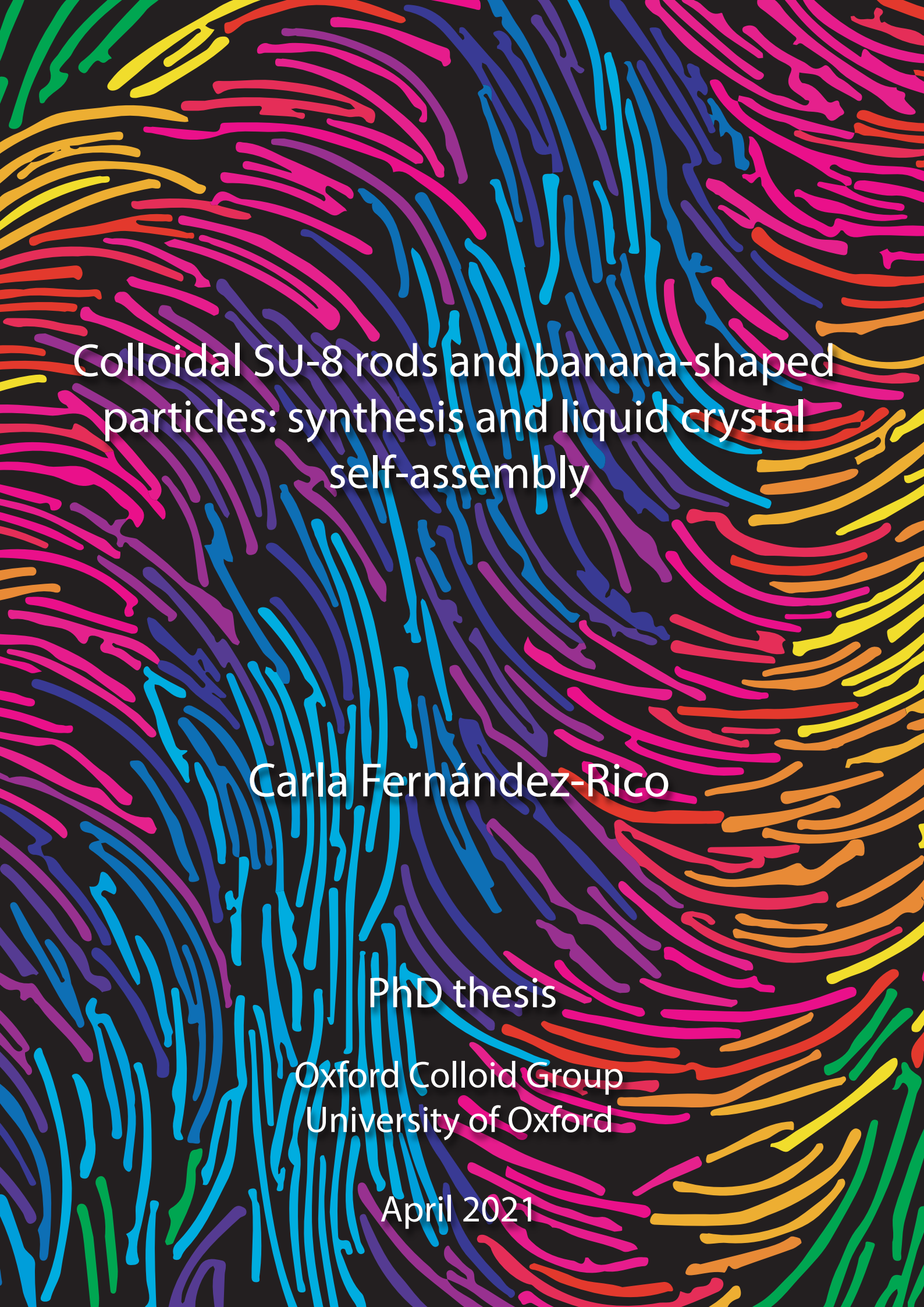




Colloidal SU-8 rods and banana-shaped particles: synthesis and liquid crystal self-assembly

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PhD thesis

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Abstract

In this thesis, we describe the development of two novel model systems of anisotropic colloidal particles and study their self-assembly into colloidal liquid crystal phases with confocal microscopy. In particular, we develop a system of colloidal rod-like and banana-shaped particles made of a polymeric material called SU-8. First, we describe the synthesis of colloidal SU-8 rods with tunable dimensions by using sonication. This simple yet, crucial step allows us to bring the SU-8 rod system – which had been limited to the granular scale – into the colloidal domain. Crucially, these rods can be fluorescently labelled and are stable in both aqueous and non-aqueous solvents. Also, their refractive index and density mismatch with the solvent can be carefully controlled. As a result, the liquid crystal behaviour exhibited by the rods can be controlled and addressed in three dimensions using confocal microscopy whilst tuning the effect of gravity. Next, we describe the synthesis of colloidal SU-8 bananas by heating the originally straight SU-8 rods. Importantly, we demonstrate that the curvature of the bananas can be controlled by tuning the rigidity of the rods. This has an enormous impact on the liquid crystal phases the colloidal bananas exhibit with respect to the colloidal rods, as the particles are now biaxial. Using confocal microscopy, we next address the liquid crystal phase behaviour of the colloidal bananas, and how it is affected by curvature, at the single-particle level. We find a library of exotic liquid crystal phases, including polar and antipolar smectic phases and even the elusive long-predicted splay-bend nematic phase. We then exploit the inherent polydispersity of the colloidal bananas to demonstrate that a hierarchical structure called the vortex phase can be assembled from polydisperse building blocks interacting via simple entropic interactions. We uncover the formation mechanism and the underlying geometrical principles dictating the structure of this hierarchical phase by systematically changing the curvature of the constituent bananas and characterising the resulting structures with confocal microscopy. Finally, we describe the fabrication of rough SU-8 rods and bananas with tunable asperity density via the nanoprecipitation of SU-8 nanospheres. With these newly developed rough particles, we provide two colloidal model systems for addressing surface-roughness related phenomena in materials composed of anisotropic particles.

Declaration

This thesis is submitted for the degree of Doctor of Philosophy in Physical and Theoretical Chemistry at the University of Oxford. No part of this thesis has been accepted or is currently being submitted for any degree, diploma, certificate or other qualification in this University or elsewhere. This thesis is wholly my own work, except where indicated.

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Chapter 1

General introduction

Among the different states in which matter can exist, the solid, liquid and gas phases are probably the most familiar. A classic example is water, which is solid below 0°C , liquid between 0°C and 100°C and gas above 100°C . When matter is composed of building blocks that can be approximated by a collection of spherical particles, only solid, liquid and gas phases are typically found [1,2]. The distinction between these states can be made by considering the degree and type of ordering shown by the constituent building blocks in each phase [1,2]. Crystalline solids are, for instance, highly ordered phases showing long-range positional order. The fixed periodic arrangement of the building blocks makes crystalline solids hard to deform and also anisotropic, meaning that their physical properties vary with direction [3]. This structural periodicity also enables crystals to interact with certain wavelengths of light [3] and exhibit a range of beautiful optical properties, such as colouration due to Bragg diffraction, as shown in Figure 1.1A.

On the contrary, liquids and gases are disordered phases where the constituent building blocks do not show any positional order, in the case of gases, or only short-range positional order, in the case of liquids. In particular, the disordered structure of liquids results in materials that are easy to deform and that have isotropic optical and mechanical properties (see Figure 1.1C). When matter is composed of anisotropically shaped building blocks, such as rod-like particles, additional states of matter between the liquid and crystalline states arise. These states are called *liquid crystal phases* and originate from the additional *orientational degrees of freedom* that anisotropic building blocks have. As a result, liquid crystal phases possess *orientational* but not (long-range) positional order and therefore show properties that are intermediate between those of liquids and crystals (see Figure 1.1B).

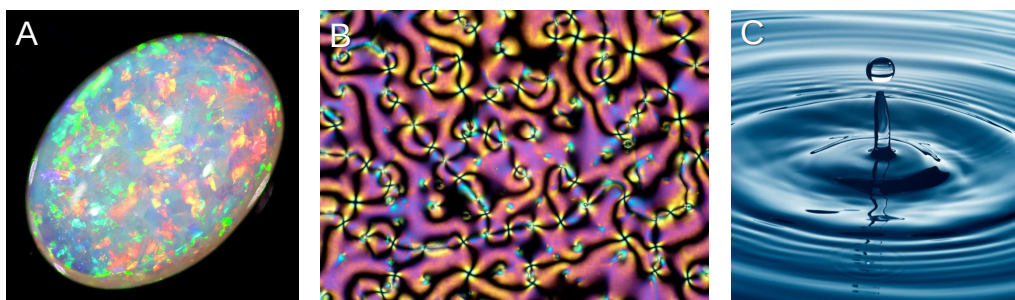


Figure 1.1: (A) Photograph of a crystalline opal stone showing iridescent colours [2]. (B) Polarised microscopy image of the Schlieren texture of nematic liquid crystal phase showing birefringence and fluidity [4]. (C) Photograph of the liquid water-air interface showing fluidity but no optical properties [5].

1.1 Liquid crystals

Liquid crystals are a fascinating state of matter that we encounter in our everyday life. For example, the cell membranes in our bodies are in a liquid crystalline state – and so are the functional materials used in displays of TVs and computers [2, 4, 6]. The reason this state of matter is a cornerstone of both living and technological materials is inherent to its unique properties: it shows order in a preferred direction, like a solid, but it also flows, like a liquid [2, 4, 6]. This means that liquid crystals exhibit a range of anisotropic physical properties, such as direction-dependant optical and mechanical responses, and that at the same time, they can be easily deformed and also respond to external stimuli, such as electric fields.

Among other factors, the shape of the liquid crystal-forming building blocks, which are typically elongated molecules, has an enormous impact on the way they arrange into different phases [1]. While simple rod-like molecules just form a handful of liquid crystal phases [2, 4], banana-shaped molecules form more than fifty [7, 8]. These ‘banana phases’ were discovered almost 30 years ago and have since then initiated a true ‘banana-mania’ in the field of liquid crystals [7–10]. The fact that even a small molecular curvature results in a new library of banana phases is not only fundamentally fascinating, but also of industrial interest, as they can switch their orientation under electric fields at ultra-fast speeds, making them ideal candidates for new highly-responsive displays.

A detailed characterisation of the inner structure of liquid crystal materials is essential to understand the relationship between the shape of the constituent microscopic building blocks and the final symmetry, and hence properties, of the phase. The most common techniques to characterise the structure of liquid crystal phases are based on birefringence and X-ray diffraction

[2, 4, 9]. These methods have been extremely useful for characterising different liquid crystal phases and have also offered great insight into their optical properties [2, 4, 9]. However, these measurements provide indirect information of the structure where single-particle details of the phases are just not available. Such levels of resolution can be especially relevant for unveiling the specific arrangement of molecules in long-debated, and even elusive phases such as the biaxial nematic [11, 12] and splay-bend nematic phases [13, 14], but also to engineer novel liquid crystal phases with pre-designed structure. Achieving single-particle resolution imaging of liquid crystals is, however, not an easy task: molecular systems are very small and move very fast and, as such, their direct imaging is extremely challenging even when using the most advanced microscopes.

1.2 Colloidal model systems

Colloidal suspensions consist of particles with a size ranging from 10 nm to 10 μm dispersed in a molecular solvent (see Figure 1.2A) [15]. While natural colloids can be found in paint, milk or even in our blood [15], colloidal particles can be also synthetically produced in a well-controlled manner and can be used as model systems for studying atomic and molecular matter [16, 17]. This is because colloidal particles are small enough to exhibit Brownian motion – a random motion arising due to collisions with the solvent molecules (see Figure 1.2A and B) – which allows them to explore the available phase space in a similar way to atomic and molecular systems [16–18]. As a result, colloids form equilibrium phases analogous to those seen in atomic and molecular matter, such as crystals or liquid crystals (see Figure 1.2C).

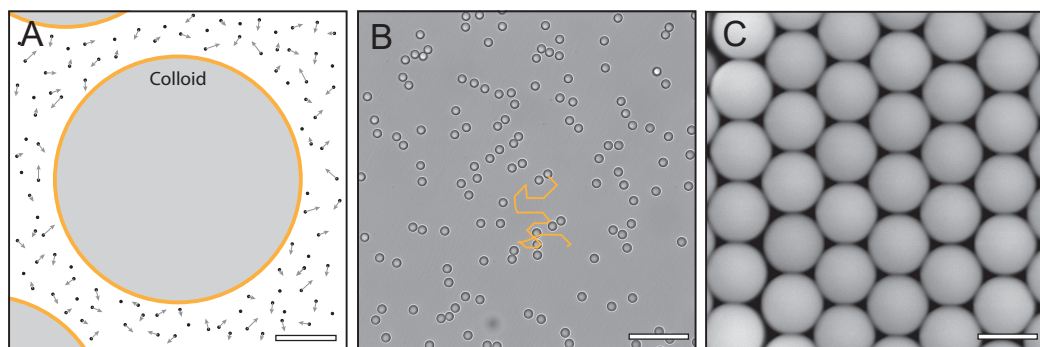


Figure 1.2: (A) Schematic representation of a colloidal suspension. The solvent molecules (black) undergo thermal motion (gray arrows) and collide with the colloidal particles (orange) giving rise to the Brownian motion of the particles. (B) Optical microscopy image of a colloidal suspension of polystyrene spheres in water. The orange line represents the random motion of a particle over time. (C) Scanning electron microscopy image of a colloidal crystal. Scales bars are (A) 150 nm, (B) 10 μm and (C) 2 μm .

The great strength of colloids is that, unlike atoms and molecules, they are large enough to be directly seen and followed with an optical microscope. Therefore, the microscopic details of their assembly into a wide variety of phases can be directly observed at the single-particle level [18, 19]. These systems have been very useful to address a range of long-standing questions in condensed-matter physics, such as the granularity of matter – with Perrin’s and Einstein’s work [20, 21] – or the largely debated crystallisation of colloidal spheres, in the absence of particle attractions, in hard spheres systems [22–24]. Furthermore, their shape and types of interactions can be also tuned and the resulting effects on structure and dynamics can be systematically studied with an optical microscope [25–27]. Their ability to spontaneously form ordered phases at the scale of visible wavelengths also makes colloids useful building blocks for optical materials such as photonic crystals [19, 28]. All of these features not only distinguish colloids as excellent and versatile model systems to address a host of fundamental processes, such as phase transitions [24, 29], interfacial phenomena [30, 31] and defect formation processes [32, 33], but also as unique building blocks to fabricate functional materials with engineered internal structure [17, 34].

1.3 Colloidal liquid crystals

In recent decades, a tremendous experimental effort in colloid science has produced a palette of colloidal systems with anisotropic shapes, leading to liquid crystal behaviour. Some of the most representative examples include colloidal Gibbsite platelets [35], silica rods [36], *fd*-viruses [37] and PMMA ellipsoids [38] (see Fig. 1.3). The combination of an exquisite control over the morphology of anisotropic colloids, their direct visualisation with optical microscopy, and their common comparison with computer simulations, has provided a deep understanding of the relationship between a particle’s shape and the final structure of the liquid crystals formed [35–39]. This has two main implications. First, it prompts the continuous development of novel anisotropic colloids with pre-designed shape to self-assemble liquid crystals with engineered structure and properties. Secondly, it motivates research to move beyond the mere optical observation of colloidal liquid crystals and towards the quantitative investigation of their structure and dynamics in three-dimensions (3D). Confocal microscopy has proven to be an excellent tool to obtain 3D information of colloidal systems at a single-particle level [40, 41]. Nevertheless, confocal microscopy places severe requirements on the particles to be used and, as we will discuss Chapter 3, these are typically not satisfied in many of the existing anisotropic colloidal systems.

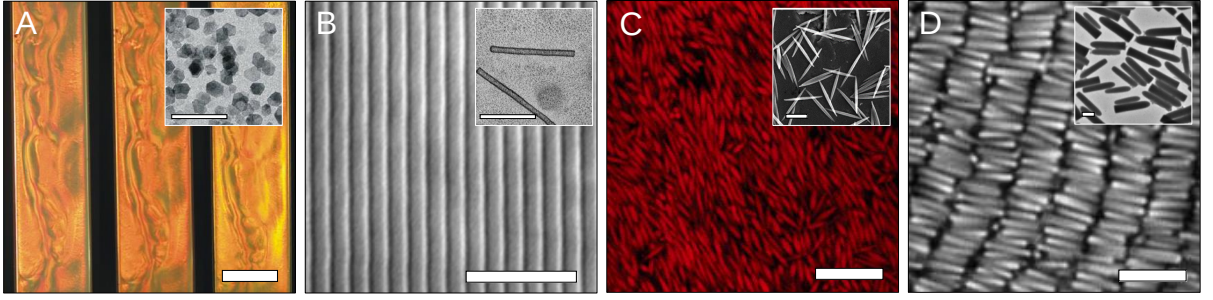


Figure 1.3: Representative examples of colloidal liquid crystals formed by (A) Gibbsite platelets (photograph of nematic phases using polarised light [35]), (B) *fd*-viruses (optical microscopy image of a smectic phase [37]), (C) PMMA ellipsoids (confocal microscopy of a nematic phase [38]) and (D) silica rods (confocal microscopy of a smectic phase [36]). All insets show SEM images of the constituent colloids. Scale bars are (A) 1 cm, (B,C) 10 μm , (D) 5 μm , and 500 nm for all insets.

1.4 Scope of the thesis

In this thesis, we describe the development of two novel model systems of anisotropic colloidal particles and study their self-assembly into colloidal liquid crystal phases with confocal microscopy. In particular, we develop a system of colloidal rods and bananas – with tunable dimensions and curvature – made of a polymeric material called SU-8. Using confocal microscopy and image analysis techniques, we study the impact of the particle shape on the structure and dynamics of different types of colloidal liquid crystals at the single-particle level.

This thesis is organized as follows. First of all, in Chapter 2, we present the basic concepts related to liquid crystals and the experimental techniques used to study them at the colloidal scale. This chapter begins with a description of the main liquid crystal phases formed by rod-like and banana-shaped particles. The physics of colloidal systems and their self-assembly into ordered phases are next discussed. Finally, the features of colloidal SU-8 systems are presented, alongside the working principles of confocal microscopy and image analysis techniques used.

In Chapter 3, the synthesis of colloidal SU-8 rods using sonication is described. Firstly, we discuss the high-shear based method used to fabricate long SU-8 rods, and then, the use of sonication to bring these into the colloidal domain. Next, the liquid crystal phase behaviour of the colloidal rods in water is addressed using confocal microscopy. In particular, we demonstrate that this system can be imaged in three-dimensions whilst carefully controlling the effect of gravity, as the refractive index and density mismatch between the particles and the solvent can be independently tuned. Finally, we show preliminary experiments on the behaviour of colloidal SU-8 rods in the presence of different external fields and added polymer.

Chapter 4 describes the development of colloidal SU-8 bananas with tuneable curvature. These are a unique addition to the existing library of anisotropic colloidal building blocks, as smoothly-curved rods were simply absent in the palette of colloidal model systems. Detailed studies of the synthesis mechanism, based on a temperature-driven buckling of straight SU-8 rods, is first discussed. Next, a full characterization of the dimensions and curvature of these particles is given. This chapter ends with an outlook showing the potential of these particles for studying, at the single-particle level, exotic liquid crystals, biofilms and other materials formed by curved, elongated building blocks.

In Chapter 5, particle-resolved confocal studies of the phase behaviour of differently curved bananas are presented. In particular, we systematically address the impact of curvature on the structure of the self-assembled liquid crystal phases using three differently curved systems of bananas. This results in a wide range of exotic phases such as biaxial nematic phases and polar/antipolar smectic phases. Particular focus is given to the phase behaviour exhibited by slightly curved rods, as they show the elusive splay-bend nematic phase. This represents the first experimental observation of this type of nematic phase, more than four decades after its first theoretical prediction.

Next, in Chapter 6, we exploit the inherent polydispersity of the colloidal bananas to assemble a hierarchical structure, termed the vortex phase, via the assembly of the particles into concentric structures, termed colloidal vortices. The impact of curvature and opening angle of the bananas on the formation mechanism of the vortex phase is firstly discussed. This includes the preparation of mixtures of differently curved bananas and the visualization of the formation of the colloidal vortices and vortex phase using confocal microscopy. This chapter ends with the characterisation of the structure and dynamics of the vortex phase.

Finally, in Chapter 7, the fabrication of rough colloidal SU-8 rods and bananas is described. We discuss how the nanoprecipitation of SU-8 in water is exploited to decorate the surface of our colloidal particles with SU-8 nanospheres. The tunability of the lobes' dimensions and lobe density is next demonstrated. With these newly-developed rough particles, we provide a colloidal model system that allows for studies addressing the impact of surface roughness on the mechanical, wetting and self-assembly properties of materials composed of anisotropic particles.

Chapter 2

Theoretical background and experimental methods

ABSTRACT

In this chapter, we introduce the basic concepts related to liquid crystals, starting with a brief historical background and then moving on to introducing the physics of liquid crystals. First, we discuss the symmetry of the main liquid crystal phases formed by rod-shaped and banana-shaped particles and also the key parameters driving their phase behaviour. We also introduce the main order parameter used to quantify liquid crystal ordering, as well as the basic elastic deformations liquid crystals can undergo. Next, the physics of colloidal particles and, in particular, of anisotropic particles is briefly discussed. We then describe the key features of our newly developed systems of colloidal SU-8 rods and bananas, and explain the principles of confocal laser scanning microscopy, which is the main experimental technique used to characterise our colloidal liquid crystals at the single-particle level. Finally, we discuss the typical image analysis routines used for extracting quantitative data from confocal images of our colloidal liquid crystals.

2.1 Liquid crystals

Liquid crystals were discovered back in 1888, when the botanist Friedrich Reinitzer observed that an organic cholesterol derivative had two melting points [42]. First, the organic material melted from a crystalline state into a cloudy liquid and then, at higher temperature, into a clear liquid. Intrigued by this behaviour, Reinitzer wrote a letter to the physicist Otto Lehmann, who a few years earlier had constructed a heating stage for his polarizing optical microscope [2]. Lehmann studied Reinitzer's material and observed that the cloudy liquid phase, while still flowing, also refracted light in a similar way to a crystal [43]. These revolutionary observations opened the field of liquid crystals [2, 44]. The interest in this kind of materials continued to grow thanks to Daniel Vörländer, who in the early 1900s synthesized many new liquid crystalline substances and identified what molecular features give rise to liquid crystallinity [45, 46]. Experimental work on the physical properties of liquid crystals was then supported by the theoretical work of Pierre de Gennes [1], Carl Oseen [47], and F. Charles Frank [48] among others, during the second half the nineteenth century. Since then, great progress has been made on explaining the structural order in liquid crystals, their behaviour under electric fields and their elastic properties [2, 4, 49].

