins to interfaces and formation of two-dimensional arrays* (Elsevier, 2001).
- [42] W. Gifford and L. Scriven, *On the attraction of floating particles*, Chem. Eng. Sci. **26**, 287–297 (1971).
- [43] V. Paunov, P. Kralchevsky, N. Denkov, and K. Nagayama, *Lateral capillary forces between floating submillimeter particles*, J. Colloid Interface Sci. **157**, 100–112 (1993).
- [44] J.-B. Fournier and P. Galatola, *Anisotropic capillary interactions and jamming of colloidal particles trapped at a liquid-fluid interface*, Phys. Rev. E **65**, 031601 (2002).
- [45] “Capillary interactions on fluid interfaces: opportunities for directed assembly,” *Soft matter self-assembly* (IOS Press, 2016), pp. 165–215.
- [46] O. D. Velev, N. D. Denkov, V. N. Paunov, P. A. Kralchevsky, and K. Nagayama, *Direct measurement of lateral capillary forces*, Langmuir **9**, 3702–3709 (1993).
- [47] I. Ho, G. Pucci, and D. M. Harris, *Direct measurement of capillary attraction between floating disks*, Phys. Rev. Lett. **123**, 254502 (2019).
- [48] H. K. Khattak, S. Karpitschka, J. H. Snoeijer, and K. Dalnoki-Veress, *Direct force measurement of microscopic droplets pulled along soft surfaces*, Nat. Commun. **13**, 4436 (2022).
- [49] L. Helseth and T. M. Fischer, *Particle interactions near the contact line in liquid drops*, Phys. Rev. E **68**, 042601 (2003).

- [50] K. Hosokawa, I. Shimoyama, and H. Miura, *Two-dimensional micro-self-assembly using the surface tension of water*, Sens. Actuator A-Phys. **57**, 117–125 (1996).
- [51] K. D. Danov and P. A. Kralchevsky, *Capillary forces between particles at a liquid interface: General theoretical approach and interactions between capillary multipoles*, Adv. Colloid Interface Sci. **154**, 91–103 (2010).
- [52] L. Botto, L. Yao, R. Leheny, and K. Stebe, *Capillary bond between rod-like particles and the micromechanics of particle-laden interfaces*, Soft Matter **8**, 4971–4979 (2012).
- [53] H. Lehle, E. Noruzifar, and M. Oettel, *Ellipsoidal particles at fluid interfaces*, Eur. Phys. J. E **26**, 151–160 (2008).
- [54] J.-C. Loudet, A. M. Alsayed, J. Zhang, and A. G. Yodh, *Capillary interactions between anisotropic colloidal particles*, Phys. Rev. Lett. **94**, 018301 (2005).
- [55] J.-C. Loudet and B. Pouligny, *Self-assembled capillary arrows*, Europhys. Lett. **85**, 28003 (2009).
- [56] L. Bragg, *A model illustrating intercrystalline boundaries and plastic flow in metals*, J. Sci. Instrum. **19**, 148 (1942).
- [57] W. L. Bragg and J. F. Nye, *A dynamical model of a crystal structure*, Proc. R. Soc. A: Math. Phys. Eng. Sci. **190**, 474–481 (1947).
- [58] N. Bowden, A. Terfort, J. Carbeck, and G. M. Whitesides, *Self-assembly of mesoscale objects into ordered two-dimensional arrays*, Science **276**, 233–235 (1997).
- [59] N. Bowden, I. S. Choi, B. A. Grzybowski, and G. M. Whitesides, *Mesoscale self-assembly of hexagonal plates using lateral capillary forces: synthesis using the “capillary bond”*, J. Am. Chem. Soc. **121**, 5373–5391 (1999).
- [60] D. B. Wolfe, A. Snead, C. Mao, N. B. Bowden, and G. M. Whitesides, *Mesoscale self-assembly: capillary interactions when positive and negative menisci have similar amplitudes*, Langmuir **19**, 2206–2214 (2003).
- [61] P. W. Rothmund, *Using lateral capillary forces to compute by self-assembly*, Proc. Natl. Acad. Sci. U.S.A. **97**, 984–989 (2000).
- [62] G. M. Whitesides and B. Grzybowski, *Self-assembly at all scales*, Science **295**, 2418–2421 (2002).

- [63] M. Boncheva and G. M. Whitesides, *Making things by self-assembly*, MRS Bull. **30**, 736–742 (2005).
- [64] J. A. Pelesko, *Self assembly: the science of things that put themselves together* (Chapman and Hall/CRC, 2007).
- [65] M. Poty, G. Lumay, and N. Vandewalle, *Customizing mesoscale self-assembly with three-dimensional printing*, New J. Phys. **16**, 023013 (2014).
- [66] J. Bae, N. P. Bende, A. A. Evans, J.-H. Na, C. D. Santangelo, and R. C. Hayward, *Programmable and reversible assembly of soft capillary multipoles*, Mater. Horiz. **4**, 228–235 (2017).
- [67] J.-C. Loudet, A. G. Yodh, and B. Pouligny, *Wetting and contact lines of micrometer-sized ellipsoids*, Phys. Rev. Lett. **97**, 018304 (2006).
- [68] J. Metzmacher, M. Poty, G. Lumay, and N. Vandewalle, *Self-assembly of smart mesoscopic objects*, Eur. Phys. J. E **40**, 1–6 (2017).
- [69] N. Vandewalle, M. Poty, N. Vanesse, J. Caprasse, T. Defize, and C. Jérôme, *Switchable self-assembled capillary structures*, Soft Matter **16**, 10320–10325 (2020).
- [70] M. Delens and N. Vandewalle, *Encoding quadrupolar capillary information into saddle-shaped objects for self-assembly*, Phys. Rev. Fluids **10**, 104003 (2025).
- [71] B. A. Grzybowski, H. A. Stone, and G. M. Whitesides, *Dynamic self-assembly of magnetized, millimetre-sized objects rotating at a liquid–air interface*, Nature **405**, 1033–1036 (2000).
- [72] W. Wen, L. Zhang, and P. Sheng, *Planar magnetic colloidal crystals*, Phys. Rev. Lett. **85**, 5464 (2000).
- [73] M. Golosovsky, Y. Saado, and D. Davidov, *Self-assembly of floating magnetic particles into ordered structures: A promising route for the fabrication of tunable photonic band gap materials*, Appl. Phys. Lett. **75**, 4168–4170 (1999).
- [74] M. Golosovsky, Y. Saado, and D. Davidov, *Energy and symmetry of self-assembled two-dimensional dipole clusters in magnetic confinement*, Phys. Rev. E **65**, 061405 (2002).
- [75] G. Grosjean, G. Lagubeau, A. Darras, M. Hubert, G. Lumay, and N. Vandewalle, *Remote control of self-assembled microswimmers*, Sci. Rep. **5**, 1–8 (2015).

- [76] G. Grosjean, M. Hubert, and N. Vandewalle, *Magnetocapillary self-assemblies: Locomotion and micromanipulation along a liquid interface*, Adv. Colloid Interface Sci. **255**, 84–93 (2018).
- [77] Y. Collard, F. N. Piñan Basualdo, A. Bolopion, M. Gauthier, P. Lambert, and N. Vandewalle, *Controlled transitions between metastable states of 2D magnetocapillary crystals*, Sci. Rep. **12**, 16027 (2022).
- [78] Y. Collard, G. Grosjean, and N. Vandewalle, *Magnetically powered metachronal waves induce locomotion in self-assemblies*, Commun. Phys. **3**, 1–10 (2020).
- [79] S. Ziegler, M. Delens, Y. Collard, M. Hubert, N. Vandewalle, and A.-S. Smith, *Metachronal coordination as a mesoscale phenomenon*, Phys. Fluids **37**, 121917 (2025).
- [80] A. Hooshanginejad, J.-W. Barotta, V. Spradlin, G. Pucci, R. Hunt, and D. M. Harris, *Interactions and pattern formation in a macroscopic magnetocapillary SALR system of mermaid cereal*, Nat. Commun. **15**, 5466 (2024).
- [81] M. Janjua, S. Nudurupati, I. Fischer, P. Singh, and N. Aubry, *Electric field induced alignment and self-assembly of rods on fluid–fluid interfaces*, Mech. Res. Commun. **36**, 55–64 (2009).
- [82] G. B. Davies, T. Krüger, P. V. Coveney, J. Harting, and F. Bresme, *Interface deformations affect the orientation transition of magnetic ellipsoidal particles adsorbed at fluid–fluid interfaces*, Soft Matter **10**, 6742–6748 (2014).