Traditionally, liquid crystals were limited to rod-like building blocks. Vörländer himself reported in 1926, that non-linear molecules were unfavourable for forming liquid crystal materials [50]. Over the years, however, both experimentalist and theoreticians realised that many other shapes can also exhibit liquid crystal phases, and in fact, that these can show unexpected and remarkable physical properties such as supramolecular chirality and/or polarity [8–10]. This is the case with some plate-like [51], dimers [52], and banana-shaped molecules [53], and it is one of the reasons as to why liquid crystal research continues to be as active as ever [7–9, 54].

A general classification of different liquid crystal phases can be obtained in terms of phase symmetry, which is based on the degree of translational and orientational order shown by the liquid crystal-forming building blocks [1, 55]. Since *the shape* of these building blocks has a strong impact on the way they arrange into different phases, in the following two sections we summarise the main liquid crystal phases exhibited by rod-like particles and banana-shaped particles, as these are the two liquid crystal systems investigated in this thesis. Note that from a symmetry prospective, we refer to the liquid crystal-forming building blocks – which are typically elongated molecules, polymers or colloids – simply as particles.

2.1.1 Rod-like liquid crystals

In systems formed by rod-like particles, four major types of phases can be distinguished based on their orientational and positional order [1, 2]. These are the *isotropic* (I), *nematic* (N), *smectic* (Sm) and *crystalline* (C) phases, whose structural arrangement is shown in Figure 2.1. In the fully liquid or *isotropic phase*, particles do not exhibit positional nor orientational order. In other words, particles do not show any translational symmetry nor a preferential average orientation, which can be respectively characterised by the random distribution of both *centre of mass* (CM) and the *long axis orientation* $\hat{\mathbf{u}}$ of the particles in the phase (Figure 2.1A) [1, 2]. In the *nematic phase* particles point on average in the same direction, which is typically characterised by the unit vector $\hat{\mathbf{n}}$ called the *director* (see Figure 2.1B). At the same time, the centres of mass of the particles are still distributed randomly, i.e. there is no positional order. In the *smectic phase*, the orientational order shown in the nematic phase is accompanied by positional order in one dimension; particles form layers (see Figure 2.1C). However, particles within the layers are still distributed in a liquid-like manner. The fashion in which particles are organized inside these layers determines the exact type of the smectic phase. As many as twelve variations have been identified but only the most common smectic phase, the smectic-A, where particles are oriented parallel to the layer normal, is shown in Figure 2.1C [1, 2]. In the fully crystalline phase, particles show both long-range positional and orientational order in all three-dimensions (see Figure 2.1D). Note that there are other liquid crystal phases, such as *columnar* phases (Co) and *cholesteric* phases (N*), which are not discussed here but also show intriguing and well-defined liquid crystal ordering (see books [2, 44] for extended details).

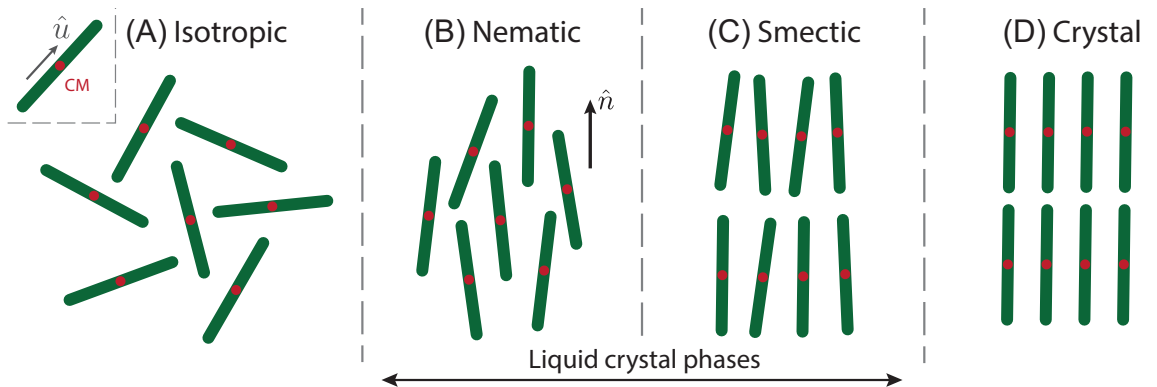


Figure 2.1: Schematic representation of the arrangement of rod-like particles in (A) the isotropic phase (no positional nor orientational order), liquid crystal phases comprising the (B) nematic and (C) smectic phases (no (fully) positional but orientational order) and the (D) crystal phase (positional and orientational order). The red dots represent the centre of mass (CM) of the particles, $\hat{\mathbf{u}}$ their orientation and $\hat{\mathbf{n}}$ the nematic director of the phase.

2.1.2 Banana-shaped liquid crystals

Banana-shaped particles exhibit a much richer liquid crystalline phase behaviour than rod-like particles, with more than fifty different liquid crystal phases [7–9]. Here, we only discuss some of most representative nematic and smectic phases shown by banana-shaped particles, which are shown in Figure 2.2. The increased structural complexity of ‘banana’ liquid crystal phases arises from the loss of symmetry along the long axis of the particles [8, 10]: banana-shaped particles are biaxial and their long and short axis orientations are described by the *orientation vector* $\hat{\mathbf{u}}$ and the *polar vector* $\hat{\mathbf{p}}$, respectively (see inset Figure 2.2A). The additional degrees of freedom associated to the orientation of the banana-shaped particles results in the formation of not only the conventional uniaxial nematic phases, with only one common direction of alignment, but also in biaxial nematic phases (N_b), where particles align along two orthogonal directions, as shown in Figure 2.2A. Note that when the $\hat{\mathbf{p}}$ vectors show alignment in the same direction, the phase exhibit polar order (see e.g. $N_b(P)$ in Figure 2.2A) [8]. Nematic phases formed by banana-shaped particles can also exhibit periodic modulations of the nematic director in space, $\hat{\mathbf{n}}(y)$, in two- and three-dimensions, and give rise to phases known as the nematic splay-bend (N_{SB}), shown in Figure 2.2A, and nematic twist bend phases (N_{TB}) [13, 14]. A detailed discussion of these phases will be presented in Chapter 4.

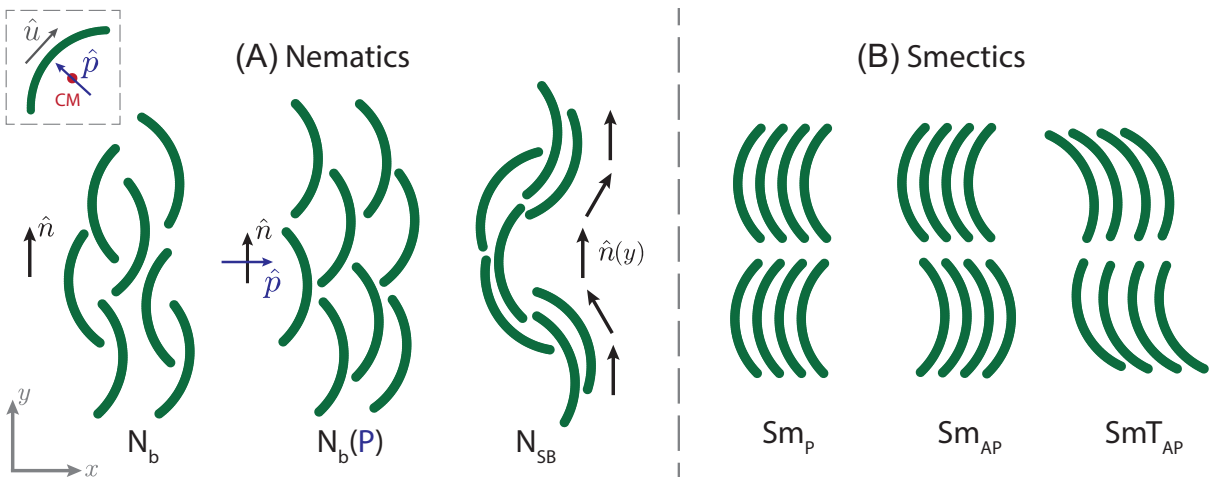


Figure 2.2: Schematic representation of the arrangement of banana-shaped particles in (A) nematic and (B) smectic phases. The nematic phases include: the biaxial (N_b), the biaxial with polar order ($N_b(P)$) and the splay-bend nematic phase (N_{SB}). The smectic phases include: the antipolar (Sm_{AP}), polar (Sm_P) and anti-polar tilted (SmT_{AP}) smectic phase. The red dot represents the centre of mass (CM) of the particles, $\hat{\mathbf{u}}$ the orientation of the long axis and $\hat{\mathbf{p}}$ of the short axis, and $\hat{\mathbf{n}}$ the nematic director of the phase, which can also vary in space $\hat{\mathbf{n}}(y)$.

In smectic phases formed by banana-shaped particles, the loss of axial symmetry also translates into many multiple ways of arranging the particles into layers [8–10]. Some of the most common banana smectic phases are shown in Figure 2.2B, which includes the antipolar smectic phase (Sm_{AP}), where the polar order in adjacent layers is opposite, the polar smectic phase (Sm_P), where neighbouring layers have polar order in the same direction, and the tilted smectic phases ($SmT_{P/A}$), with also polar or anti-polar order. Note that the geometrical features of the particles, such as their opening angle – which is a measure of the curvature of the particles – or their aspect ratio, have a huge impact on the phases they form (see reviews in [9, 10, 56]).

From a symmetry point of view, the most striking discovery in banana-shaped liquid crystals is that chiral phases, such as the twist-bend nematic [14, 57] and chiral smectic phase [7], can be spontaneously formed by achiral banana particles. This is both fundamentally and technological relevant, as it was thought that macroscopic chirality could only arise from chiral building blocks and also, because chiral molecules are very commonly used in liquid crystal displays but are relatively expensive to synthesise [11]. From a microscopic point of view, i.e. when the electronic properties of the molecules are considered, the biaxial shape of the particles leads to a net dipolar moment along the short axis of the particles. This promotes the formation of structural arrangements with specific interactions between the individual dipolar moments. The resulting coupling between the electronic properties of the banana molecules and the structure of the phase leads to fascinating phenomena not seen in conventional liquid crystals. This includes spontaneous polarisation and flexoelectricity [53]. For instance, in ferroelectric smectic phases of banana particles, there is a spontaneous electric polarisation of the phase – meaning that it is induced in the absence of an electric field –, whose direction can be reversed at extremely fast speeds upon applying an external electric field. This remarkable feature promises applications of these banana phases in new generations of optoelectronic devices [8, 10].

2.1.3 Thermotropic and lyotropic liquid crystals

For a given system of liquid crystal-forming building blocks, their phase behaviour can depend on either the temperature of the system or on the concentration of the particles in the dispersion [2, 6] (see Figure 2.3A). Based on the parameter inducing the phase transitions between different states, liquid crystalline materials can be classified into two distinct types: the *thermotropic* and *lyotropic* liquid crystals [2, 6]. *Thermotropic* liquid crystals are usually composed of molecules and the various phase transitions are controlled by varying the temperature of the system. These

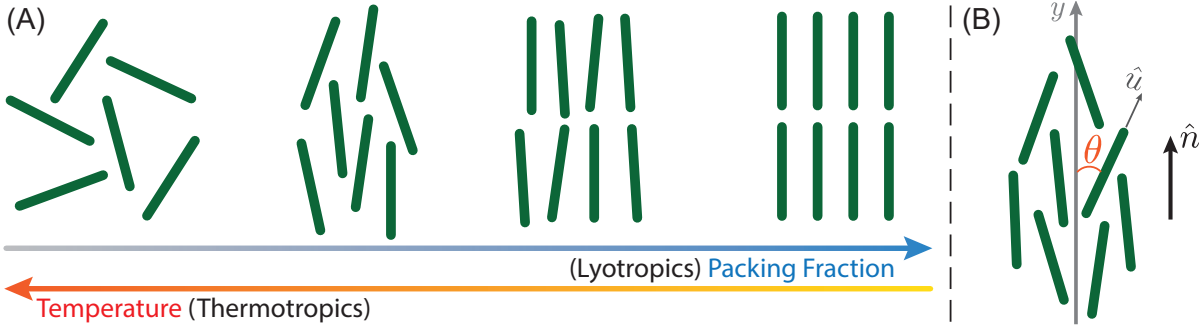


Figure 2.3: (A) Schematic representation the phase behaviour of liquid crystals as a function to temperature and packing fraction. In thermotropic liquid crystals, as the temperature increases, the system transitions from the ordered crystalline phase to the disordered liquid phase. On the contrary, lyotropic liquid crystals increase their degree of ordering by increasing the concentration of the constituent particles. (B) Orientation of rod-like particles $\hat{u}$ in a nematic phase with nematic director $\hat{n}$. θ is the angle between the orientation of the particles and the nematic director.

are the liquid crystals discovered back in 1888 by Reinitzer and Lehman [43], and are nowadays at the heart of technological materials finding a widespread use in optoelectronic applications [2]. It is important to note that the physical properties of thermotropic liquid crystals depend both on the arrangement of the molecules in the phase and also on the electronic structure of the molecules [2].

The ordering in *lyotropic* liquid crystals, which can¹ be composed of colloidal particles and hence also called *colloidal liquid crystals*, is controlled by the concentration of the particles in the dispersion (see Figure 2.3A). Colloidal liquid crystals were first reported in the 1925 by Zöcher [58], and their properties do not depend as much on the microscopic details of the particles but on their structural arrangement in the phase [59]. In this thesis, we shall restrict ourselves to *colloidal liquid crystals* as our building blocks are in the colloidal domain, but it must be noted that research done with them here is driven by the aim of gaining fundamental understanding of thermotropic liquid crystals.

2.1.4 Orientational order parameter for nematic liquid crystals

The degree of orientational order exhibited by a liquid crystal phase is typically quantified by using orientational order parameters [4, 49, 60, 61]. There are multiple ways of defining orientational order parameters depending on, for instance, the symmetry of the liquid crystal phase or on whether it is a local or a global measurement of orientation [14, 62, 63]. A second rank tensor is typically used to characterise the orientational order of the rod-like particles in a

¹Note that lyotropic liquid crystals can also be composed of amphiphilic molecules, and their phase behaviour depend both on the concentration and temperature of the system.

nematic phase [49, 60]. However, when the nematic phase is uniaxial (see Figure 2.3B), a scalar order parameter can be used to characterise the degree of alignment of the particles along $\hat{\mathbf{n}}$. This order parameter is known as the global nematic order parameter, S_2 , and is defined by

$$S_2 = \left\langle \frac{d \cos^2(\theta) - 1}{d - 1} \right\rangle, \quad (2.1)$$

where θ is the angle between the orientation of the rods $\hat{\mathbf{u}}$ and the director $\hat{\mathbf{n}}$ [4, 49, 60, 61] (see Figure 2.3B) and d the dimension of space. The order parameter S_2 can take values ranging from $-1/2$, in the case all particles are perpendicular to the director, to 1, in the case all particles are parallel to the director, i.e. a nematic phase. In the isotropic phase, S_2 is approximately 0.

2.1.5 Deformations in nematic liquid crystals

A uniaxial nematic phase typically finds its most stable state when the average orientation of the particles is characterised by a uniform director field, $\hat{\mathbf{n}}$, i.e. when the orientation of the director does not vary in space (see example in Figure 2.3B) [2, 60]. However, there are multiple situations where liquid crystals are constrained to adopt configurations in which the director field is not uniform [2, 60]. For instance, chemically treated sample cells force liquid crystal molecules to orient parallel to their surfaces [2, 60]. This leads to the deformation of liquid crystals in space as their molecules have to satisfy the alignment constraints to all of the surfaces [64]. Similar behaviour occurs in the presence of external electric and magnetic fields [2, 60]. The resulting change of the orientation of the director field, $\hat{\mathbf{n}}(r)$, can be either continuous, creating deformations, or it can change abruptly, creating disclinations or defects [2, 65].

There are three main types of deformations that can occur in a liquid crystal upon applying an external force. These are the *splay*, *twist* and *bend* deformations (see Figure 2.4) and were first

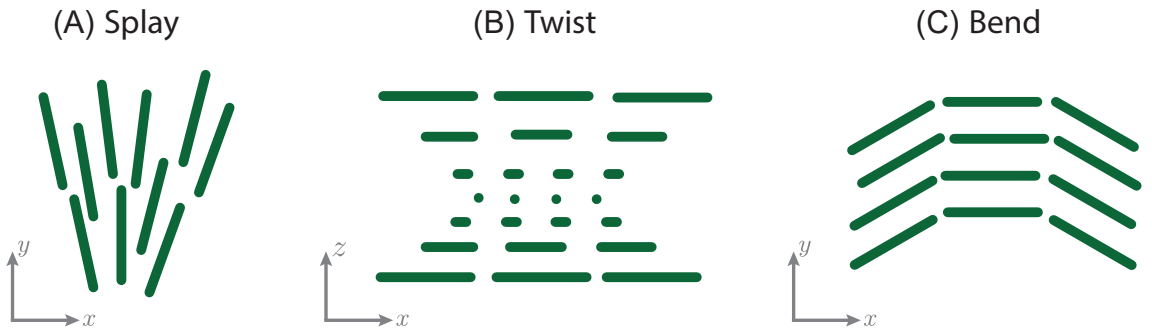


Figure 2.4: Schematic representation of the (A) splay, (B) twist and (C) deformations in nematic liquid crystals. Note that the dots in (B) represent particles pointing out of the plane.

formulated by Oseen and Frank in their famous theory on the elasticity of liquid crystals [47,48]. All these three distortions have an associated energy cost, which is typically characterised by an elastic constant [47,48]. Combinations of the splay, twist and bend deformations are also possible, but they are typically associated with a higher energetic penalty, which makes complex nematic phases energetically unfavourable and hence unstable [2]. However, in the last forty years, scientists realised that liquid crystal molecules with complex shapes could stabilise complex non-uniform nematic director fields in the absence of external forces [8,13,53,66]. An example relevant for this thesis, is the work pioneered by Meyer [66] and Dozov [13], who postulated that a system of banana-shaped particles could spontaneously form nematic phases with splay-bend or twist-bend deformations due to the bent geometrical features of the particles.

2.2 Physics of colloidal particles

2.2.1 Brownian motion

When colloidal particles are dispersed in a solvent, the molecules of the solvent constantly collide with the surface of the particles due to thermal agitation. This results in a random walk of the colloidal particles, which allows them to continuously sample the available phase space [16–18]. Also known as Brownian motion, this phenomenon was first discovered in 1827 by Robert Brown, who studied the movement of pollen grains in water using a optical microscope. A theoretical explanation of Brownian motion was provided few decades after by Albert Einstein [21], who used statistical mechanics tools, such as the Boltzmann distribution, to describe the random motion of colloidal particles and their distribution in gravitational fields. In 1909, Jean Perrin provided the experimental confirmation of Einstein’s theory, as he was able to measure the Boltzmann’s constant and Avogadro’s number from a set of beautiful experiments using colloidal particles and an optical microscope [20]. This work had an enormous impact at the time, as it proved the actual granularity of matter and hence the definitive existence of atoms and molecules. Not surprisingly, Perrin and Einstein received a Nobel Price in 1926 for their work on ‘the discontinuity of matter’. The work of Perrin and Einstein also laid the foundations for the ‘Colloids as big atoms’ paradigm [16,18], as they showed that colloids can also explore configurational space and reach equilibrium distributions in an analogous way to atoms and molecules, and as such, their phase behaviour can be studied using the same statistical mechanical framework.

As first formulated by Einstein, the dynamics of a Brownian particle can be characterised using the mean squared displacement (MSD), which measures the typical area $\langle \Delta r^2 \rangle$, explored by the particle over a time lag τ . For a free diffusive Brownian particle its MSD is given by

$$\langle \Delta r^2(\tau) \rangle = 2dD\tau, \quad \text{with} \quad D = \frac{k_B T}{\xi}, \quad (2.2)$$

where d is the dimension of space, D is the diffusion coefficient, $k_B T$ is the thermal energy with k_B the Boltzmann's constant and T the temperature of the system, and ξ is the friction coefficient of the particle in the fluid [21]. For a colloidal sphere of diameter a , the friction coefficient is given by the Stokes' formula $\xi = 3\pi\eta a$, where η is the viscosity of the solvent, giving rise to famous the Stokes-Einstein formula describing the diffusion coefficient of a sphere [16]. When considering an anisotropic shape, such as a colloidal rod, the expression of the friction coefficient is no longer a linear expression but a tensor, as now it depends on the longitudinal or transverse direction with respect to the long axis of the rod [60, 67]. As a result, the diffusion coefficient of a colloidal rod, or in a more general sense, of any anisotropic particle, is also extended to a diffusion tensor with various degrees of complexity depending on the symmetry of the particle [60, 68–72].

The characteristic time scale of Brownian motion is given by the Brownian time, τ_B , which is the time taken for a particle to move a distance equal to its own diameter [15]. In three dimensions this time is given by

$$\tau_B = \frac{a^2}{6D}. \quad (2.3)$$

Because the typical length scale associated to colloids is on the order of few micrometers, the resulting Brownian time of colloidal particles is on the order of few seconds [16, 17]. These relatively large time and length scales makes colloids very useful experimental systems to be studied with optical microscopy, as they can be resolved in real space and time at the single-particle level [16].

Another relevant phenomenon occurring in colloidal suspensions is the sedimentation of colloidal particles due to the earth's gravitational field [16]. Sedimentation occurs when the mass density of the particles is larger than that of the dispersing solvent. Similarly to gas molecules, colloids also show a barometric height distribution in which the number density of the particles,

n , as a function of height, z , is characterised by an exponential distribution [73],

$$n(z) = n(0) \exp\left(-\frac{z}{L_g}\right), \quad \text{with} \quad L_g = \frac{k_B T}{\Delta m g}. \quad (2.4)$$

Here, the decay length of the exponential distribution is called the *gravitational length*, L_g , which quantifies the effect of gravity in the system. In other words, it gives a measure for the height to which a particle is lifted due to its thermal energy $k_B T$ in the presence of a gravitational field [16]. Note that Δm is the buoyant mass of the colloid particles and g the gravitational acceleration constant. The effect of gravity in colloidal systems is therefore strongly dependent on the mass density mismatch between the particles and the solvent, and on the size of the particles. While for some colloidal suspensions the gravitational height can be several kms, for some others it can be on the order of the particle size or even smaller [16]. For instance, colloidal systems with a small L_g can be very useful for studying systems in two dimensions [29], but can also lead to kinetic arrested phases if the system is studied in three-dimensions [15].

2.2.2 Colloidal interactions

In colloidal suspensions, particles can interact with one another via a range of attractive and repulsive forces [60]. The origin of these forces depends on many factors including the material they are made of, the nature of the solvent, the presence of salt or polymer in solution and the use of external fields [16]. Inter-particle interactions are usually described by a pair potential, $U(r)$, which is the interaction energy of two particles as a function of their relative position, r . One of the most relevant pair potentials in colloid science is the Derjaguin-Landau-Verwey-Overbeek (DLVO) potential, which describes the stability of slightly charged colloidal particles in suspension [15] (see Figure 2.5A and Equation 2.5). The potential energy of this interaction consist of an attractive part, $U_{att}(r)$ and a repulsive part, $U_{rep}(r)$, whose competition dictates the stability of the suspension. The DLVO potential is written as:

$$U_{DLVO}(r) = U_{att}(r) + U_{rep}(r) \propto -\frac{1}{r} + \exp\left(-\frac{r}{\kappa}\right), \quad (2.5)$$

where κ^{-1} , is the Debye length and characterises the decay of the $U_{rep}(r)$ [15]. The attractive part of the DLVO potential, originates from the Van der Waals (dispersion) forces acting between the molecules constituting the colloidal particles. These attractive forces play an important role

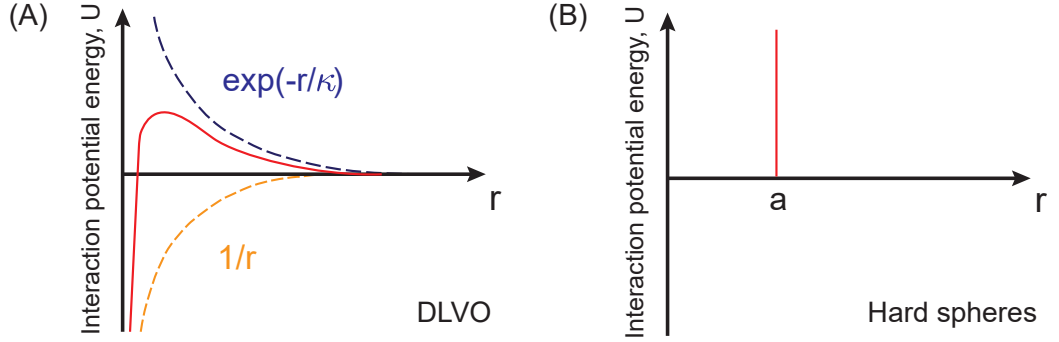


Figure 2.5: Schematic representation of the interaction potential energy U , as a function of the inter-particle distance r , in a system of (A) slightly charged spheres and (B) hard spheres. a is the diameter of the colloidal particle.

at short inter-particle distances (see $1/r$ dependence in Equation 2.5), as the interaction between the millions of molecules forming the colloidal particles can lead to the irreversible aggregation of the particles [60]. Van der Waals attractions are, however, usually opposed by repulsive electrostatic forces. Colloidal particles typically carry charged surface groups which become ionised when suspended in water [15]. The charge of the particles is typically screened by the counter-ions present in the dispersion medium, which form an electric double-layer around the colloidal particles. As a result, the surface charge decays exponentially with a typical length scale characterised by the Debye length κ^{-1} (see Equation 2.5). Since κ^{-1} depends on the amount of ions present in the system [15, 60], the strength and range of the repulsive electrostatic forces, and hence its competition with the constant attractive Van der Waals forces, can be controlled via tuning the salt concentration in solution [15, 60].

The interactions between colloidal particles can be also tuned such that, for instance, they resemble to what are so-called *hard* or *excluded volume* interactions [74]. In hard particle systems, the potential energy between two particles is considered infinite if they overlap and zero otherwise (see Equation 2.6 and Figure 2.5B). This is experimentally achieved by screening the charges of the particles [40, 75] or by grafting onto the particles's surface a polymer layer, whose chains are much shorter than the typical size of the particles [24, 76]. This gives rise to short-range repulsive interactions, which allows the particles to come into close proximity without compromising their stability [77].

$$U_{HS}(r) = \begin{cases} \infty & \text{if } r \leq a \\ 0 & \text{if } r > a \end{cases}, \quad (2.6)$$

Finally, it is important to mention that nowadays colloidal interactions can be also engineered such that they are directional. This means that particles can experience forces in specific parts of their surface and hence interact with an orientational dependence [78, 79]. Directional interactions are typically achieved by coating specific parts of the particles with attractive or repulsive functionalities, such as DNA-strands or hydrophobic molecules [78–81].

2.3 Self-assembly and entropy-driven phase transitions

Self-assembly of colloidal systems is the process by which colloidal particles – continuously jiggling around in suspension due to thermal energy – self-organise into structures with a higher degree of order than that of the initial state [19]. This includes the self-assembly of, for instance, colloidal crystals [24, 82] and liquid crystals [27, 83], but also the formation of non-close-packed structures, such as colloidal molecules [84, 85] and open crystalline structures [25, 80]. The structural complexity of self-assembled structures depends mainly on the type of inter-particle interactions and the shape of the particles. In the context of self-assembly of liquid crystals, it is particularly relevant to examine the simplest case, where colloidal rods interact via hard interactions. Lars Onsager was the first to theoretically study this system and realise that a system of hard rods could transition from an isotropic to a nematic phase at a remarkably low packing fraction of rods [86]. Onsager’s theory, which was published in 1949, represented a hallmark in the field of condensed matter physics, and also in the liquid crystal community [2, 60]. For the first time, it was shown that phase transitions from a disordered state to an ordered state could be explained in the absence of inter-particle attractions, and that only particle shape anisotropy was enough to explain liquid crystal ordering. To fully appreciate the importance of Onsager’s findings and how it relates to colloidal liquid crystals, it is worth revisiting a few key concepts of (statistical) thermodynamics.

From a thermodynamic perspective, colloidal particles are statistical systems that find their equilibrium state by minimising their free energy $F = U - TS$, where U is the internal energy, T is the temperature and S is the entropy of the system [17, 60]. In hard-core systems, the interaction potential is infinite if two particles overlap and zero elsewhere (see Equation 2.6). As a consequence, the Boltzmann weight of a configuration of hard spheres is either zero, in the case of overlap, or unity otherwise. In other words, the only relevant configurations are the ones without particle-particle overlaps, and all of them are equally probable. As a result, the internal

energy does not play any role in the free energy minimisation of the system². This implies that the phase behaviour of hard systems is essentially dominated by entropy, and perhaps surprisingly, that entropy is maximised by the organisation of hard particles into ordered phases at increasing packing fraction. The fact that these type of phase transitions could occur in the absence of particle interactions was a topic of a huge debate 70 years ago, however, after several crucial pieces of work on hard spheres [23, 24] and hard rods [86], they are now widely accepted and carefully examined both experimentally and with computer simulations.

The crucial idea required to understand entropy-driven phase transitions relies on the microscopic definition of entropy, which instead of being linked to the idea of disorder, is connected to the number of configurational states available in the system. As first postulated by Boltzmann, Gibbs and Planck, the more microstates accessible are to a system, the larger the entropy [19, 87, 88]. The relation between entropy, phase behaviour and particle shape is best illustrated by a system of hard rods. Onsager proposed that the isotropic-nematic transition occurring in a system of hard rods could be understood as the result of a competition between the orientational entropy and the translational entropy of the rods [86, 89]. When the particle concentration increases, the rods align because despite losing orientational entropy, they increase the available space per particle – or translational entropy – by aligning. As a result of this ordering, the total entropy, i.e. the total number of configurational states, of the system increases and hence drives the phase transition from a disordered to an orientationally ordered phase. Comprehensive derivations of Onsager’s theory can be found in [60, 90, 91].

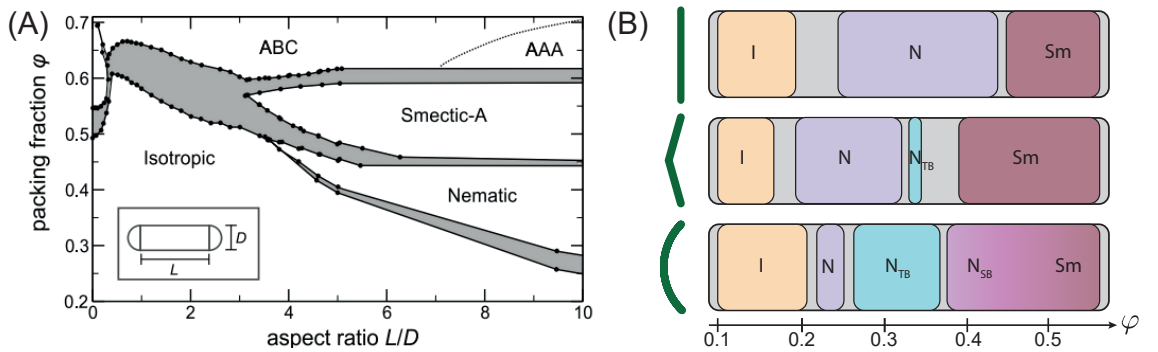


Figure 2.6: (A) Phase diagram of hard spherocylinders of length L and diameter D (see inset) as a function of the packing fraction ϕ and aspect ratio L/D [92]. Isotropic liquid, nematic, smectic and crystal (ABC and AAA) phases are found. The shaded areas denotes biphasic coexistence regions. (B) Phase diagram hard spherocylinders, boomerangs and smoothly curved spherocylinders with $L/D = 10$ and opening angle of 150° as a function of packing fraction [14].

²Note that the internal energy also contains kinetic part, U_k , which is constant and therefore does not affect the phase behaviour of the system.

The experimental confirmation of Onsager’s theory came in 1992 with a colloidal system hard-like boehmite rods [93], which upon increasing the particle concentration, exhibited nematic phases. Computer simulations have further shown that not only nematic phases, but also smectic and crystalline phases can occur in systems of hard spherocylinders [92] (see Fig. 2.6A). These findings have been also experimentally confirmed with colloidal liquid crystals composed of Gibbsite platelets [35], silica rods [83] and SU-8 rods [27]. More recently, the research has moved towards the investigation hard systems with more complex shapes as they have proven to form remarkably complex structures, such as quasi-crystals [94] or exotic liquid crystals [14]. This is nicely illustrated by the work of Damasceno et. al [95], who carefully studied the impact of shape in systems of hard polyhedra and revealed the formation of more than twenty different liquid crystal phases. Another example includes the work of Chiappini et al. [14], who studied the phase behaviour of slightly bent rods with both a sharp kink and a smooth curvature (see Figure 2.6B), and revealed the stability of splay-bend and twist-bend nematic phases [14]. Both examples showcase the fact that complex phases can arise from building blocks that simply interact via ‘their shape’.

It is not surprising that computational work usually precedes experiments; this is due to the fact that fabricating complex particles at the colloidal scale is not an easy task. In this thesis, we contribute to the field of colloid science and liquid crystals by developing two novel model system of colloidal rods and bananas, whose assembly can be experimentally studied at the single-particle level. These systems can be used to compare the resulting self-assembled structures to computer simulations and vice-versa, and also to create new self-assembled structures with pre-designed internal structural complexity.

2.4 Experimental methods

2.4.1 Colloidal model systems

Our newly developed model systems consist of colloidal SU-8 rods and bananas, whose structure and dynamics can be imaged at the single-particle level with confocal microscopy, as shown in Figure 2.7. A full discussion of the synthesis details of these two systems, as well as their potential for studying liquid crystals is given in Chapter 3 and 4. Here, we summarise the main properties of the colloidal SU-8 particles, the material properties of SU-8 and the previous work related to the bulk fabrication of non-Brownian SU-8 rods [96, 97]. Firstly, the dimensions of

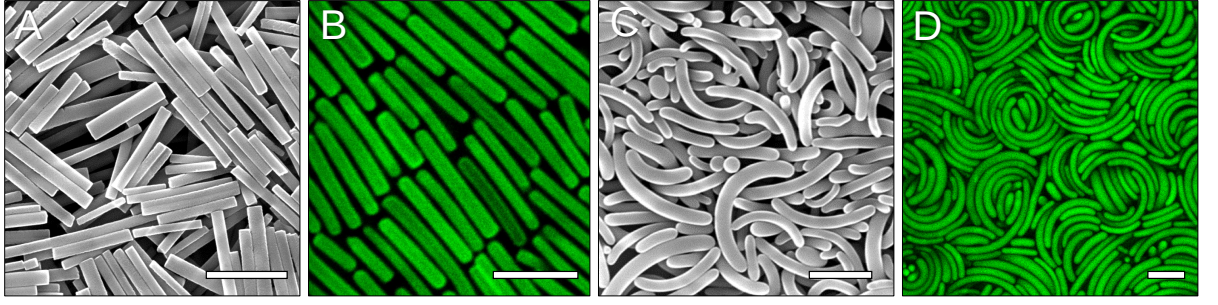


Figure 2.7: Scanning electron microscopy images and confocal microscopy images of the (A-B) colloidal SU-8 rods and (C-D) bananas, respectively. Note that in the confocal microscopy images the particles have been fluorescently dyed. Scale bars are $5\mu\text{m}$.

our colloidal SU-8 particles can be tuned with lengths ranging from 4 to $15\mu\text{m}$ and diameters from 0.4 to $1.2\mu\text{m}$. In the case of the bananas, their curvature can be continuously tuned from $0.25\mu\text{m}^{-1}$ to zero. In addition, both systems can be easily fluorescently dyed and are stable in aqueous and organic solvents. By varying the composition of the organic solvent mixture, the difference in refractive index and mass density between the particles and the solvent can be independently controlled. This enables the use of confocal microscopy for imaging dense phases of colloidal rods and bananas in three-dimensions, whilst controlling of the effect of gravity - which is important for the dynamics of colloidal suspensions and hence liquid crystal formation.

SU-8 photoresist as a material

SU-8 is UV-curable, epoxy-based photo-resist commonly used in photolithographic processes [98, 99] (see Figure 2.8A). The main components of SU-8 photoresist are (i) SU-8 oligomers, with an average number of eight epoxy groups, (ii) an organic solvent (γ -butyrolactone, GBL) and (iii) a salt-based photo-acid generator (triarylsulfonium salt), as schematically shown in Figure 2.8B and C. There is a wide range of commercially available formulations of SU-8 in which the content and type of solvent varies, resulting in varying viscosity values [98, 100]. In this thesis, we use SU-8 50 from Microchem [101], which consists of 63% of SU-8 oligomers and 27% of GBL using triarylsulfonium hexafluoroantimonate salt.

Upon UV-exposure, the cross-linking of SU-8 takes place via a cationic polymerisation reaction [100, 102], as schematically shown in Figure 2.8D. Firstly, the photo-acid generator is decomposed into a strong acid upon UV-exposure (see Figure 2.8D(i)). This acid initiates the cationic polymerisation reaction by ring-opening the epoxy groups, which subsequently undergo cross-linking with other epoxy groups [102, 103], as shown in Figure 2.8D(ii). A post-exposure

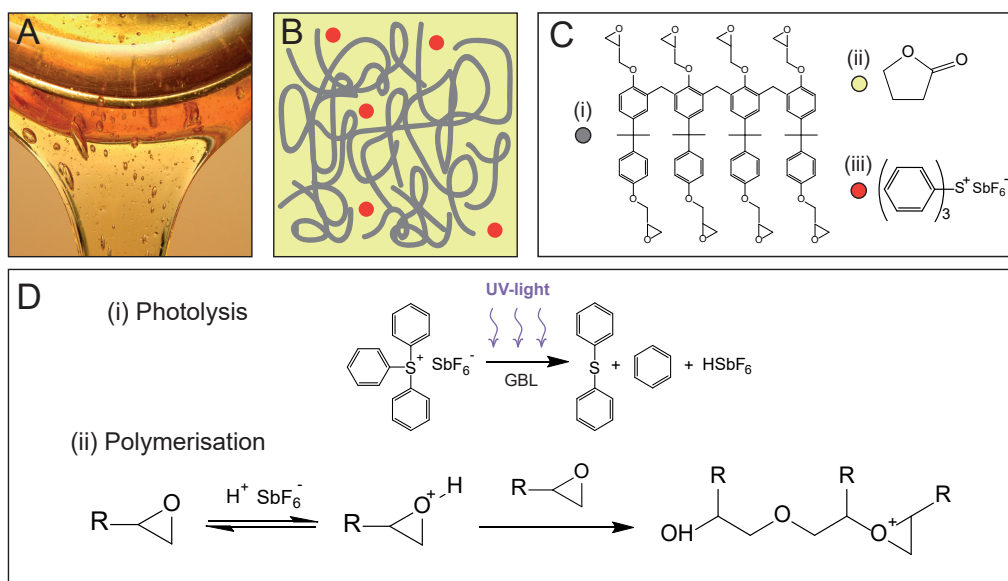


Figure 2.8: (A) Photograph of the SU-8 photo-resist showing its characteristic high viscosity [101]. (B,C) Schematic representation of the three main components of SU-8 photoresists: (i) SU-8 oligomers, (ii) the solvent and (iii) the photo-initiator. (D) Scheme of the photo cross-linking reaction of SU-8. (i) The photo-acid generator is activated upon UV-exposure. (ii) The polymerisation starts when the acid protonates the epoxy groups. The activated oligomers then react with neutral epoxy groups [102].

thermal treatment is typically conducted to increase the mobility of the photo-acid and SU-8 oligomers, and hence accelerate the polymerisation rate [102, 104, 105]. Due to the large number of epoxy functionalities per oligomer, UV-cured SU-8 photo-resists possess a high degree of cross-linking. This results in highly stable mechanical and chemical structures with a typical Young's modulus of $E \approx 4\text{GPa}$ and a glass transition temperature of $T_g \approx 200^\circ$ [98, 100]. Importantly, when fully cross-linked, SU-8 photoresists have a mass density of $\rho_{\text{SU8}} = 1.2\text{g/mL}$ and refractive index $n_{\text{SU8}} \approx 1.6$ [98, 100]. The value of these bulk properties makes SU-8 a good material candidate for fabricating colloidal model particles, as they can be matched with the mass density and refractive index of common solvents used in colloid science [106].

Bulk synthesis of SU-8 microparticles

SU-8 photo-resists are traditionally used in lithographic processes where SU-8 acts as negative resist [98, 102]. In these processes, micro-fabricated masks are used to selectively expose parts of SU-8 to UV-light: the exposed parts become cross-linked and hence solid, while the unexposed parts remain soluble and can be washed away during the development. This technique allows to produce micron-sized features in SU-8 films, which find common applications in the field of microfluidics [98, 102]. Photolithography of SU-8 has also been exploited to fabricate colloidal

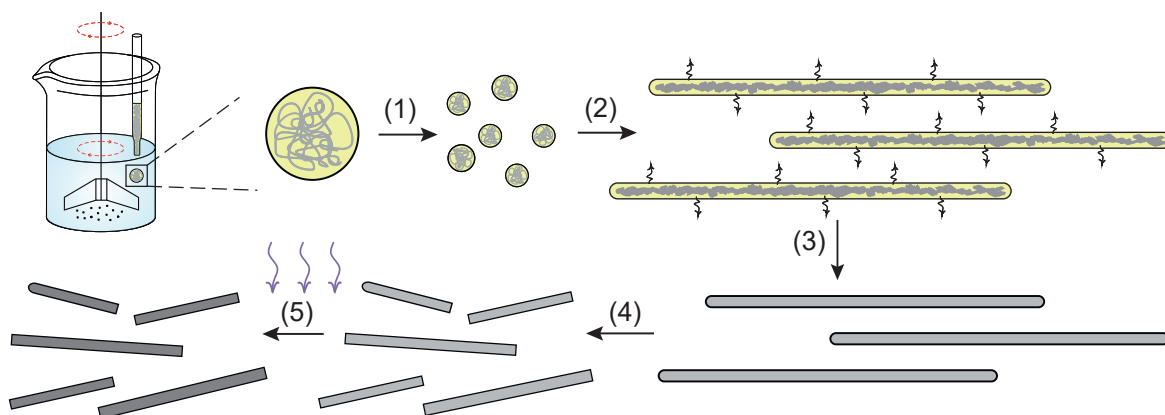


Figure 2.9: Schematic representation of the stages involved in the SU-8 microrod formation mechanism. (1) Emulsification of the polymer droplets. (2) Elongation of the liquid droplets under shear flow and simultaneous transferring of the GBL into the dispersion media. (3) Solidification of the SU-8 cylinders. (4) Break-up of the long and solid cylinders into shorter pieces under shear. (5) Photo cross-linking of the microrods via illumination with UV-light.

SU-8 particles with various shapes, including spirals [107], discs [108] and rod-like shapes [109]. However, the 2D nature of this procedure limits the possibilities to obtain high particle yields, which are required to prepare dense colloidal suspensions, and also, it only produces particles with high aspect ratio when their diameter is on the order of tens of micrometers [100, 107–109].

An alternative route to obtain SU-8 microparticles was firstly explored by Alargova et al. in 2004, who showed that long SU-8 rods could be obtained in *bulk* via shearing an emulsion of SU-8 droplets in a highly viscous medium [96, 97]. This method consists of five main steps which are schematically shown in Figure 2.9. First, a small amount of concentrated SU-8 solution in γ -butyrolactone (GBL) is added to a viscous organic liquid medium (such as glycerol or its mixtures with alcohols) that is being subjected to high-shear flow. The insolubility of SU-8 in the dispersion media and the high-shear rates facilitate the formation of an emulsion of micron-sized polymer solution droplets (see Figure 2.9, step 1). Under high shear, these droplets are deformed into long cylinders (see Figure 2.9, step 2). At the same time, the solvent diffuses out of the sheared polymer droplets leaving the solid polymer behind. The latter process is assisted by the fact that the solvent for the SU-8, GBL, is soluble in the dispersion media. When the transfer of GBL into glycerol has been (partially) completed, the long, thin liquid cylinders solidify and any recovery of the initial spherical shape is prevented (see Figure 2.9, step 3). As a result, the solid character of the cylinders leads to the breaking of the long cylinders into shorter rod-like particles under high shear (see Figure 2.9, step 4) [97]. The breaking-up of the cylinders is confirmed by SEM analysis, where it is shown that most of the rods have straight edges and

just a very few of them have hemispherical ends. This feature that would not be possible if every drop would deform and solidify into a single-particle [96,97]. In the last step, the SU-8 rods are typically cross-linked by means of UV-illumination (see Figure 2.9, step 5), which results into chemically extremely stable polymer particles.