- [83] N. Aubry and P. Singh, *Physics underlying controlled self-assembly of micro-and nanoparticles at a two-fluid interface using an electric field*, Phys. Rev. E **77**, 056302 (2008).
- [84] N. Aubry, P. Singh, M. Janjua, and S. Nudurupati, *Micro-and nanoparticles self-assembly for virtually defect-free, adjustable monolayers*, Proc. Natl. Acad. Sci. U.S.A. **105**, 3711–3714 (2008).
- [85] I. B. Liu, N. Sharifi-Mood, and K. J. Stebe, *Capillary assembly of colloids: Interactions on planar and curved interfaces*, Annu. Rev. Condens. Matter Phys. **9**, 283–305 (2018).
- [86] E. P. Lewandowski, J. A. Bernate, P. C. Searson, and K. J. Stebe, *Rotation and Alignment of Anisotropic Particles on Nonplanar Interfaces*, Langmuir **24**, 9302–9307 (2008).

- [87] M. Cavallaro Jr, L. Botto, E. P. Lewandowski, M. Wang, and K. J. Stebe, *Curvature-driven capillary migration and assembly of rod-like particles*, Proc. Natl. Acad. Sci. U.S.A. **108**, 20923–20928 (2011).
- [88] I. B. Liu, M. A. Gharbi, V. L. Ngo, R. D. Kamien, S. Yang, and K. J. Stebe, *Elastocapillary interactions on nematic films*, Proc. Natl. Acad. Sci. U.S.A. **112**, 6336–6340 (2015).
- [89] Y. Peng, Y. Jiao, C. Li, S. Zhu, C. Chen, Y. Hu, J. Li, Y. Cao, and D. Wu, *Meniscus-Induced Directional Self-Transport of Submerged Bubbles on a Slippery Oil-Infused Pillar Array with Height-Gradient*, Langmuir **38**, 15001–15007 (2022).
- [90] C. Zeng, M. W. Faaborg, A. Sherif, M. J. Falk, R. Hajian, M. Xiao, K. Hartig, Y. Bar-Sinai, M. P. Brenner, and V. N. Manoharan, *3D-printed machines that manipulate microscopic objects using capillary forces*, Nature **611**, 68–73 (2022).
- [91] M. Poty and N. Vandewalle, *Equilibrium distances for the capillary interaction between floating objects*, Soft Matter **17**, 6718–6727 (2021).
- [92] H. Cooray, P. Cicuta, and D. Vella, *Floating and sinking of a pair of spheres at a liquid–fluid interface*, Langmuir **33**, 1427–1436 (2017).
- [93] N. Vandewalle, L. Clermont, D. Terwagne, S. Dorbolo, E. Mersch, and G. Lumay, *Symmetry breaking in a few-body system with magnetocapillary interactions*, Phys. Rev. E **85**, 041402 (2012).
- [94] G. Lagubeau, G. Grosjean, A. Darras, G. Lumay, M. Hubert, and N. Vandewalle, *Statics and dynamics of magnetocapillary bonds*, Phys. Rev. E **93**, 053117 (2016).
- [95] R. Chinomona, J. Lajeunesse, W. H. Mitchell, Y. Yao, and S. E. Spagnolie, *Stability and dynamics of magnetocapillary interactions*, Soft Matter **11**, 1828–1838 (2015).
- [96] G. Grosjean, M. Hubert, G. Lagubeau, and N. Vandewalle, *Realization of the Najafi-Golestanian microswimmer*, Phys. Rev. E **94**, 021101 (2016).
- [97] M. Delens and N. Vandewalle, *Data and STL files supporting article: Encoding Quadrupolar Capillary Information into Saddle- Shaped Objects for Self-Assembly* (2024).
- [98] B. Madivala, J. Fransaer, and J. Vermant, *Self-assembly and rheology of ellipsoidal particles at interfaces*, Langmuir **25**, 2718–2728 (2009).

- [99] Z. Zhang, P. Pfliegerer, A. B. Schofield, C. Clasen, and J. Vermant, *Synthesis and directed self-assembly of patterned anisometric polymeric particles*, J. Am. Chem. Soc. **133**, 392–395 (2011).
- [100] E. P. Lewandowski, M. Cavallaro Jr, L. Botto, J. C. Bernate, V. Garbin, and K. J. Stebe, *Orientation and self-assembly of cylindrical particles by anisotropic capillary interactions*, Langmuir **26**, 15142–15154 (2010).