This method allows to produce SU-8 rods with tunable dimensions ranging from diameters between 0.5 and 1.5 μm and lengths between 20 μm and 200 μm , resulting in aspect ratios ranging from 25 to 125. Alargova et. al demonstrated that key parameter controlling both the rod formation and their dimensions is the *shear stress*, τ [96,97]. The shear stress is defined as the product of the media viscosity μ_o and the shear rate G :

$$\tau = \mu_o G . \quad (2.7)$$

Here, the shear flow produced in the reaction vessel is simply modelled as the flow induced in the gap between two concentric cylinders [96,97]. There are other parameters, such as the concentration of SU-8 in GBL, which also play a role on the synthesis of SU-8 rods. For instance, a minimum concentration of SU-8 in GBL is required for the formation of rods. This is related to the viscosity of the SU-8 droplets, which needs to be high enough to enable their deformation into long cylinders under the shear flow. Other experiments showed the versatility of the method by producing microrods using mixtures of polymers, including SU-8 mixed with polystyrene [97].

While Alargova's results have provided an experimental system of rods with a host of applications [96,110], the large dimensions of the produced particles prevents the rods to undergo Brownian motion. As a consequence, the long SU-8 rods can not be used as colloidal model systems to study liquid crystal behaviour. However, in Chapter 3 and 5 of this thesis, we introduce the development of a system of colloidal SU-8 rods and bananas by modifying Alargova's original protocol via using sonication and heat. With our newly developed systems, we are able to investigate the assembly of colloidal liquid crystal phases with confocal microscopy.

2.4.2 Confocal laser scanning microscopy

Developed by Marvin Minsky in 1957 [111], confocal laser scanning microscopy (CLSM) is an imaging technique frequently used in colloid science to obtain three-dimensional (3D) information in real space on the structure and dynamics colloidal dispersions with single-particle resolution [40,106,112]. When conventional optical microscopy is used to image optically dense

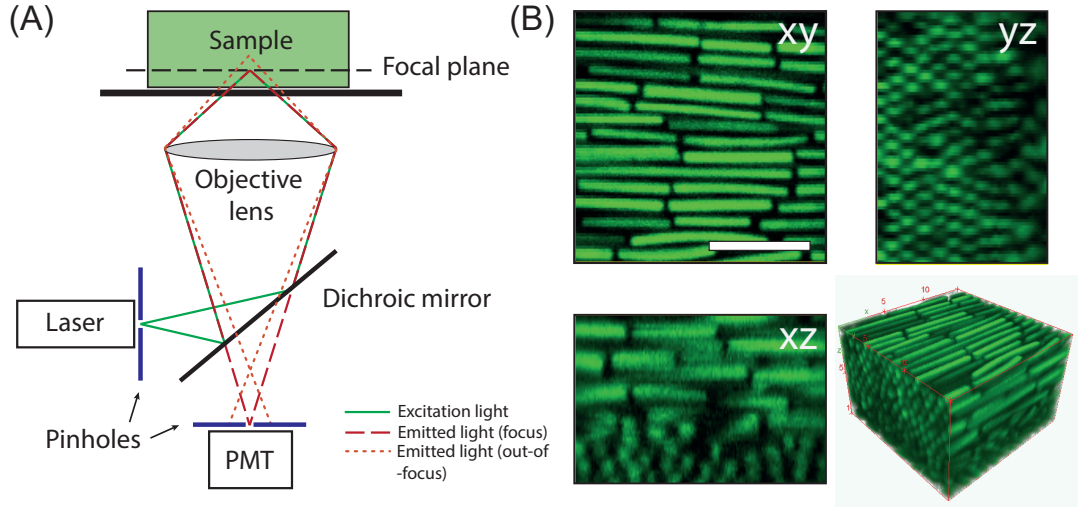


Figure 2.10: (A) Schematic illustration of the operating principle of a confocal microscope. Laser light (green lines) is first passed through a source pinhole aperture. This allows only a small central portion of the light pass through the aperture. The light is then focused by the objective lens into a small area on the sample. The fluorescent light originating from the focal plane, depicted as the red dashed lines, is focused at the detector pinhole by the collector lens and reaches the PMT detector. The out-of-focus fluorescent light, depicted as dotted red lines, is prevented from reaching the detector by the detector pinhole. (B) Example of xy , yz , xz views obtained from confocal imaging a sample of colloidal SU-8 rods in the nematic phase, and the resulting 3D snapshot. Scale bar is $5\ \mu\text{m}$.

systems, such as dense colloidal suspensions, the light coming from planes that are not in focus contribute to the image formation, resulting into blurry images [106]. Confocal microscopy, circumvents this problem by using pinhole apertures in the optical imaging set-up, as schematically shown in Figure 2.10A. Firstly, the excitation light is restricted to that of a diffraction limited point by placing a pinhole in front of the laser light. Secondly, any out-of-focus light is rejected by placing a pinhole aperture in front of the detector at the conjugate focal plane. This allows to obtain two-dimensional (2D) optical cross-section images of dense systems with a significantly higher contrast than using optical microscopy [106]. The extension to 3D imaging is subsequently achieved by acquiring 2D-cross section images at different heights in the sample (see Figure 2.10B). In the work described in this thesis, we typically use a confocal microscope consisting of a 12 kHz resonant scanner head (Thorlabs) and a 532 nm laser, coupled to an Olympus IX73 inverted microscope equipped with a $60\times$ ($\text{NA} = 1.42$) oil immersion objective (Olympus). This results in an approximate resolution of 250 nm in xy and 400 nm in z and a scanning speed of approximately 30 frames per second for a 512×512 pixel field of view.

Colloidal particles are very suitable for CSLM studies mainly because of three particular features [106,113]. Firstly, micron-sized colloidal particles can be made fluorescent by incorporating fluorescent dyes, such as FITC or RITC, during their synthesis [75]. In fact, 3D quantitative

studies on the structure and dynamics are further facilitated by using particles with core-shell morphology [40, 112], as they ensure the spacing between the fluorescent signals to be equal or larger than the optical resolution of the microscope. Secondly, the refractive index of the particles can be readily matched with the refractive index of the solvent. When colloidal particles are optically matched with the solvent, the scattering of light is strongly suppressed [106, 113]. As a result, the excitation light can penetrate deep into the bulk of the sample, and similarly, the emitted fluorescent light can reach the PMT from deep within sample. Thirdly, the resolution and typical speed at which the confocal operates falls within the colloidal domain – with typical length scales of microns and time scales of seconds (see Section 2.2.1)– and as a result, the particles can be tracked in 3D and in real time [106, 113].

The combination of confocal microscopy and colloidal model systems has enabled for further quantitative 3D studies of fundamental condensed matter phenomena, such as nucleation and growth of colloidal crystals [106, 112]. However, most advances in understanding the properties of colloidal materials by CLSM have been made for systems of spherical particles. Only few anisotropic experimental systems have been used in confocal microscopy studies. These include PMMA ellipsoids, [114, 115], silica rods [116, 117] and *fd*-virus particles [64].

Sample cells for confocal microscopy

To study the colloidal liquid crystals formed by our colloidal rods and bananas, we prepare dense particle suspensions in either rectangular VitroCom capillaries ($0.1\text{ mm} \times 0.2\text{ mm} \times 5\text{ cm}$) or home-made sample cells. Home-made sample cells are prepared by UV-gluing rectangular #1 cover slips (Menzel-Gläser) onto a microscope slide, creating a small horizontal channel. A third rectangular microscope #1 coverslip is then UV-glued on the top of the channel. These samples are filled, via capillary forces, with colloidal SU-8 particle dispersions with a typical initial packing fraction, ϕ_0 , in the range of $0.10 - 0.20$ and subsequently sealed using epoxy glue. At these low packing fractions the system is in the isotropic phase where the particles can freely rotate and translate, thereby minimizing kinetic arrest and also flow alignment effects. After filling the sample cells, the colloidal particles typically sediment, over the course of a day, towards the bottom of the sample cell where the packing fraction gradually increases.

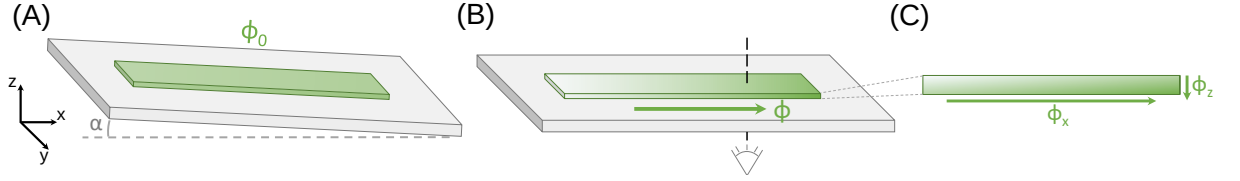


Figure 2.11: Schematic illustration of (A) the equilibration and (B) the imaging of the sample cell used for the study of the phase behaviour of the colloidal bananas with confocal microscopy. ϕ_0 is the initial volume fraction of the colloidal dispersion. (C) Side-view of the capillary illustrating the two packing fraction gradients, one in the x -direction (ϕ_x) and the other in z (ϕ_z), established in the sample cell.

Samples are typically equilibrated for at least two weeks before imaging. A small tilt ($2 - 3^\circ$) is used during the equilibration to induce a small packing fraction gradient along the channel, i.e. along the x -axis (see Fig. 2.11A). This enables us to access to the concentration-dependent phase behaviour of the system using a single sample (see Figure 2.11B). At the same time, a second gradient in the packing fraction is established in the vertical direction, z , as the colloidal particles sediment over time (see Figure 2.11C).

The solvent in which the particles are dispersed determines, among other aspects, the dimensionality of our confocal microscopy imaging of the system. If particles are dispersed in water, the large refractive index mismatch, between the particles ($n_{SU8} \sim 1.6$) and the solvent ($n_{H_2O} \sim 1.33$) only allows for imaging the system in two dimensions. This is due to large light scattering effects, which originate from within the sample. In this case, the imaging is typically done relatively close to the bottom wall of the sample cell, where light scattering is minimised. To address the three-dimensional nature of the phases formed by our colloidal particles, we need to use solvents that closely match the refractive index of SU-8. There are solvents, such as carbon disulfide ($n_{CS_2} \sim 1.63$), which have a very similar refractive index to SU-8, however, these are often highly volatile and hazardous solvents. Instead, we typically use tetralin ($n_{tet} = 1.54$), as it allows us to image approximately $30 - 40 \mu\text{m}$ deep into the bulk of the sample and also keep the colloidal suspensions for long periods of time.

We use the dispersants OLOA 1200 or OLOA 11000 (4-5wt%) to stabilize the particles in organic solvents. OLOA is a proprietary polyisobutylene succinic anhydride (PIBSA) stabiliser with two effects: it adsorbs onto the particles to form a steric brush layer [118], and it also forms charged micelles in solution which can act as a screening agent and undergo charge exchange with the surface. Previous work using particles made of TPM [119], PMMA and polystyrene [120] all show that concentrations of OLOA between 4-5wt%, lead to a screened Yukawa potential [15].

2.4.3 Image analysis

SEM images

Prior to studying the self-assembly of colloidal SU-8 rods and bananas into liquid crystalline phases, we first determine the average dimensions of the particles. To this end, we use custom-written image analysis routines in Mathematica to determine the length, diameter and curvature of the rods and bananas from scanning electron microscopy (SEM) images (see Figure 2.12). SEM images typically are taken with a JSM-6010LV electron microscope working at 15 kV. Samples are prepared by depositing a droplet of aqueous particle dispersion onto a 1 cm² silicon wafer. The solvent is then evaporated using a heat lamp. Prior to the imaging, a thin layer of palladium is deposited on the sample using a Quorum Sputter Coater. Note that we typically take low magnification images (1000 $\times$) of diluted samples to maximise inter-particle distances and facilitate the particle-resolved image analysis procedure (see Figure 2.12C₁ and D₁).

Our image analysis routine of SEM images consists of multiple steps, as shown in Figure 2.12. First, we binarise the SEM images with a locally adaptive threshold using the ‘LocalAdaptiveBinarize’ built-in function (see Figure 2.12C₂ and D₂). This reduces the effect of intensity

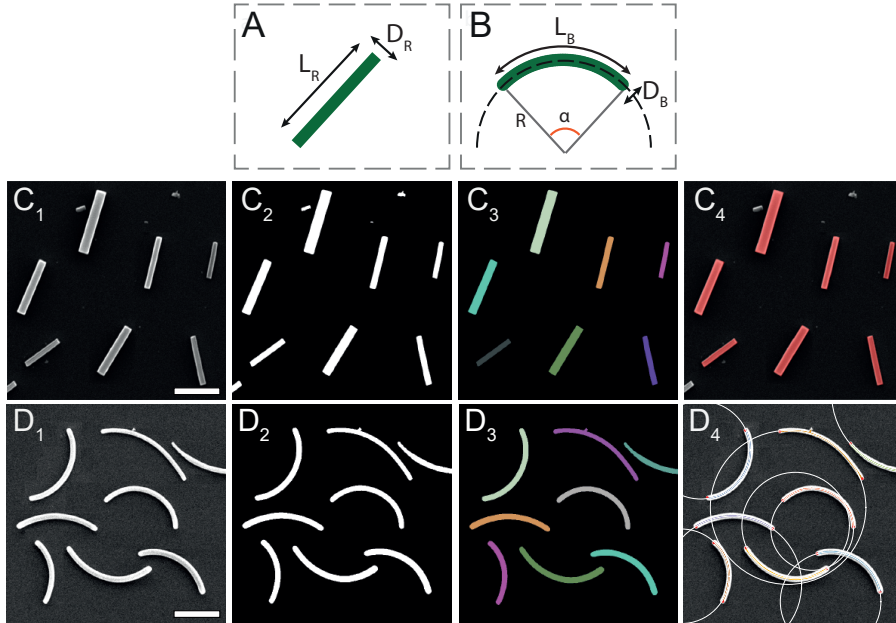


Figure 2.12: Step-wise image analysis procedure to extract the length, diameter and curvature of colloidal rods and banana from scanning electron microscopy (SEM) images. (A,B) Schematic of the typical dimensions of the rods and bananas. (C₁,D₁) Original SEM images, (C₂,D₂) binarised images and (C₃,D₃) segmented images, where the different colours represent different particles. (C₄) Rods enclosed by minimal bounding boxes (red). (D₄) original image overlaid with the skeletons of the bananas (thin coloured lines), the end points (red dots) and the fitting circles (in white). Scale bars are 5 μm .

variations in the images. Next, we segment the binarized images using the ‘MorphologicalComponents’ function, which results in images where the different colours correspond to different particles (see Fig. 2.12C₃ and D₃). At this point, we use an upper and lower bound on the pixel count based on a histogram of all the detected particles to discriminate very big or small particles. Next, to determine the length, L_R , and diameter, D_R of the rod-like particles (see Figure 2.12A), we use the ‘MinimalBoundingBox’ function which find the best fit for a box enclosing a rectangular particle as shown in Figure 2.12C₄. From the dimensions of this box we extract the particle length (long side of the box) and the particle diameter (short side of the box).

To determine the length of the banana-shaped particles L_B , we first determine the radius of curvature R_B and the opening angle of the particles α which is calculated as $L_B = \alpha R_B$ (see Figure 2.12B). To this end, we first skeletonize the segmented images using the ‘Skeletonize’ built-in function to obtain the backbones of the particles (see coloured skeletons in Figure 2.12D₄). Then, we fit circles to the backbone pixels using a custom-written algorithm that minimises the distance between the circles and the pixels of the particles (see Figure white circles in 2.12D₄). The radius of the fitting circle R is taken to be the radius of curvature of the particle. Note that in this thesis we also refer to the particle curvature using κ , which is simply the inverse of R . Finally, we find the coordinates of the end points of the particles (see red dots in Figure 2.12D₄) and compute the opening angle, α , using the coordinates of the center of curvature (see Figure 2.12). The diameter of the particles was calculated using the area of the bananas, which is extracted as the pixel count of the (non-skeletonised) segmented images and its already calculated length. Note that we approximate the area of a banana to be the same as that of a rectangle with $A_B \approx L_B D_B$.

Confocal images

Structural studies of the colloidal liquid crystal phases formed by our colloidal rods and bananas are performed by analysing confocal microscopy images of the different phases. Similarly to the analysis of the SEM images, we use custom-written routines in Mathematica to extract single-particle features, such as particle positions and orientation (see Figure 2.13A and B), from the microscopy images. In Chapters 3 and 5, we provide a detailed description of the analysis procedure, however, here we summarise the main steps used, which are shown in Figure 2.13. The initial steps of the analysis of confocal images include binarisation and segmentation steps (not shown here), as described for SEM images. For both the rods and bananas, the position of

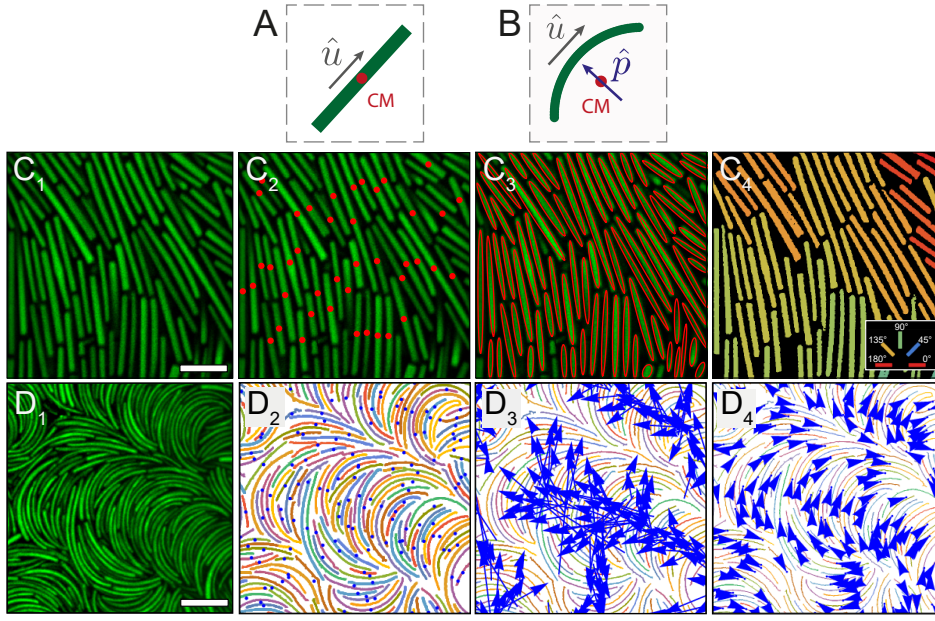


Figure 2.13: Step-wise image analysis procedure to extract the position and orientation of colloidal rods and bananas from confocal microscopy images. (A,B) Schematic of the centre of mass and orientation of the particles. (C₁,D₁) Original confocal images overlaid with (C₂,D₂) the centre of mass, (C₃) the fitting ellipsoids, (D₃) polar vectors and (D₄) orientation vectors. In (C₄) rods are coloured according to their orientation as indicated in the legend.

the particles is given by their centre of mass, which is calculated from the pixel coordinates of each particle using the ‘Centroid’ function (see Figure 2.13C₂ and D₂). The orientation of the rods and the bananas is next calculated in slightly different ways. For the rods, the orientation of the particles, $\hat{\mathbf{u}}$ (see Figure 2.13A), is calculated by fitting ellipsoids to the particles and then measuring their orientation with respect to the horizontal axis (see Figure 2.13C₃). In the case of the bananas, the particle orientation in two dimensions is characterised by the polar vector $\hat{\mathbf{p}}$, which is associated to the short axis of the banana, and the orientation vector $\hat{\mathbf{u}}$ which is associated to the long axis of the banana (see Figure 2.13B). The polar vector, is calculated using the average vector originating from all the vectors starting from the centre of curvature and ending at the backbone of the banana (see Figure 2.13D₃). The orientation vector, $\hat{\mathbf{u}}$, is then simply calculated by rotating the polar vector by $\pi/2$ (see Figure 2.13D₄). Note that this analysis is valid in two-dimensions and as long as the imaging plane is parallel to the long axis of the bananas.

Acknowledgments

Louis Cortes and Adam Edward Stones are thanked for assistance with the development of the image analysis routines.

Chapter 3

Synthesis of colloidal SU-8 rods using sonication

ABSTRACT

In this chapter, we describe the bulk synthesis of fluorescent colloidal SU-8 polymer rods with tuneable dimensions. The colloidal SU-8 rods are prepared by first shearing an emulsion of SU-8 polymer droplets and then exposing the resulting non-Brownian rods to ultrasonic waves, which breaks them into colloidal rods with typical lengths of 4–10 μm . The rods are stable in both aqueous and apolar solvents, and by varying the composition of apolar solvent mixtures both the difference in refractive index and mass density between particles and solvent can be independently controlled. As a result, these colloidal SU-8 rods can be used in both three dimensional confocal microscopy and optical trapping experiments whilst carefully tuning the effect of gravity.

3.1 Introduction

Colloidal dispersions of rod-like particles are widely accepted as convenient model systems to study the phase behaviour of liquid-crystal (LC) forming systems [25]. This is due to the fact that colloidal rods exhibit analogous phase behaviour to that of elongated molecules, while they can be directly observed by optical microscopy [25, 59]. Almost 70 years ago, Onsager already predicted that a system of hard rods undergoes an entropy-driven isotropic-nematic phase transition at a remarkably low packing fraction [86]. Since then, a great deal of theoretical and experimental work has been done on identifying and studying the key parameters influencing the LC phase behaviour of rods, see e.g. [59, 92, 121–124]. Computer simulations have shown that systems of hard (sphero)cylinders can also exhibit smectic, columnar and crystalline phases depending on their volume fraction, aspect ratio and size polydispersity [92, 121–123]. Experimentally, much insight has been gained by studying colloidal rod-like model systems such as TMV and *fd*-virus particles [124–126], PMMA ellipsoids [115, 127], boehmite rods [93] and silica rods [36, 83].

Detailed insight into the three-dimensional (3D) structure and dynamics of dense colloidal phases at the particle level can be obtained using 3D confocal microscopy [40, 41, 106]. This technique has also been applied to study dense suspensions of rods including, *fd*-virus particles [64, 128], PMMA ellipsoids [114, 129] and silica rods [36, 116]. Using *fd*-virus particles, for example, the director field of colloidal liquid crystals in wedge-shaped confinement was measured by adding fluorescent *fd*-virus particles in a host suspension of non-fluorescent *fd*-virus particles [64]. Confocal microscopy was also used to study at the single-particle level the structure of sediments of PMMA ellipsoids [114, 129], the phase behaviour of silica rods external fields [36, 116, 130] and the structure of sedimentation-diffusion equilibria in mixtures of silica spheres and rods [63].

Confocal microscopy, however, does put severe constraints on the colloidal model system to be used. Firstly, the refractive index of the particles needs to be matched to that of the dispersing solvent ($\Delta n \approx 0$) in order to minimize scattering effects when imaging deep into the bulk of concentrated samples. Secondly, it is beneficial to be able to tune the effect of gravity by adjusting the mass density difference between the particles and the solvent, $\Delta\rho$. In this way, for instance, fluctuating interfaces [30], sedimentation-diffusion equilibria ($\Delta\rho > 0$) [131] or the 3D structure of crystalline phases ($\Delta\rho \sim 0$) [132, 133] can be monitored over time using the

same colloidal particles. For rods specifically, the small dimensions of the *fd*-viruses and the high mass density of silica rods make tuning the effect of gravity in these systems cumbersome. While this is possible for PMMA ellipsoids, they are typically produced in low yields and deviate from the ideal rod-like shape, as a result of which smectic, columnar or crystalline phases have not been observed in concentrated suspensions of these ellipsoids [114].

Here, we describe the bulk synthesis of fluorescent colloidal SU-8 polymer rods with tuneable length and diameter that are stable in both aqueous and apolar solvent mixtures. By varying the composition of the solvent mixture, both the difference in refractive index and mass density between the particles and the solvent can be independently controlled. This enables the use of colloidal SU-8 rods in both 3D confocal microscopy ($\Delta n \approx 0$) and optical trapping ($\Delta n \neq 0$) experiments, and even in experiments combining both techniques. Crucially, the effect of gravity can be carefully tuned in all of these experiments via $\Delta\rho$. We demonstrate this by imaging the liquid crystalline phases and the isotropic-nematic interface formed by the colloidal SU-8 rods using confocal microscopy in various solvent mixtures. In addition, we show the optical trapping of a single SU-8 rods in water and the simultaneous optical manipulation and confocal imaging of multiple rods in the isotropic phase. Finally, we present preliminary results on the functionalisation of SU-8 rods with magnetic nanoparticles and their behaviour in the presence of external electric and magnetic fields.

3.2 Experimental methods

3.2.1 Materials

SU-8 50 (Microchem), gamma-butyrolactone (GBL, $\geq 99\%$, Sigma-Aldrich), glycerol ($\geq 99\%$, Sigma-Aldrich), ethylene glycol ($\geq 99\%$, Sigma-Aldrich), tetralin ($\geq 99\%$, Sigma-Aldrich), Carbon disulfide ($\geq 99\%$, Sigma-Aldrich), PEG-PPG-PEG pluronic F-108 (Sigma-Aldrich), OLOA 11000 (Azelis) and cyanine-3 and BDP fluorescent dyes (Lumiprobe) are used as received. Deionized water obtained directly from a purification system (Direct-Q 3 UV, Millipore) is used for all the experiments conducted in aqueous media.

3.2.2 Synthesis of colloidal SU-8 rods

The synthesis of our colloidal SU-8 polymer rods is adapted from the method described by Alargova et al. [96,97]. The experimental set-up we typically use is shown in Figure 3.1A and consists of three main parts: the homogeniser mixer, the impeller and the reaction vessel containing the viscous media. In typical synthesis, a 250 mL beaker with an inner diameter of 5 cm is filled with 110 mL of glycerol. A mixer (Heidolph RZR 2021) equipped with a half-moon impeller with a diameter of 3.5 cm is then introduced into the glycerol such that the impeller is located approximately 1 cm above the bottom wall of the beaker (see Figure 3.1B). Next, the homogenisation process at 1500 rpm – corresponding to a shear stress of 518 Pa – is started (see Figure 3.1C). Note that the impeller should be placed in the centre of the beaker, in order to produce a relatively uniform shear flow during the homogenisation. Approximately 0.1 g of SU-8 50 viscous photoresin (Microchem) is dropped from a spatula into the gap between the inner wall of the beaker and the impeller, resulting in a turbid dispersion. As shown in [96,97], the shear stress can be varied in order to tune the resulting dimensions of the rods. It is also important to note, that a minimum shear rate, whose value depend on the viscosity of the media used, is needed for emulsify the injected SU-8 droplet [96,97].

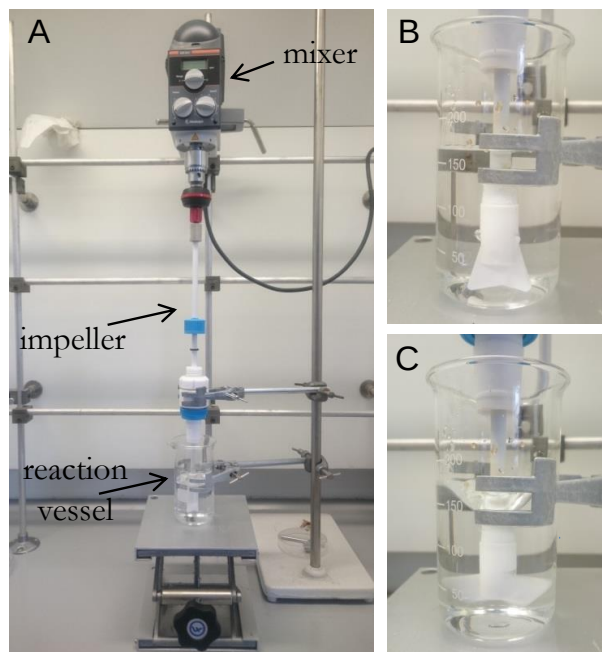


Figure 3.1: (A) Image of the experimental set-up used for the synthesis of colloidal SU-8 rods, which consists of a high-speed mixer, an impeller and a reaction vessel. Magnified images of the reaction vessel (B) before and (C) during the homogenization of the dispersion media at 1500 rpm. Image of the experimental set-up where the three main elements are highlighted: the mixer, impeller and reaction vessel.

For the synthesis of fluorescent SU-8 rods a fluorescent dye is simply mixed with the SU-8 50 at a mass ratio of 10 mg dye/ g SU-8 50. The high-shear mixing of the glycerol and the SU-8 50 is continued for 10 min. The resulting non-Brownian SU-8 rod-like particles in glycerol are directly exposed to sonication (VWR ultrasonic cleaner, 45 kHz, 80 W) for 1 to 3 hours in order to break to them into smaller colloidal rods. These colloidal SU-8 rods are subsequently photo-crosslinked by exposing them to UV-light with a wavelength of 365 nm (Spectroline 14A/FB) for 30 min. To remove the glycerol, the colloidal SU-8 rods are washed by repeated centrifugation and redispersion cycles at 3000 g for 40 minutes using water containing 0.5 wt% Pluronic F-108. Any large or irregularly shaped rods are easily removed by sedimentation in water under gravity for an hour. Very small rods are removed by centrifuging three times at 3000 g for 15 minutes. Long and thick rods are typically removed by spinning at 600 g for 15 min. Finally, the resulting colloidal SU-8 rods are kept in water containing 0.5 wt% Pluronic F-108.

3.2.3 Size characterization of colloidal SU-8 rods

The size distributions of the colloidal SU-8 rods is determined by measuring the length and diameter of at least 200 rods from scanning electron microscopy (SEM) images of dilute suspensions of rods using custom-written image analysis software in Mathematica described in Section 2.4.3. Note that the polydispersity of the rods is defined as $\sigma_i = \delta_i / \langle i \rangle$, where $\langle i \rangle$ is the mean value of the length L or the diameter D and δ_i is its standard deviation.

3.2.4 Refractive index and mass density determination of colloidal SU-8 rods

The refractive index of the colloidal SU-8 rods is determined by dispersing the particles in mixtures of decalin (*DEC*, $n = 1.481$) and carbon disulfide (CS_2 , $n = 1.627$) of different compositions (see Table 3.1) [133–135]. Inspection of the optical transparency of particle dispersions using bright field microscopy allows us to determine whether the refractive index of the particles is higher or lower than that of the solvent mixture. When particles appear completely transparent, their refractive index is considered to be the same as that of the solvent mixture.

Table 3.1: Refractive indices of the solvent mixtures of decalin (*DEC*, $n = 1.481$) and carbon disulfide (CS_2 , $n = 1.627$) as a function of the solvent composition in v/v%.

<i>DEC:CS₂</i> (v/v%)	1:4	1:6	1:8	1:10	1:12	1:14
refractive index	1.598	1.606	1.611	1.614	1.616	1.617

The mass density of the colloidal SU-8 rods is determined by dispersing them in carefully prepared mixtures of decalin ($\rho = 0.896$ g/mL) and trichloroethylene (*TCE*, $\rho = 1.460$ g/mL) at different compositions (see Table 3.2) [36,133–135]. The dispersions are subsequently centrifuged at 8000 g for 10 min. The mass density of the rods is equal to that of the solvent by identifying the transition point between sedimentation and creaming of the rods.

Table 3.2: Densities of the solvent mixtures of decalin (DEC, $\rho = 0.896$ g/mL) and trichloroethylene (*TCE*, $\rho = 1.460$ g/mL) as a function of the solvent composition in v/v%.

<i>DEC:TCE</i> (v/v%)	1:1.4	1:1.6	1:1.8	1:2.0	1:2.2	1:2.4	1:2.6
densities (g/mL)	1.225	1.243	1.259	1.272	1.284	1.294	1.303

3.2.5 Solvent transfer from aqueous to non-aqueous solvents

Because SU-8 is a hydrophobic polymer, the synthesized rods have a tendency to aggregate in aqueous media [96]. As a result some aggregates can be observed in an aqueous dispersions of colloidal SU-8 rods 7 days after sample preparation. To stabilise the rods in water, two surfactants are used: the anionic surfactant sodium dodecyl sulfate (SDS) at a mass fraction of 0.2 wt% and the non-ionic surfactant, Pluronic F-108 at a mass fraction of 0.5 wt%.

When particles are transferred from an aqueous medium to a low dielectric non-aqueous medium, a step-wise solvent transfer procedure via an intermediate solvent is performed [120, 133]. Directly transferring the rods from water to organic media results in the formation of an oil-water emulsion and irreversible particle aggregation. We also note that particles that are not sufficiently crosslinked during the UV-exposure step tend to aggregate in non-aqueous solvents. Therefore, fully cross-linked rods in water are successfully dispersed in non aqueous solvents by transferring them from H_2O containing 0.5 wt % Pluronic to a 50:50 (v/v) H_2O :isopropanol, then to pure isopropanol (step repeated at least 3 times to remove all the water), then to 50:50 (v/v) isopropanol:organic, and finally into the 100% organic medium typically containing 1 wt % of OLOA 1200 [120, 133] or OLOA 11000 dispersant. Isopropanol (IPA) is chosen as the intermediary solvent as it is miscible with both water and low dielectric solvents. The transfer procedure involved the sedimentation of the particles by centrifugation, removing the supernatant and replacing it by the new solvent mixture. Particles are then redispersed in the new solvent by sonication and vortexing.

3.2.6 Confocal imaging of colloidal SU-8 rods

Confocal microscopy images are obtained using 12 kHz resonant scanner head (Thorlabs) coupled to an Olympus IX73 inverted microscope using $60\times$ ($\text{NA} = 1.42$) and $100\times$ ($\text{NA} = 1.40$) oil immersion objectives (Olympus). Images with 16-bit pixel-depth are acquired using either 488 nm or 532 nm laser sources depending on the dye used. When the refractive index mismatch between the particles and the solvent is relatively large ($\Delta n > 0.1$) imaging is done close to the wall. For small refractive index mismatches, 3D image stacks are obtained using typical xyz dimensions of $160 \times 160 \times 170$ pixels.

Samples of the colloidal SU-8 rods at a given volume fraction are typically prepared by filling home-made sample cells as described in Section 2.4.2. For the imaging of the isotropic-nematic interface, the sample was equilibrated and imaged in a vertical configuration.

3.3 Results and discussion

3.3.1 Synthesis of colloidal SU-8 rods

To synthesize the fluorescent colloidal SU-8 polymer rods, we adapt the procedure for the fabrication of non-Brownian SU-8 rods described in [96,97]. In that work, ten to a hundred microns long SU-8 rods were obtained by vigorously shearing an emulsion of SU-8 polymer droplets in a viscous medium. Here, we use sonication to break the non-Brownian SU-8 rods into smaller colloidal SU-8 rods, as shown schematically in Figure 3.2A. This simple, yet crucial step opens up the use of SU-8 rods in the colloidal domain. To enable the imaging of the colloidal SU-8 polymer rods with 3D confocal microscopy, we incorporate a fluorescent dye (e.g. RITC) in the initial SU-8 photoresin, which results in uniformly labelled and highly fluorescent colloidal SU-8 rods (see Section 3.2.2). Finally, UV-light exposure is used to cross-link the colloidal SU-8 rods, which yields chemically highly stable particles that can be dispersed in both aqueous and non-aqueous solvents.

Figures 3.2B and C show typical scanning electron microscopy images of the colloidal SU-8 polymer rods obtained after sonication. First of all, the dimensions of the rods are clearly within the colloidal domain with an average length of $L \approx 4.5 \mu\text{m}$, diameter of $D \approx 0.5 \mu\text{m}$

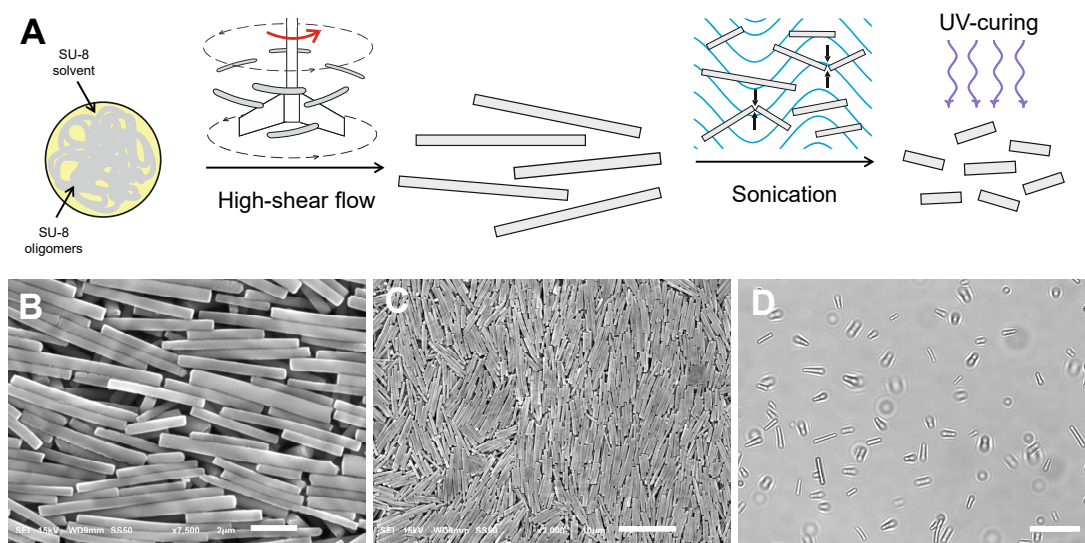


Figure 3.2: (A) Schematic representation of the synthesis of the colloidal SU-8 polymer rods. Under high-shear flow, a macroscopic droplet of SU-8 polymer solution in glycerol is emulsified into smaller droplets that are subsequently elongated into cylinders of tens of micrometres long. Subsequent exposure to sonication breaks the long SU-8 rods into shorter colloidal SU-8 rods. Finally, exposing the rods to UV-light photo-crosslinks the SU-8 and yields chemically highly stable colloidal SU-8 rods. Scanning electron microscopy (SEM) images (B,C) and an optical microscopy image (D) of the colloidal SU-8 rods obtained at a shear stress of 518 Pa after a sonication time of 3 hours. Scale bars are (B) 2 μm , (C) 10 μm and (D) 20 μm .

and hence an aspect ratio of $L/D \approx 9$. While the rods are rather polydisperse, cycles of sedimentation and centrifugation in water can be used to reduce their size polydispersity down to approximately 20% in length, 15 % in diameter and 20 % in aspect ratio (see Appendix A.2 for sorting experiments). Shape-wise, the obtained rods have an almost ideal cylindrical shape with flat ends, which is due to the sonication-induced breakage of the brittle SU-8 rods that are obtained after the shearing process. Figure 3.2D shows an optical microscopy image of an aqueous dispersion of colloidal SU-8 rods, where the random positions and orientations are reminiscent of the translational and rotational Brownian motion exhibited by the colloidal rods.

The dependence of the average length, diameter and aspect ratio of the SU-8 rods on the sonication time is shown in Figure 3.3. Importantly, there is a clear decrease in the average rod length, especially during the first hour of sonication, while the rod diameter remains roughly constant. However, the rod diameter can be independently tuned from 0.4 up to 1 μm during the first step of the synthesis where increasing the applied shear stress leads to thinner rods, as shown in Figure 3.4 and [96,97]. The aspect ratio of the colloidal SU-8 rods can thus be fully tuned by the duration of the sonication. Interestingly, the change in the distributions in Figure 3.3d–f shows that the length reduction during sonication is mainly driven by the breakage of

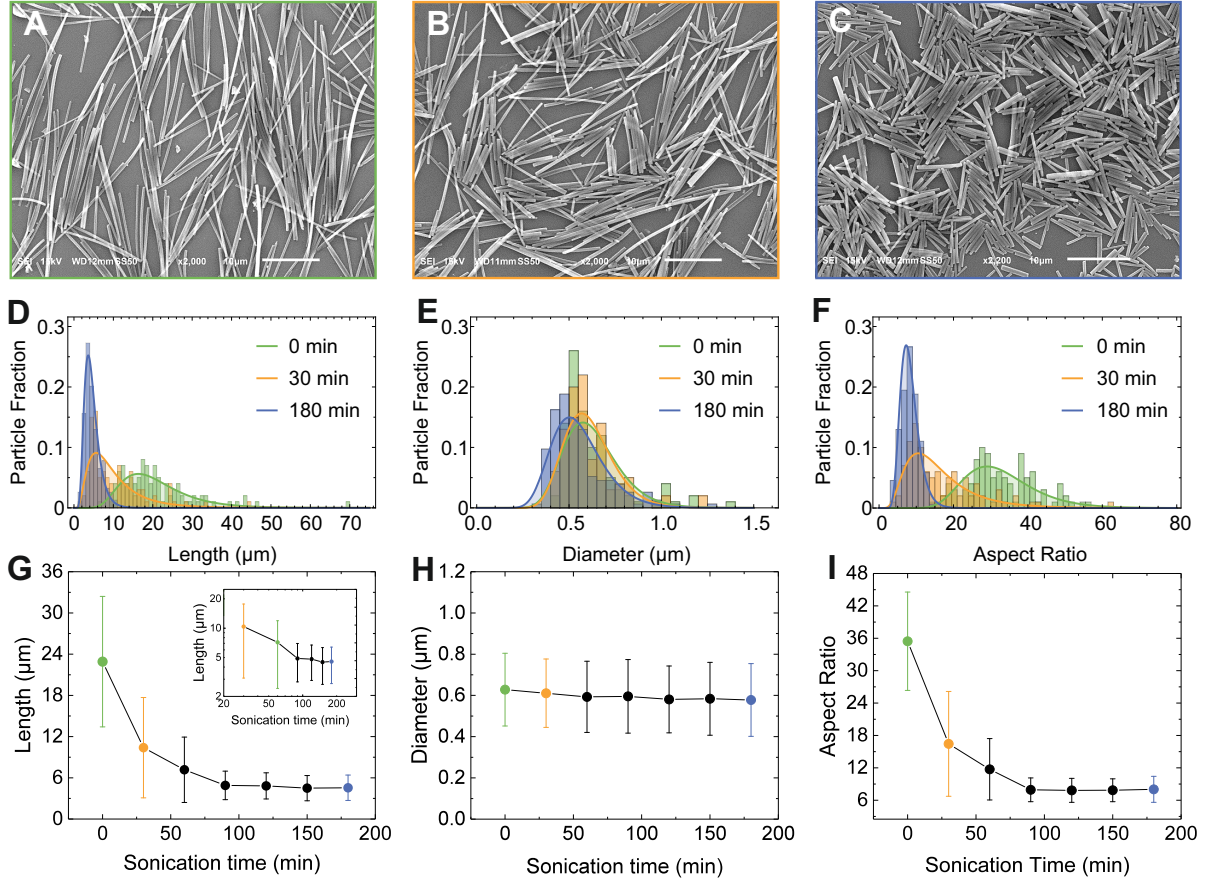


Figure 3.3: Representative SEM images of the SU-8 rods (A) before and after (B) 30 and (C) 180 minutes of sonication. Scale bars are 20 μm . (D-F) Length, diameter and aspect ratio distributions of the SU-8 rods at 0, 30 and 180 min of sonication. (G-H) Evolution of the average length, diameter and aspect ratio of SU-8 rods as a function of the sonication time. Inset: log-log plot of length as a function of the sonication time. Error bars represent the standard deviation of the average value.

the initially long rods into shorter rods due to the violent hydrodynamic shear flows produced around the collapsing cavitation bubbles created in the dispersion during sonication [136, 137]. Indeed, the peaks of the length and aspect ratio distributions shift towards smaller values and the tails of both distributions are greatly reduced. This is also reflected by the decrease of the standard deviation in the mean values, represented by the error bars in Figure 3.3g–i. We note that the sonication time required for the rods to reach their final average length depends on the sonication parameters: increasing the power or decreasing the sonication frequency leads to faster rod-breakage [136, 137] (see Figure A.2 in the Appendix for sonication experiments). While the dimensions of the colloidal SU-8 rods synthesized in this paper are optimized for their study with 3D confocal microscopy, we anticipate that the minimum rod-dimensions could be further reduced by increasing the shear stress applied during the first step of the synthesis or decreasing the SU-8 polymer concentration of the initial SU-8 solution as discussed in [97].