- [101] S. J. Thomson, J.-W. Barotta, and D. M. Harris, *Non-equilibrium thermodynamics in driven macroscopic self-assembly* (2025).
- [102] H. Cooray, P. Cicuta, and D. Vella, *The capillary interaction between two vertical cylinders*, J. Phys. Condens. **24**, 284104 (2012).
- [103] C. Semprebon, P. Forsberg, C. Priest, and M. Brinkmann, *Pinning and wicking in regular pillar arrays*, Soft Matter **10**, 5739–5748 (2014).
- [104] J. Cappello, B. Scheid, F. Brau, and E. Siéfert, *Bioinspired shape shifting of liquid-infused ribbed sheets*, Proc. Natl. Acad. Sci. U.S.A. **120**, e2216001120 (2023).
- [105] J. Bico, U. Thiele, and D. Quéré, *Wetting of textured surfaces*, Colloids Surf. A: Physicochem. Eng. Asp. **206**, 41–46 (2002).
- [106] D. Quéré, *Wetting and roughness*, Annu. Rev. Mater. Res. **38**, 71–99 (2008).
- [107] Y. Yang, X. Li, X. Zheng, Z. Chen, Q. Zhou, and Y. Chen, *3D-printed biomimetic super-hydrophobic structure for microdroplet manipulation and oil/water separation*, Adv. Mater. **30**, 1704912 (2018).
- [108] J. Jurin, *II. An account of some experiments shown before the Royal Society; with an enquiry into the cause of the ascent and suspension of water in capillary tubes*. Phil. Trans. R. Soc. **30**, 739–747 (1717).
- [109] M. Delens, A. Franckart, D. M. Harris, and N. Vandewalle, *GRASP-LAB/3D-printed-spines: Code and STL supporting our article "3D-Printed Spines for Programmable Liquid Topographies and Micro-manipulation"* (2025).
- [110] X. Liu, W. Zhou, F. Tang, H. Zheng, and S. W. Joo, *Capillary tweezer for programmable droplet manipulation*, Sens. Actuators B Chem. **370**, 132380 (2022).

- [111] C. Zeng, F. Brau, B. Davidovitch, and A. D. Dinsmore, *Capillary interactions among spherical particles at curved liquid interfaces*, Soft Matter **8**, 8582–8594 (2012).
- [112] J. L. Eatson, J. R. Gordon, P. Cegielski, A. L. Giesecke, S. Suckow, A. Rao, O. F. Silvestre, L. M. Liz-Marzán, T. S. Horozov, and D. M. A. Buzza, *Capillary Assembly of Anisotropic Particles at Cylindrical Fluid–Fluid Interfaces*, Langmuir **39**, 6006–6017 (2023).
- [113] F. Jülicher, A. Ajdari, and J. Prost, *Modeling molecular motors*, Rev. Mod. Phys. **69**, 1269 (1997).
- [114] S. Wildeman, *Real-time quantitative Schlieren imaging by fast Fourier demodulation of a checkered backdrop*, Exp. Fluids **59**, 97 (2018).
- [115] Q. Xie, G. B. Davies, F. Günther, and J. Harting, *Tunable dipolar capillary deformations for magnetic Janus particles at fluid–fluid interfaces*, Soft Matter **11**, 3581–3588 (2015).
- [116] P. D. Ravazzoli, A. G. Gonzalez, J. A. Diez, and H. A. Stone, *Buoyancy and capillary effects on floating liquid lenses*, Phys. Rev. Fluids **5**, 073604 (2020).
- [117] Y. Sun, H. Zhang, Y. Zhao, J. Wu, Y. Zhu, M. Li, and L. Wang, *Locally Reprogrammable Magnetic Micropillars with On-Demand Reconfiguration and Multi-Functionality*, Adv. Mater. Technol. **8**, 2300773 (2023).
- [118] M. Poty, F. Weyer, G. Grosjean, G. Lumay, and N. Vandewalle, *Magnetoelastic instability in soft thin films*, Eur. Phys. J. E **40**, 1–5 (2017).
- [119] H. Ishii, D. Leithinger, S. Follmer, A. Zoran, P. Schoessler, and J. Counts, *TRANSFORM: Embodiment of “Radical Atoms” at Milano Design Week*, 687–694 (2015).