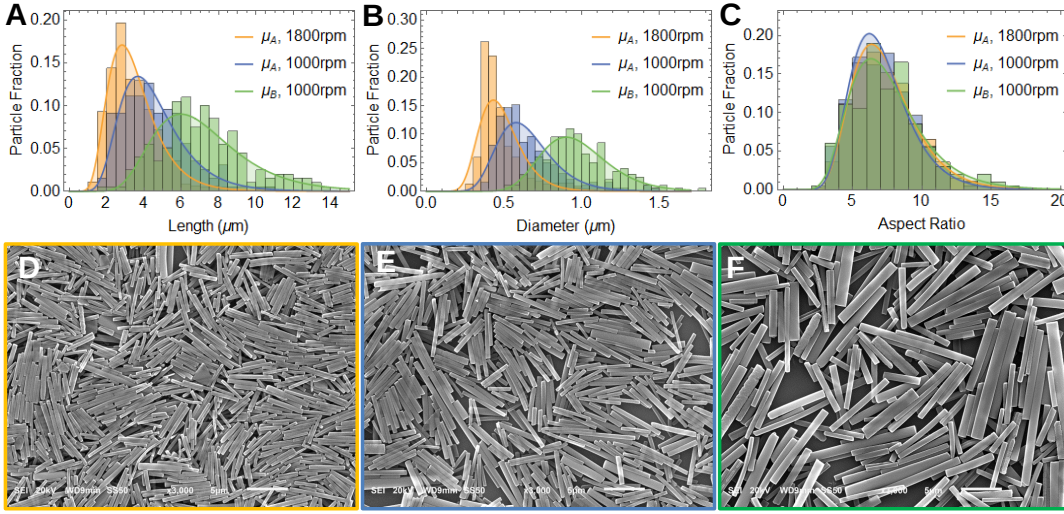


Figure 3.4: Size distributions of the (A) length, (B) diameter and (C) aspect ratio of the colloidal SU-8 rods obtained after 90 min of sonication. SEM images of the colloidal SU-8 rods obtained using (D) pure glycerol (and viscosity μ_A) at 1800 rpm, (E) pure glycerol at 1000 rpm and (F) a mixture of 80% glycerol and 20% ethylene glycol (μ_B) at 1000 rpm. Scale bars are 5 μm .

3.3.2 Liquid crystal phase behaviour of colloidal SU-8 rods

Stable aqueous dispersions of colloidal SU-8 rods in water are obtained by adding small amounts of ionic (SDS) or non-ionic (Pluronic F-108) surfactants. The resulting colloidal stability is further confirmed by the observed self-assembly of the colloidal SU-8 rods in water into various liquid crystalline phases, as shown in Figure 3.5. In order to form these phases, we slightly tilt the sample, thereby inducing a packing fraction gradient. At low packing fractions, the rods exhibit no translational or orientational ordering, reminiscent of the isotropic phase, while at higher packing fractions the rods orient in the same direction corresponding to nematic ordering (Figure 3.5B). At even higher packing fractions, the rods self-assemble into a smectic-like structure (Figure 3.5C). This may seem surprising as the typical rod-length polydispersity of the SU-8 rods $\sim 30\%$ is above the terminal polydispersity of 18%, where the smectic phase is predicted to no longer be stable for a system of hard spherocylinders [123]. However, a rod-length count performed in the smectic-like phase shows that the local length-polydispersity has significantly decreased to about 20% due to fractionation [138, 139], which facilitates the formation of a smectic-like phase like the one shown in Figure 3.5c.

To observe the structure and dynamics of the colloidal SU-8 rods using 3D confocal microscopy, the refractive index of the particles and the solvent mixture should be closely matched ($\Delta n \approx 0$), while ideally the degree of mass density matching, $\Delta\rho$, is carefully controllable. By

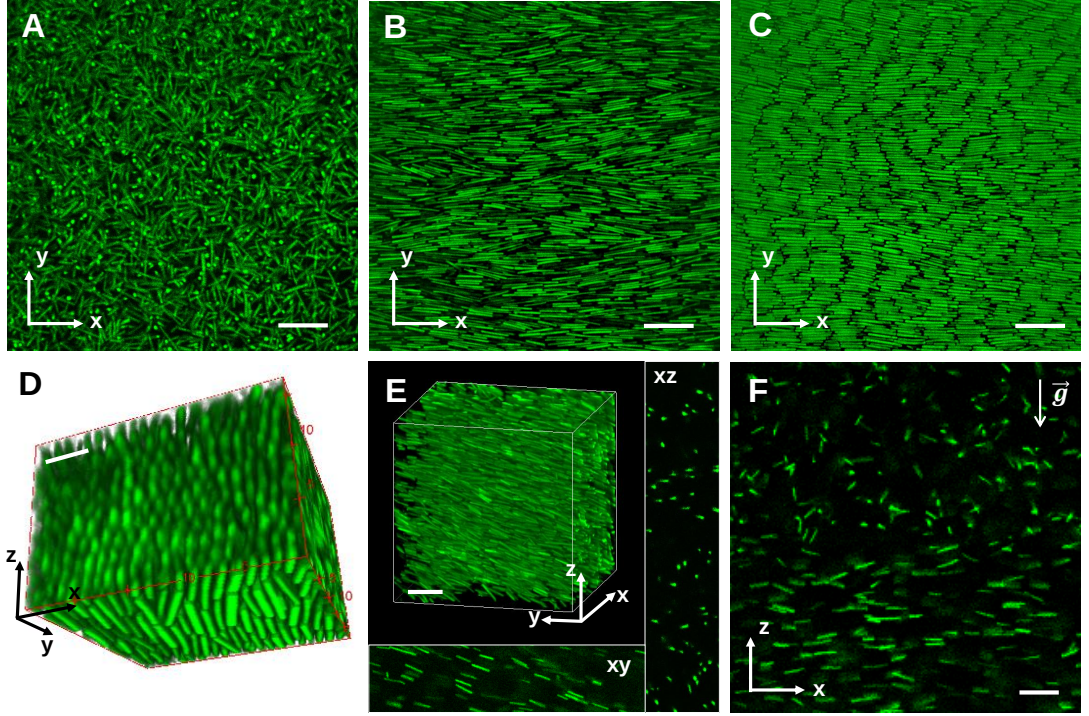


Figure 3.5: (A-C) Confocal microscopy images of a tilted sample containing an aqueous dispersion of fluorescent SU-8 rods with $L = 5.3 \mu\text{m}$ ($\sigma_L = 29.1\%$), $D = 0.62 \mu\text{m}$ ($\sigma_D = 16.1\%$), $L/D = 8.8$ ($\sigma_{D/L} = 29.5\%$): (A) isotropic, (B) nematic and (C) smectic-like ordering upon increasing volume fraction. (D) 3D confocal image ($20 \times 20 \times 17 \mu\text{m}^3$) of the nematic phase of fluorescent colloidal SU-8 rods in tetralin ($L_g \approx 2 \mu\text{m}$). (E) 3D confocal image ($50 \mu\text{m}^3$) of the nematic phase of a 1:50 mixture of fluorescent and non-fluorescent colloidal SU-8 rods in a 1:11 mixture of TCE:CS₂ ($L_g \approx 200 \mu\text{m}$). The side and bottom panels show the xy and xz cross-sections, respectively. (F) Confocal image of an isotropic-nematic interface of a 1:30 mixture of fluorescent and non-fluorescent colloidal SU-8 rods in a 1:4 DEC:CS₂ ($L_g \approx 6 \mu\text{m}$). Scale bars are $10 \mu\text{m}$.

identifying the maximum optical transparency and the transition point between sedimentation and creaming, the refractive index and mass density of the colloidal SU-8 rods are found to be $n = 1.614$ and $\rho \approx 1.28 \text{ g/mL}$ (see Section 3.2.4). Conveniently, with these values, various mixtures of common organic solvents (see Table 3.3) can be used to independently, and hence simultaneously or not, match the refractive index and the mass density of the colloidal SU-8 rods. This allows the effect of gravity, as quantified by the gravitational length of the rods, $L_g = k_B T / V_p \Delta \rho g$, to be systematically varied from $\sim 1 \mu\text{m}$ up to $\sim 200 \mu\text{m}$ in nearly refractive index matched dispersions. Here, $k_B T$ is the thermal energy, V_p is the volume of the rods and g is the acceleration due to gravity.

The controllability of gravity in our colloidal SU-8 rod system is demonstrated in Figures 3.5D–F, where 3D confocal microscopy images of rods with different gravitational lengths are shown. Figure 3.5d shows a 3D image of the fluorescent rods in the nematic phase in tetralin

Table 3.3: Characteristics of typical solvent mixtures that can be used to tune the refractive index and mass density mismatch (Δn , $\Delta \rho$) between the particles and the solvent. The fraction of tetralin (TET), carbon disulfide (CS_2), trichloroethylene (TCE) and tetrachloroethylene (PERC) is given in v/v% ratios. The dimensions of the rod used to calculate L_g are $L = 5 \mu\text{m}$ and $D = 0.5 \mu\text{m}$.

Solvent	TET	CS_2	TCE	PERC	Δn	$\Delta \rho$ (g/mL)	L_g (μm)
1	1	0	0	0	0.073	0.314	1.4
2	1	5	0	0	0.001	0.067	6.3
3	1	0	1.6	0	0.112	0.012	34.3
4	1	0	0	0.9	0.089	0.005	82.8
5	0	11	1	0	-0.001	0.002	233.0

(solvent 1, Table I), which demonstrates the imaging of all the particles at the single-particle level, where particle coordinates and orientations may potentially be extracted using existing images processing algorithms, as described in [116]. Next, in Figure 3.5e the composition of the solvent is such that both Δn and $\Delta \rho$ are very close to zero. Here, a 3D snapshot of the nematic phase formed in a 1:50 mixture of fluorescent and non-fluorescent colloidal SU-8 rods in solvent 5 is shown (note that $L_g \gg$ field of view). Since refractive index matching was almost perfect ($\Delta n \approx 0$), imaging of the rods was easily achieved 50 μm deep into the sample without significant loss of fluorescence intensity. Next, the mass density mismatch is increased to induce a sedimentation-diffusion equilibrium in which the L_g of the rods is tuned such that the isotropic-nematic interface can be directly observed as shown in Figure 3.5f. From a corresponding 3D confocal z-stack, we estimated the isotropic-nematic transition to occur at an approximate volume fraction of 0.25 (see Figure A.5 in the Appendix). While this value only represents a rough estimate, it is comparable to earlier reports [83], and is also consistent with the value reported for hard spherocylinders at the appropriate aspect ratio [92].

3.3.3 Further applications of the colloidal SU-8 rods

The versatility of our colloidal SU-8 rods warrants further applications in a wider range of experiments. The independent tunability of the refractive index and mass density mismatch facilitates, for example, the optical manipulation of the rods with, again, controllable effects of gravity. Figure 3.6A shows the dynamic manipulation of a colloidal SU-8 rod in water using two different optical traps acting on either end of the rod, which can, for example, be used to measure the friction coefficient of a rod as a function of its distance to the surface [99]. In Figure 3.6B, we show preliminary results on the simultaneous confocal imaging and optical

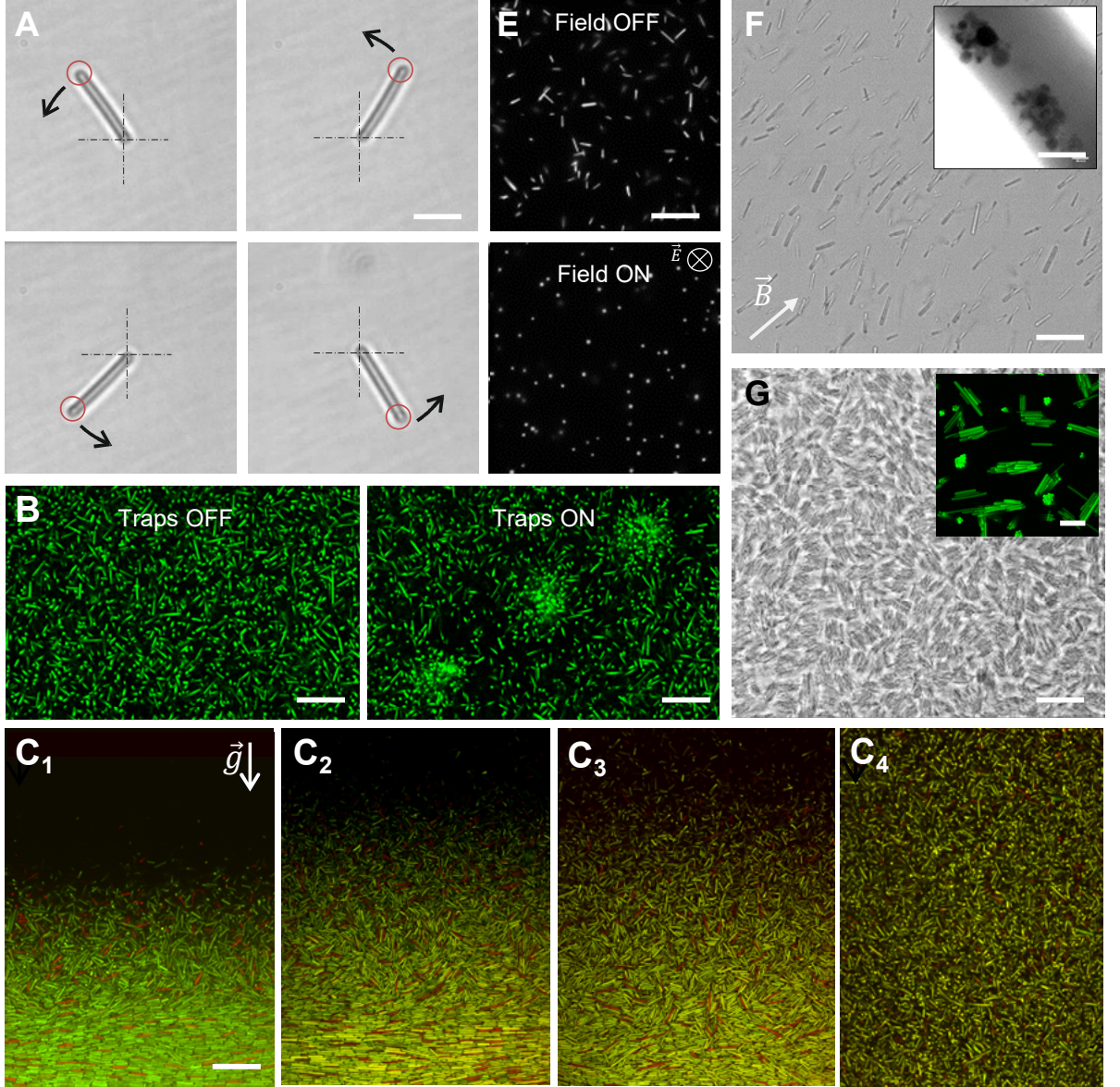


Figure 3.6: (A) In-plane optical manipulation of a single SU-8 rod in water using two optical traps. (B) Simultaneous optical manipulation and confocal imaging of a collection of colloidal SU-8 rods in tetralin using three independent optical traps. The optical axis of the traps is perpendicular to the image plane, which is 10 μm above the sample wall. (C) Confocal images of the isotropic-nematic interface at decreasing density mismatch from left to right. (E) Fluorescence microscopy images showing the effect of a 1 kHz AC electric field ($E \sim 0.01\text{V}/\mu\text{m}$) in a dilute dispersion of colloidal SU-8 rods. (f) Bright field image of magnetic rods aligning with an external magnetic field, $\hat{B}$. The inset shows TEM of SU-8 rods functionalised with magnetite nanoparticles. (G) Depletion effect in aqueous systems of colloidal rods. Scale bars are (A) 2 μm and (B-G) 20 μm . Scale bars in insets are (F) 500 nm and (G) 5 μm .

manipulation of a collection of SU-8 rods in the isotropic phase. This is achieved by choosing an organic solvent (solvent 1, Table I) with a refractive index mismatch small enough to image tens of micrometres deep into the sample, but still large enough to use holographic optical tweezers to manipulate the particles [140]. Interestingly, the three optical traps clearly induce local orientational (nematic) ordering, with the rods aligning along the optical axis [141], at higher

packing fractions than that of the background isotropic phase. This effect may be exploited to systematically study the nucleation of nematic droplets (tactoids) in the isotropic phase [142]. We also prepare samples with progressively larger gravitational length, and qualitatively address the impact on the isotropic-nematic interface. We observe that this interface becomes less well-defined as the system approaches density matching (see Figure 3.6C). Note that overall packing fraction of rods is roughly constant. Quantitative analysis of these experiments may lead to a measurement of the interfacial tension of the system [143–145]. In addition, we note that manipulating the isotropic-nematic interface using optical tweezers, in principle, also allows for a measurement of the interfacial tension or the study of the pinch-off of tactoids from the bulk nematic phase, as was shown for the colloidal liquid-gas interface [31]. Furthermore, we show that the colloidal SU-8 rods can also be aligned using external electric fields, see Figure 3.6E, as was also done for silica rods [36]. Also, we note that the composition, and hence the optical and chemical properties, of the colloidal SU-8 rods can be readily varied by incorporating other polymers and/or nanoparticles as reported in [97, 146]. In particular, the incorporation of silver or magnetic nanoparticles would make the rods conductive and/or magnetic (see example Figure 3.6F) which could be then used, for example, in sensing applications [147, 148] or studies of self-assembly in the presence of external magnetic fields [130]. We also qualitatively study the optical properties of our colloidal rods with polarised optical microscopy, and find that liquid crystalline phases show some structural birefringence, and also, that rods in the isotropic phase act as little waveguides (see Figure A.6 in the Appendix for birefringent measurements). Finally, we show that the inter-particle interactions of the colloidal SU-8 can be readily tuned, as shown in Figure 3.6G, where the presence of non-adsorbing polymer leads to the formation of depletion-induced liquid crystalline tactoids [26, 149, 150].

3.4 Conclusions

In summary, we have shown the successful bulk synthesis of colloidal SU-8 polymer rods with tunable dimensions that are stable in aqueous and apolar solvents. Dense suspensions of the SU-8 rods exhibit the classic range of colloidal liquid crystalline phases including nematic and smectic-ish phases. By changing the composition of the solvent mixtures used, both the refractive index and mass density mismatch between the particles and the solvent can be independently controlled. This enables the use of the SU-8 rods in confocal microscopy and optical trapping

experiments while tuning the effect of gravity. As a result, both bulk liquid crystal phases and also isotropic-nematic interfaces can be studied at the single-particle level with different gravitational lengths. In addition, we demonstrate that the SU-8 rods can be externally manipulated by using optical tweezers, electric and magnetic fields. In general, the dimensions, composition, stability and tunability of this novel system, as well as the ease of synthesis, combined with the wealth of knowhow available for tuning interparticle interactions in colloidal systems, promise a wide range of applications of colloidal SU-8 rods in condensed matter experiments.

Acknowledgments

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Chapter 4

Synthesis of colloidal SU-8 banana-shaped particles

ABSTRACT

In this chapter, we develop a strategy to produce colloidal banana-shaped particles in bulk. Our method is based on the buckling of initially straight SU-8 polymer rods by applying heat. Crucially, both the dimensions and curvature of the resulting ‘colloidal bananas’ can be precisely controlled by tuning the initial rigidity of the rods before the heating step. This is achieved by controlling the cross-linking density of the rods using UV-light. In fact, by controlling the interplay between the rigidity of the rods and the interfacial forces that arise during the heating, allows us to not only produce bananas, but also other particle shapes including colloidal SU-8 spheres and spherocylinders. We demonstrate the potential of our new colloidal bananas by directly visualising complex polar smectic phases, liquid crystal defects and depletion-induced banana clusters using confocal microscopy.

4.1 Introduction

Introducing curvature to rod-like microscopic building blocks has an enormous impact on their functionality and self-assembly [17, 25]. In the biological world, for instance, curved rod-shaped bacteria outperform their straight counterparts in surface-colonization and swimming efficiency, which makes them ubiquitous in marine environments [151, 152]. Also, many cellular functions, such as cell division or endocytosis, rely on the ability of ‘banana-shaped’ proteins to generate curvature in cell membranes [153, 154].

Curvature is also of key importance at the molecular scale, where, for example, bent-core molecules exhibit liquid crystalline phases never seen before in rod-like liquid crystals [8]. In fact, over the past two decades, more than fifty new banana-shaped liquid crystalline phases have been reported depending primarily on the molecular curvature [7, 8, 10]. These include chiral nematic and polar or antipolar smectic phases, which are promising candidates for display technologies [7, 8, 10]. While most of these molecular liquid crystal phases are typically characterised using birefringence or X-ray diffraction techniques [7, 8, 10], their structure and dynamics are not accessible at the molecular level. This prompts the need for a colloidal analogue, where this information is readily available using optical microscopy. However, despite the abundance of liquid crystal-forming colloidal particles such as rods, boomerangs or platelets [27, 35, 155], there is no system of smoothly curved colloidal rods available. As such, the rich liquid crystal phase behaviour of banana-shaped particles has yet to be experimentally uncovered at the single-particle level.

In this Chapter, we develop a powerful method to produce, in bulk, fluorescent curved colloidal rods – *colloidal bananas* – with tuneable dimensions and curvature. Our method relies on the temperature-driven buckling of initially straight SU-8 rods into colloidal bananas. The extent of the shape deformation, and hence the final curvature of the particles, is controlled by the rigidity of the SU-8 rods during the heating. In fact, this subtle balance results not only in colloidal bananas, but in an entire family of colloidal SU-8 particles with different shapes, including spheres and spherocylinders. The exciting potential of our colloidal model bananas is illustrated by the direct observation of exotic liquid crystalline structures such as polar smectic phases, liquid crystal defects and depletion-induced banana clusters, all of them resolved at the single-particle level using confocal microscopy.

4.2 Experimental methods

4.2.1 Synthesis of colloidal SU-8 banana-shaped particles

The synthesis of our colloidal SU-8 banana-shaped particles starts with the preparation of long straight SU-8 rods following the slightly modified method first described by Alargova et al. [96,97] described in Section 3.3.2. The main difference is that for the preparation of colloidal bananas, the long SU-8 rods obtained after the high-shear flow process are not sonicated but firstly exposed to UV-light and then heated in a 95°C oven. To this end, we typically transfer the SU-8 rods to multiple 15 mL glass vials with an inner diameter of 2 cm and expose them, in glycerol, to low-intensity UV-light using a fluorescent lamp (L36W/835, Osram, see next subsection for specifications of the lamp), placed at approximately 120 cm away from the vials, for a typical UV-exposure times of 45 min (see Figure 4.1A). The partially cross-linked rods are then heated, in glycerol, in a 95°C pre-heated oven for typically 30 min to induce the particle shape deformations. After the heating, the particles are fully cross-linked via 30 min UV-light exposure using a UV-bench lamp (Analytik Jena 15W/365nm), which is placed at approximately 5 cm away from the vials. To remove the glycerol, the particles are washed by repeated centrifugation and redispersion cycles at 3000 g for 15 minutes using water containing 0.5 wt% Pluronic F-108 (Sigma Aldrich). Cycles of centrifugation are also used to remove large particles. Finally, the resulting colloidal SU-8 particles are kept in water containing 0.5 wt% Pluronic F-108.

Characterisation of the UV-exposure of the SU-8 rods

During the second step of the synthesis of banana-shaped particles, the SU-8 rods are exposed to UV-light using a fluorescent lamp consisting of two 36-watt bulbs (Osram L36W/835 lamp). In order to characterise the main features of this lamp, we first consider its spectral power distribution, which is shown in Figure 4.1B. From this spectrum, we calculate the power of the Osram lamp in the range 350–370 nm, corresponding to the range of wavelengths where SU-8 absorbs, to be 0.19 watt per fluorescent bulb. This value is obtained by calculating the integral of the spectrum between 350 and 370 nm and then dividing this by the total integral over all wavelengths, while assuming an efficiency of 30%, which is typical for fluorescent lights. Finally,

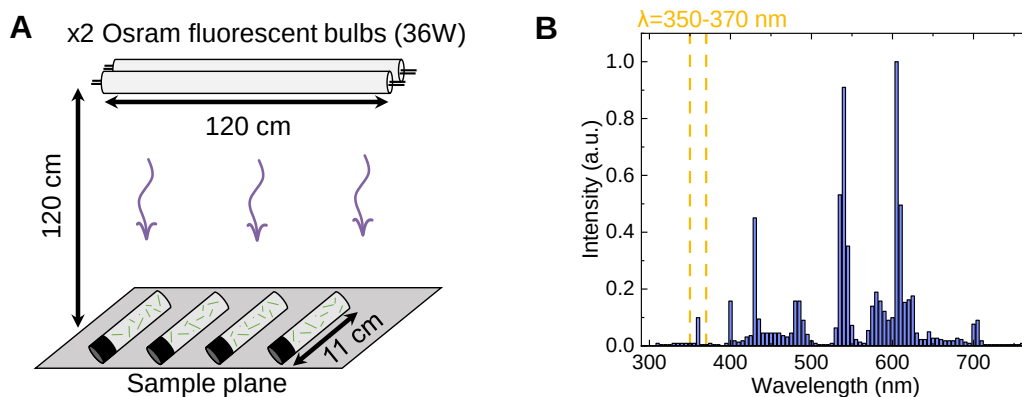


Figure 4.1: (A) Schematic of the experimental set-up used for the UV-exposure of the SU-8 rods after their synthesis. (B) Spectral power distribution of the L36W/835 Osram fluorescent lamp.

we approximate the irradiance to be $4.2 \mu\text{W}/\text{cm}^2$ at the plane of the samples (see Figure 4.1A) taking into account that (i) the sample was 120 cm away from the light source and (ii) the light was emitted over a hemisphere due to the reflective cover behind the bulbs.

Infrared spectroscopy

Infrared spectroscopy (IR) spectra of the SU-8 rods –prior the heating– are recorded at different UV-exposure times using a Perkin Elmer FT-IR Frontier Spectrometer in attenuated total reflectance mode. The measurements are performed on powders obtained by evaporating the solvent of the colloidal dispersion by air-exposure. To prevent UV cross-linking of the SU-8 during drying, samples are covered with aluminium foil all the time.

4.2.2 Size characterization of colloidal SU-8 banana-shaped particles

The size distributions of the colloidal SU-8 particles are determined by measuring the length, diameter and curvature of at least 200 particles from scanning electron microscopy (SEM) images using custom-written image analysis software in Mathematica as described in Section 2.4.3. In brief, the particle curvature, κ , is found by calculating the inverse of the radius, R , of the circle fitting the long axis of the banana (see schematic in Figure 2.12B). The opening angle of the particles, ψ is defined as the angle subtended by the particle from the centre of curvature.

4.2.3 Confocal imaging and polarised optical microscopy

Confocal microscopy images with a 16-bit pixel depth are acquired using a 12 kHz resonant scanner head (Thorlabs) and a 532 nm laser, coupled to an Olympus IX73 inverted microscope equipped with a $60\times$ ($\text{NA} = 1.42$) oil immersion objective (Olympus). Dense particle suspensions of the colloidal bananas are prepared by filling either rectangular VitroCom capillaries ($0.1\text{ mm} \times 0.2\text{ mm} \times 5\text{ cm}$) with aqueous dispersions of colloidal SU-8 bananas, as described in Section 2.4.2.

The visualization of the temperature-driven shape deformations is performed in epoxy glue-sealed rectangular glass capillaries coupled to a custom-made heating stage. This consisted of a peltier element (RS components) attached to the glass capillaries with thermal conductive paste. A thermocouple is then attached to the capillary to monitor the temperature in the capillary during the heating. Note that the same custom-made heating stage is also used to image the deformation of the rods in a bright field microscopy mode.

Polarised optical microscopy (POM) imaging of the liquid crystals formed by our colloidal bananas is typically conducted by preparing thin samples of colloidal bananas in water, which are subsequently imaged using an Olympus IX73 inverted microscope equipped with pair of cross-polarisers (Thorlabs).

4.2.4 Colloidal clusters

The depletion-induced clusters are studied by preparing mixtures of colloidal bananas and xanthan gum ($M_w = 4.5 \cdot 10^6\text{ g/mol}$, Sigma-Aldrich) in water. First, we prepare a polymer stock solution containing 2 mg/mL xanthan in water. We typically use gentle magnetic stirring overnight to ensure a complete dissolution of the xanthan in water. A given volume of polymer solution is then added to a dilute aqueous dispersion of colloidal SU-8 banana-shaped particles to reach a final polymer concentration of 1 mg/mL. The mixture is homogenized using a micro-pipette and loaded into rectangular VitroCom capillaries. The ends of the capillaries are sealed with epoxy glue onto a microscope slide and left equilibrating for at least 2 hours prior to imaging with optical or confocal microscopy, if particles are fluorescent.

4.3 Results and discussion

4.3.1 Synthesis of colloidal SU-8 banana-shaped particles

Our method to produce colloidal SU-8 banana-shaped particles consists of three main steps, which are illustrated in Figure 4.2A: (I) the synthesis of rods, (II) the UV-exposure and (III) the heating. In the first step, polydisperse straight SU-8 rods ($L \sim 20 \mu\text{m}$, see Fig. 1B) are synthesised by vigorously shearing an emulsion of SU-8 droplets in a viscous medium [96, 97]. During the second step, the resulting rods are partially cross-linked via the ring-opening reaction of the epoxy groups under low-intensity UV-light. The degree of cross-linking in the rods is controlled by the UV-exposure time, t_{UV} , as confirmed by the IR spectra shown in Figure 4.3A, where the peak corresponding to the epoxy groups clearly decreases with increasing exposure time (see Figure 4.3B). In the third step, the deformation into banana-shaped particles is induced by heating the rods in a 95°C oven after UV-exposure, resulting in smoothly curved polydisperse colloidal bananas (see Figure 4.2C and D, $t_{\text{UV}} = 45 \text{ min}$). Finally, the particles are fully cross-linked via high intensity UV-light exposure, yielding highly stable particles that can be dispersed in both aqueous and non-aqueous solvents.

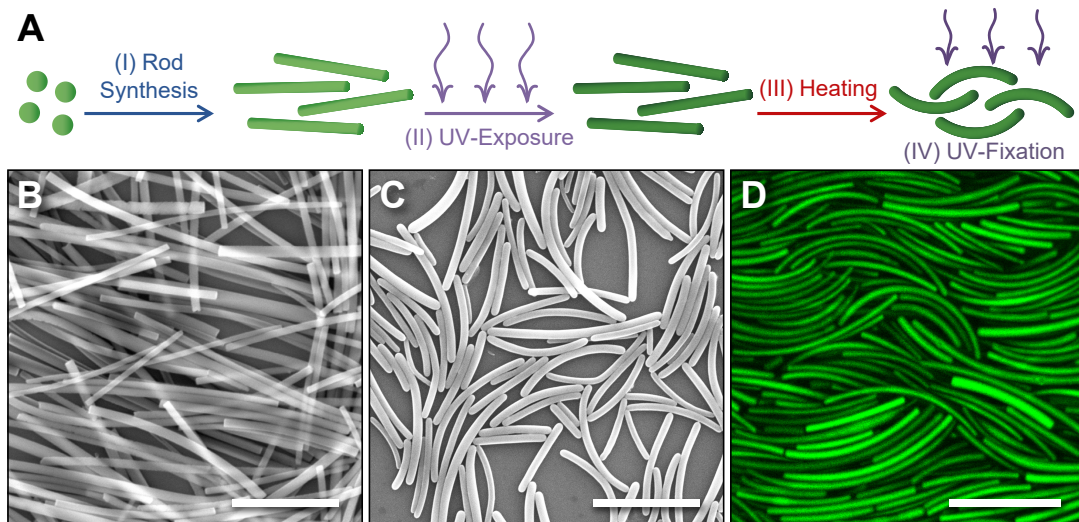


Figure 4.2: Synthesis of colloidal SU-8 banana-shaped particles. (A) Schematic showing the synthesis of SU-8 banana-shaped particles. In the first step, straight SU-8 rods are synthesised by shearing an emulsion of SU-8 droplets [96, 97]. In the second step, the rods are partially cross-linked via exposure to UV-light. In the third step, the partially cross-linked rods are heated to induce a shape deformation into banana-shaped particles, before they are UV-cured in the fourth step. Scanning electron microscopy images of (B) the rods obtained after the synthesis with no heating and (C) the colloidal SU-8 bananas ($t_{\text{UV}} = 45 \text{ min}$) obtained with heating. (D) Confocal microscopy image of the fluorescent colloidal SU-8 bananas. Scale bars are $10 \mu\text{m}$.

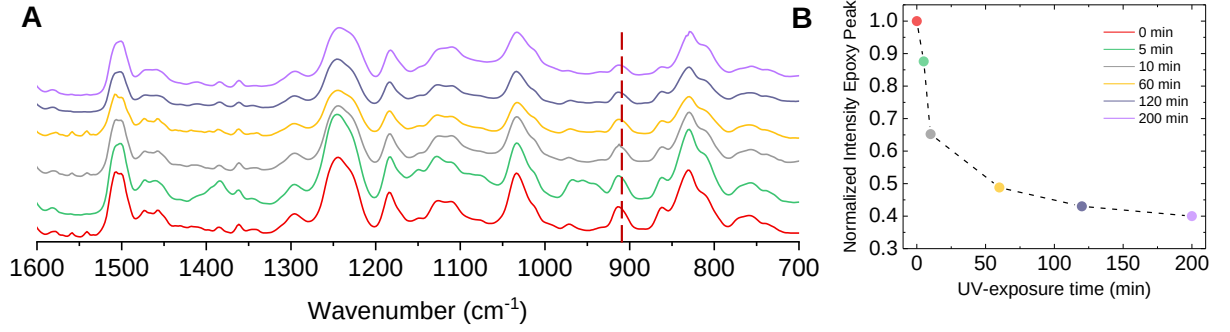


Figure 4.3: Evolution of infrared (IR) spectra of rods with UV-exposure time. (A) Evolution of the IR spectra of the rods with UV-exposure time. All the spectra are normalized to the peak at 1500 cm^{-1} . The dotted line indicates the 915 cm^{-1} epoxy peak. (B) Evolution of the epoxy peak intensity at 915 cm^{-1} with UV-exposure time.

The formation of banana-shaped particles is controlled by the interplay between the cross-linking density of the SU-8 rods, tuned by the UV-exposure time, and the interfacial forces induced during the heating step [156,157]. The cross-linking density of SU-8 dictates its rigidity and glass transition temperature, and both increase with longer UV-exposures [105,158]. In our experiments, we can actually observe three distinct thermoelastic responses depending on the UV-exposure time. At short exposure times ($t_{\text{UV}}=1$ min, Figure 4.4A), i.e. low cross-linking densities, the heating of the rods results in the rounding of their sharp edges (see Figure 4.4C), suggesting that the rods are heated to a temperature above their glass transition temperature. The interfacial forces associated with the hemispherical particle ends drive the collapse of the rods into spheres, rather than bananas, in order to minimise their surface energy [156,157,159]. This collapse takes place via a sphero-cylindrical intermediate state, as shown by the snapshots taken during heating in Figure 4.4A and as similarly seen in [156]. From the corresponding scanning electron microscopy (SEM) images, shown in Figure 4.4C, we find that the particle length decreases, and the diameter increases (see Figure 4.4F), but that the particle volume remains constant during heating.

At intermediate exposure times ($t_{\text{UV}}=25$ min, Figure 4.4B), the heating of the rods still results in the formation of round edges (see Figure 4.4D), which leads to an initial decrease of the rod length and an increase of the rod diameter (Figure 4.4F). However, the increased cross-linking density of the rods, i.e. the higher rigidity, leads to the formation of banana-shaped particles via buckling, as directly visualised during the heating process using confocal microscopy (see Figure 4.4B). The buckling clearly manifests itself by the appearance of curvature after heating for 20 min, where the particle length and diameter no longer change significantly (see Fig. 4.4F).

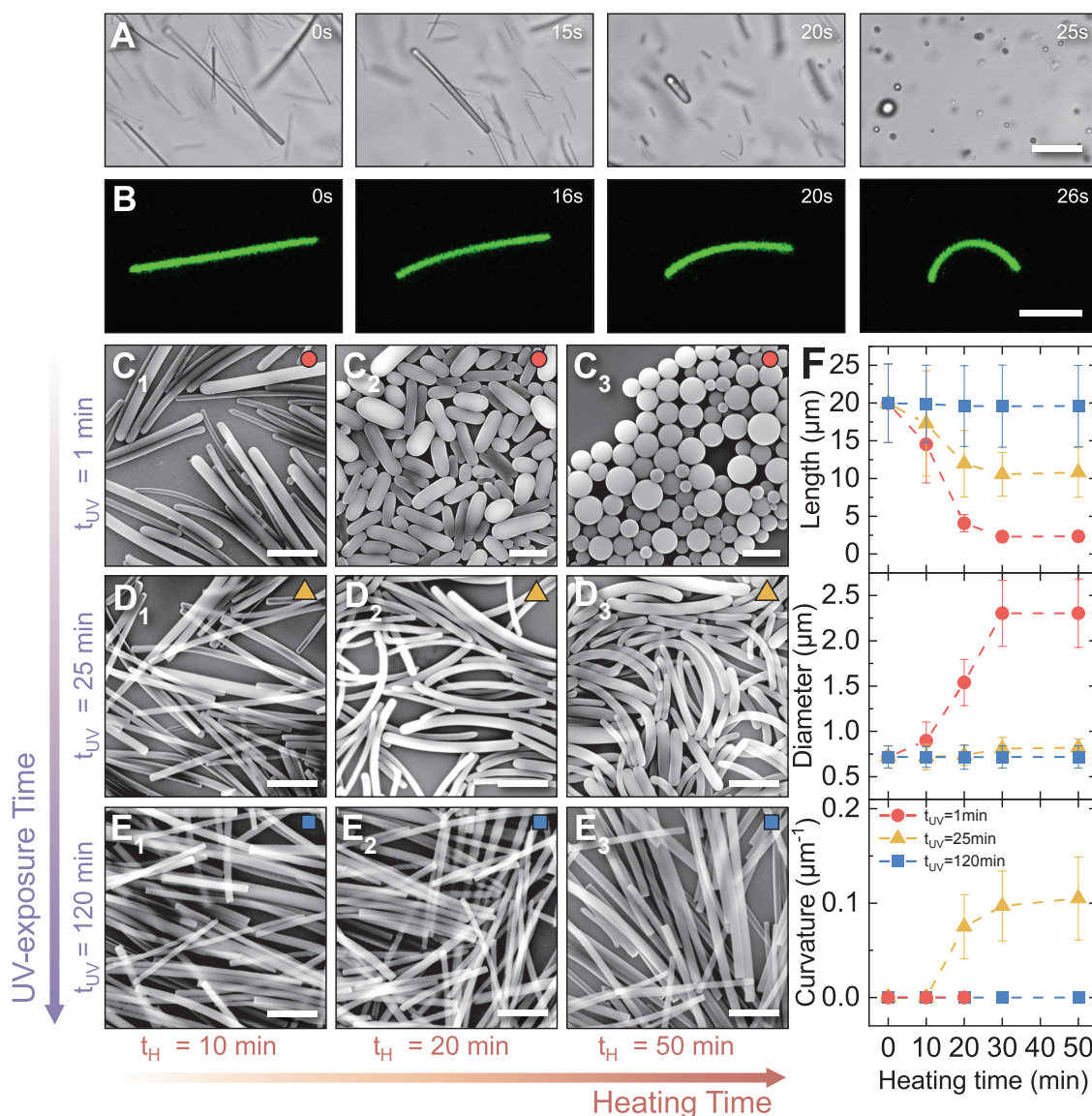


Figure 4.4: Particle shape deformations during heating. (A) Bright field and (B) confocal microscopy snapshots of the deformation of an SU-8 rod during heating at 95°C using a heating stage, for (A) $t_{UV} = 1$ min and (B) $t_{UV} = 25$ min. Representative SEM images of the shape evolution of the SU-8 polymer rods during heating in a 95°C oven for (C) $t_{UV} = 1$ min, (D) $t_{UV} = 25$ min and (E) $t_{UV} = 120$ min. (F) Evolution of the dimensions and curvature of the originally straight SU-8 polymer rods during heating in a 95°C oven for $t_{UV} = 1$ min (circles), $t_{UV} = 25$ min (triangles) and $t_{UV} = 120$ min (squares). Error bars represent the standard deviation of the mean value. Scale bars are (A-B) 10 μm and (C-E) 5 μm .

At large exposure times ($t_{UV}=120$ min, Figure 4.4E), i.e. high cross-linking densities, no rounding of the edges is observed, suggesting that the rods are heated to temperatures below their glass transition temperature. Consequently, no shape deformation is observed and the length, diameter and curvature are all constant during the heating (see Figure 4.4F). Finally, in

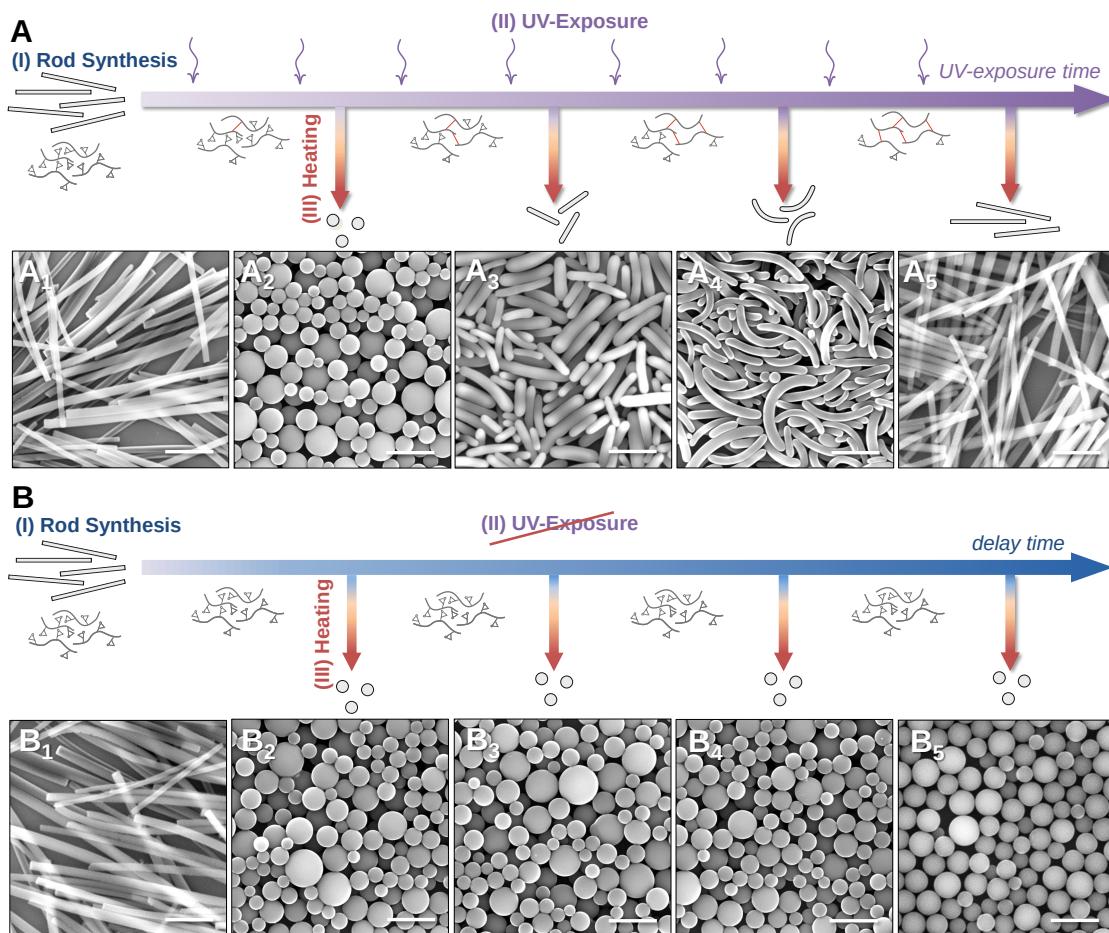


Figure 4.5: Effect of heating in experiments in the absence of UV-light exposure. In (A) rods are exposed to UV-light, which after $t_{UV}=1, 5, 15$ and 120 min and heating, they become (A_2) spheres, (A_3) spherocylinders, (A_4) bananas and (A_5). In (b), the time has between the synthesis and the heating has taken place, i.e. $1, 5, 15$ and 120 min, but they have not been exposed to UV-light. As a result, spheres are always obtained after heating ($B_2 - B_5$). Scale bars are $5\mu\text{m}$.

Figure 4.5 we show the results when carrying out the same experiments in the dark, i.e. when no cross-linking takes place. We observe that instead of obtaining spheres, spherocylinders, bananas and straight rods after the heating at increasing t_{UV} (see Fig. 4.5A), spheres are always obtained in the absence of UV-exposure (see Fig. 4.5B). These results confirm the key importance of the cross-linking degree of the rods in determining the particle shape after obtained the heating.

4.3.2 Morphological state diagram

The ability to systematically control the final particle shape of our new colloidal SU-8 particles using both –UV-exposure and heating time– is summarised in the morphological state diagram shown in Figure 4.6A. This includes SU-8 spheres, spherocylinders, bananas and rods (see Figure A.9 in the Appendix for confocal images of all the differently shaped SU-8 particles).

Importantly, within the banana regime, we show that both the dimensions and curvature of the resulting banana-shaped particles can be carefully controlled by tuning the UV-exposure time at constant heating time. This is clearly observed in the SEM images presented in Figure 4.6C-E, where the bananas obtained using UV-exposure times of $t_{UV}=15, 25$ and 45 min, respectively, are shown for a fixed heating time of 30 min. From these images, we find that with longer UV-exposure times, the particle length L (see inset Fig. 4.6D), increases from $8\text{ }\mu\text{m}$ to $14\text{ }\mu\text{m}$, while the diameter and curvature decrease from $1\text{ }\mu\text{m}$ to $0.7\text{ }\mu\text{m}$ and from $0.25\text{ }\mu\text{m}^{-1}$ to $0.07\text{ }\mu\text{m}^{-1}$, respectively (see Fig. 4.6B). This corroborates the fact that the rigidity of the rods increases and thus the extent of buckling decreases with UV-exposure time. Inherent to the polydisperse nature of the initial SU-8 rods, the resulting colloidal bananas are also polydisperse in length, diameter and curvature, with typical polydispersities of 30%, 20% and 30%, respectively. These banana-shaped particles are a unique and exciting addition to the existing library of colloidal building blocks, in particular, as it opens up the route towards experimentally uncovering the rich self-assembly behavior predicted for banana-shaped particles at the particle level.

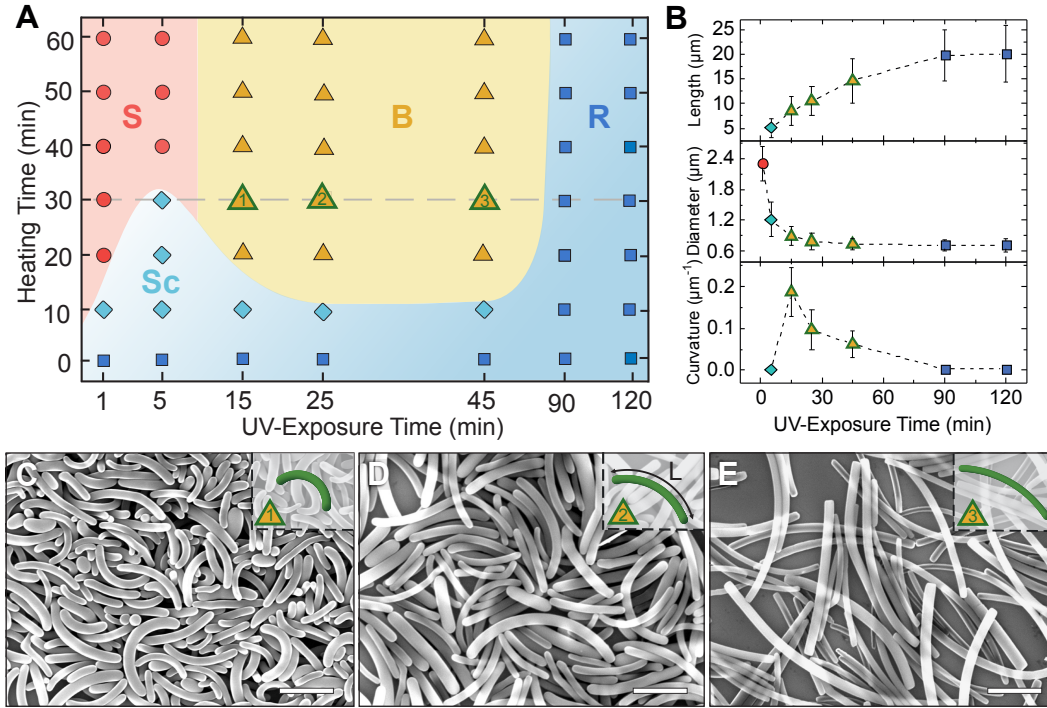


Figure 4.6: Tuning particle shape and controlling the curvature and dimensions of banana-shaped particles. (A) Morphological state diagram of the SU-8 polymer particles as a function of UV-exposure and heating time with a heating temperature of 95°C , where S, B, R and Sc denote the sphere, banana, rod and sphero-cylinder regimes, respectively. (B) Length, diameter and curvature of the SU-8 particles after heating for 30 min, see dashed line in (A), in a 95°C oven for $t_{UV} = 5, 15, 25, 45, 90$ and 120 min. Error bars represent the standard deviation of the mean value and the different colors of the symbols correspond to the different regimes in (A). (C-E) SEM images of banana-shaped particles with decreasing curvature obtained when $t_{UV} = 15, 25$ and 45 min. Scale bars are $5\text{ }\mu\text{m}$.

4.3.3 Applications of the colloidal SU-8 bananas

To illustrate the potential of our new colloidal model system, the self-organisation of differently-curved bananas into colloidal liquid crystalline phases is explored by preparing concentrated samples of fluorescently labelled particles. In Figure 4.7 we show confocal microscopy images of the resulting structures obtained using (A) highly curved bananas ($\kappa = 0.25 \mu\text{m}^{-1}$) and (B) bananas with a relatively low curvature ($\kappa = 0.07 \mu\text{m}^{-1}$). While isotropic ordering is observed for the high curvatures (see Figure 4.6A), polar smectic-like ordering is observed for bananas with lower curvature (see Figure 4.6B). To the best of our knowledge, this is the first experimental observation of banana-shaped colloidal liquid crystals with single-particle resolution. Since the smooth curvature of banana-shaped particles has been predicted to promote bend deformations in concentrated samples [13, 14], our particles should allow us to experimentally probe the existence of the elusive splay-bend nematic phase [13, 14], and the observation of the chiral twist-bend nematic phase [14, 57] at the colloidal length scale. Since these particles can

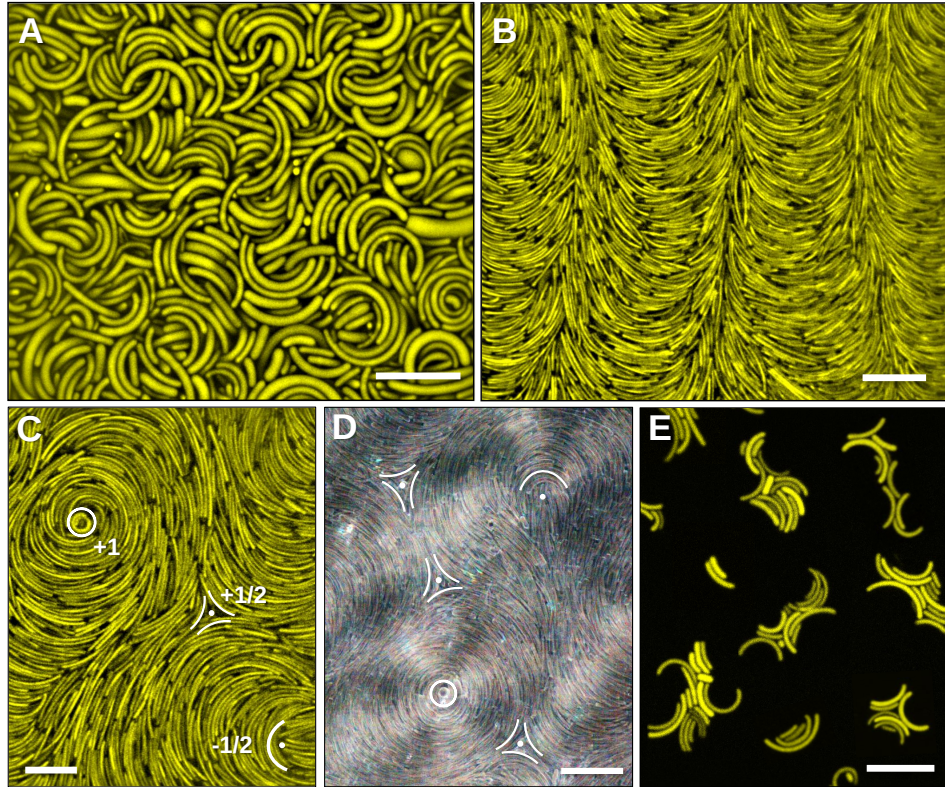


Figure 4.7: Self-assembly of banana-shaped particles. Confocal microscopy images of concentrated samples of banana-shaped particles in the (A) isotropic phase ($\kappa = 0.25 \mu\text{m}^{-1}$) and the (B) smectic phase ($\kappa = 0.07 \mu\text{m}^{-1}$). (C) Various topological defects observed in liquid crystals formed by colloidal bananas with $\kappa = 0.07 \mu\text{m}^{-1}$. (D) Polarized optical microscopy image showing both the structure and birefringence in banana-shaped liquid crystals. (E) Banana clusters obtained using depletion interactions in a mixture of bananas and polymer. Scale bars are (A-D) $10 \mu\text{m}$ and (E) $20 \mu\text{m}$.

be density and refractive index matched with mixtures of organic solvents [27], it will be also possible to observe the three dimensional structure of these complex phases. In addition, we can directly visualise the structure of different types of topological defects in banana-shaped liquid crystals (see Figure 4.6C), enabling us to elucidate, for instance, how they interact with each other and with their surrounding liquid crystalline structure [160, 161]. In fact, as shown in Figure 4.6D, we can also visualise the birefringent signal exhibited by the sample using polarized optical microscopy while simultaneously observing the underlying structural details of defects found in banana-shaped liquid crystals [160, 161] (see Figure A.7 in the Appendix for more birefringent measurements). Finally, we show that dynamic clusters of banana-shaped particles can be assembled via depletion interactions (see Figure 4.6E). This will allow us to study structural rearrangements and the population of different energy states in anisotropic colloidal clusters [162], which resemble the structures exhibited by banana-shaped bacteria when forming biofilms [163, 164].

4.4 Conclusions

In summary, we have introduced a new bulk strategy to produce colloidal SU-8 banana-shaped particles with tunable dimensions and curvature. These particles are an new addition to the existing library of anisotropic colloidal shapes, and promise a range of opportunities for studying – at the single-particle level – systems formed by microscopic banana-shaped building blocks. This includes, for instance, detailed studies of the assembly of banana-shaped liquid crystals and how their phase behaviour is affected the by particle curvature. The colloidal bananas could be also used to mimic structural aspects of some biological systems, such as proteins or bacteria, allowing to address, for example, their interaction with lipid vesicles, and the subsequent deformation of the vesicle’s membrane [165, 166], or the visualisation of the structural details of biofilm-resembling structures [163]. Furthermore, the shape tunability of this system and the already established methods to control inter-particle interactions [25], promises the design of novel structural self-assembled materials with pre-engineered optical and mechanical properties.

Acknowledgments

This work was done in collaboration with Taiki Yanagishima, Heidi de Sousa and Dirk Aarts. Adam Edward Stones, Nicholas Orr and Joris Sprakel are thanked for useful discussions.

Chapter 5

Phase behaviour of colloidal SU-8 banana-shaped particles

ABSTRACT

In this chapter, we study the liquid crystalline phase behaviour of colloidal banana-shaped particles with different curvatures using confocal microscopy. In particular, we measure the distribution of the particle orientations and positions for three differently curved colloidal bananas at various packing fractions. We find that while highly curved bananas only form isotropic phases, less curved bananas exhibit very rich phase behaviour including biaxial nematic, polar and antipolar smectic-like phases. Crucially, we also find that slightly bent bananas exhibit the elusive splay-bend nematic phase, whose very existence is thus finally experimentally established more than four decades after its first theoretical prediction. These results demonstrate the potential of the colloidal bananas for unveiling the structural details of banana-shaped molecular liquid crystals.

5.1 Introduction

The shape of liquid crystal-forming molecules plays a crucial role on the final symmetry of their condensed phases [11, 167]. Compared to the conventional liquid crystal (LC) phases shown by rod-like molecules, including nematic (N), smectic (Sm) and columnar (C) phases, molecules with a bend in their structure show a remarkable richer phase behaviour with more than fifty different liquid crystal phases [7, 8, 10]. These biaxial molecules, which are known as *banana-shaped molecules*, have generated a lot of interest in the last 20 years since they exhibit exotic liquid crystalline phases with distinctive features such as supramolecular chirality and polarity [7, 8, 10]. Banana-shaped liquid crystals are not only attractive from a technological point of view, promising faster switchability speeds in LC displays [8], but also from a fundamental prospective, as they are ideal systems to study, for instance, the spontaneous chiral symmetry breaking in systems of achiral molecules [13, 168–170].

Over the past two decades, the vast majority of reported banana-shaped liquid crystal phases are smectic (Sm) phases, as the curved shape of the constituting molecules promotes their locking into smectic layers [7, 8, 10]. The large stability of Sm phases has also been observed in experiments of colloidal ‘boomerang-like’ particles [155], and in computer simulations of similarly shaped particles [14]. The rather uncommon observation of nematic phases in banana-shaped systems [171, 172] has been the subject of intense research for the past 20 years, not least because of their potential to form chiral and biaxial nematic phases [11, 14, 170, 173]. Examples of chiral and biaxial nematic phases are the twist-bend (N_{TB}) and the splay-bend (N_{SB}) nematic phases, respectively, in both of which the particle orientation is modulated in space. While in the N_{TB} phase the particles exhibit a periodic twist in space resulting in a chiral phase, the N_{SB} phase exhibits periodic splay and bend modulations of the particle orientation in a single plane, therefore showing biaxiality but not chirality [13].

The N_{TB} and N_{SB} phases were postulated over forty years ago by Meyer [66], and later independently by Dozov [13], who suggested that bend deformations in the orientation field of banana-shaped particles should be accompanied either by twist or splay deformations to fill 3D space. While the N_{TB} phase has been observed in thermotropic liquid crystals (see e.g. [57, 174, 175]) the very existence of the N_{SB} phase is still to be confirmed experimentally. Recently, computer simulations suggested that the N_{SB} phase can be found in systems of hard boomerangs,

i.e. rod-like particles with a sharp kink, if the Sm phase is destabilised by polydispersity in the particle length or by smooth curvature in the particle shape [14]. Experimentally studying the impact of polydispersity and curvature on the microscopic structure of banana-shaped systems is thus crucial for a deeper understanding of the formation and properties of these phases. However, banana-shaped liquid crystals are typically characterised using birefringence and X-ray diffraction techniques, where direct information about structural details is not available at the molecular scale.

Here, we use our recently developed *colloidal bananas* (see Chapter 4) to study the phase behaviour of banana-shaped liquid crystals at the single-particle level. Using confocal microscopy, we elucidate the phase behaviour of three differently curved banana-shaped particles at different packing fractions. While isotropic phases are mostly found for highly curved bananas, very rich phase behaviour, including biaxial nematic, and polar and antipolar smectic-like structures, is observed for less curved bananas. Crucially, we find that the least curved bananas exhibit the elusive splay-bend nematic phase, whose very existence is thus finally experimentally established more than four decades after its first theoretical prediction.

5.2 Experimental methods

5.2.1 Differently curved colloidal SU-8 bananas

The three average particle curvatures used in this Chapter are $0.25\mu\text{m}^{-1}$, $0.10\mu\text{m}^{-1}$ and $0.07\mu\text{m}^{-1}$ (see Figure 5.1). Upon decreasing curvature the corresponding lengths of the colloidal bananas slightly decrease with values of 8, 11 and 14 μm , while their diameter is roughly constant at 0.8 μm . It is important to note that our bananas are polydisperse in both dimensions and curvature, with polydispersity values of 30%, 20% and 30% in length, diameter and curvature, respectively (see Table 5.1).

Table 5.1: Mean length (L), diameter (D), aspect ratio (L/D), curvature (κ), opening angle (ψ), and polydispersity (%) of the different batches of SU-8 banana-shaped particles used. The polydispersity (%) of the particles is defined as $\sigma_i = \delta_i/\langle i \rangle$, where δ_i is the standard deviation of the mean value $\langle i \rangle$.

Batch number (min)	L (μm)	D (μm)	L/D	κ (μm^{-1})	ψ ($^\circ$)
1	8.1 (30.2%)	0.94 (16.9%)	9.5 (25.9%)	0.25 (29.8%)	113.4 (12.7%)
2	10.9 (31.7%)	0.80 (19.7%)	14.3 (27.5%)	0.10 (29.5%)	148.3 (11.5%)
3	14.0 (30.4%)	0.74 (19.3%)	19.1 (26.7%)	0.07 (28.4%)	151.0 (8.5%)

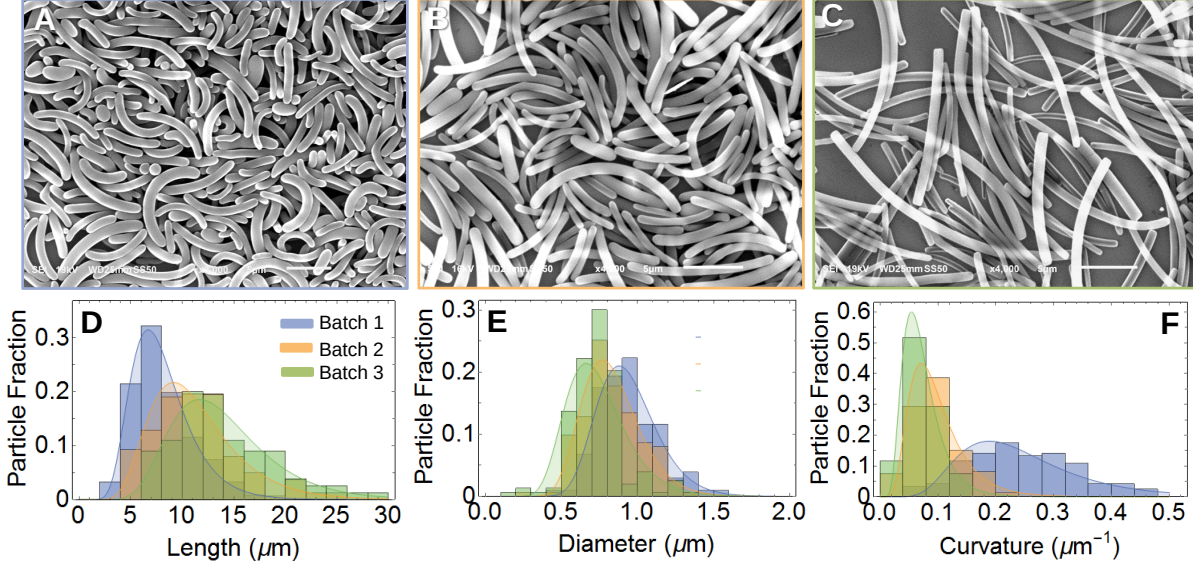


Figure 5.1: (A-B) Scanning electron microscopy images of the three differently curved bananas used in this work. Distributions of the (D) length, (E) diameter and (F) curvature of the three batches of particles used: (blue) batch 1, (orange) batch 2 and (green) batch 3. Scale bars are 5 μm .

5.2.2 Confocal imaging of dense suspensions of colloidal SU-8 bananas

Confocal microscopy images with a 16-bit pixel depth are acquired using a 12 kHz resonant scanner head (Thorlabs) and a 532 nm laser, coupled to an Olympus IX73 inverted microscope equipped with a 60 $\times$ (NA = 1.42) oil immersion objective (Olympus) (see Section 2.4.2).

Dense particle suspensions of the colloidal bananas are prepared by filling home-made sample cells as described in Section 2.4.2. As a recap, all samples are let to equilibrate for roughly two weeks while slightly tilted at a small angle ($2 - 3^\circ$) in order to induce a weak gradient in packing fraction (see Figure 5.2A). This enables us to access to the concentration-dependent phase behaviour of the system using a single sample (see Figure 5.2B). At the same time, a second gradient in the packing fraction is established in the vertical direction, z , as the colloidal particles sediment over time (see Figure 5.2C). While the equilibrated samples have a typical thickness of $\sim 50 \mu\text{m}$, we image the system relatively close to the bottom wall to which the bananas align (see Figure 5.2D), as this facilitates the quantitative two-dimensional structural analysis at the particle level. As such, we use the packing fraction gradient in the x -direction to quantitatively study the phase behaviour of the colloidal bananas.

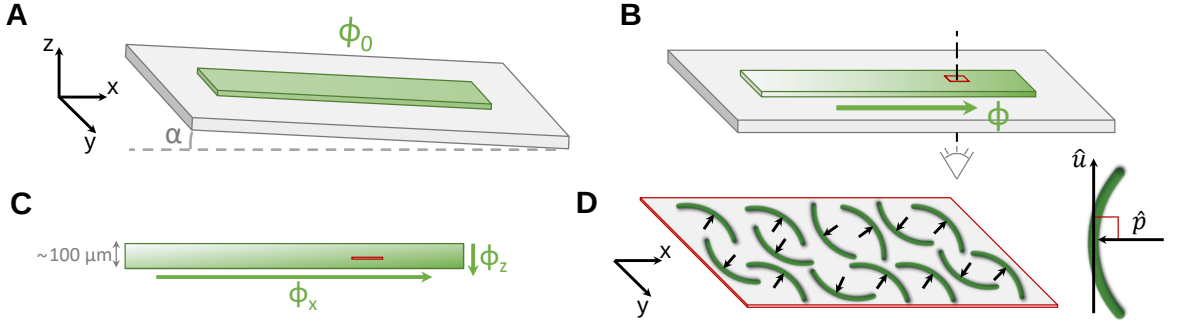


Figure 5.2: Schematic illustration of (A) the equilibration and (B) the imaging of the sample cell used for the study of the phase behaviour of the colloidal bananas with confocal microscopy. ϕ_0 is the initial packing fraction of the colloidal dispersion. (C) Side-view of the capillary illustrating the two packing fraction gradients, one in the x -direction (ϕ_x) and the other in z (ϕ_z), established in the sample cell. (D) Schematic of a typical confocal image of the bananas close to the wall, illustrating how the bananas align to it. Note that in this configuration, the polar orientation, $\hat{p}$, and the long axis orientation, $\hat{u}$, of the banana-shaped particles are always orthogonal to each other.

5.2.3 Analysis of the positions and orientations of the colloidal SU-8 bananas

The positions and orientations of the banana-shaped particles are determined from the confocal microscopy images using the custom-written image analysis routine in Mathematica introduced in Section 2.4.4. In this work, our image analysis routine consists of multiple steps, as shown in Figure 5.3. First, we binarize the confocal microscopy images with a locally adaptive threshold using the ‘LocalAdaptiveBinarize’ built-in function to reduce the effect of intensity variations in the image (see Figure 5.3B). Next, we segment the binarized image using the ‘Morphological-Components’ built-in function (see Figure 5.3C). From the segmented images, we can calculate the position and orientation of the corresponding particles, but also other characteristic parameters such as their curvature or length. This is useful to determine, for instance, local fractionation in the particle curvature or length in a specific region of our field of view.

To calculate the curvature of the banana-shaped particles, we first skeletonize the segmented image using the ‘Skeletonize’ built-in function to obtain the backbones of the particles. Then, we fit circles to the backbone pixels using a custom-written algorithm that minimizes the distance between the circles and the pixels of the particles (see Figure 5.3D). The curvature of the particles, κ , is calculated as the inverse of the fitting radius, R . The length of the particles, L , is obtained by first finding the coordinates of the end points of the particles (see Figure 5.3E) and then computing the opening angle, α , of each particle using the coordinates of the center of curvature. The particle length is then given by $L = \alpha R$.

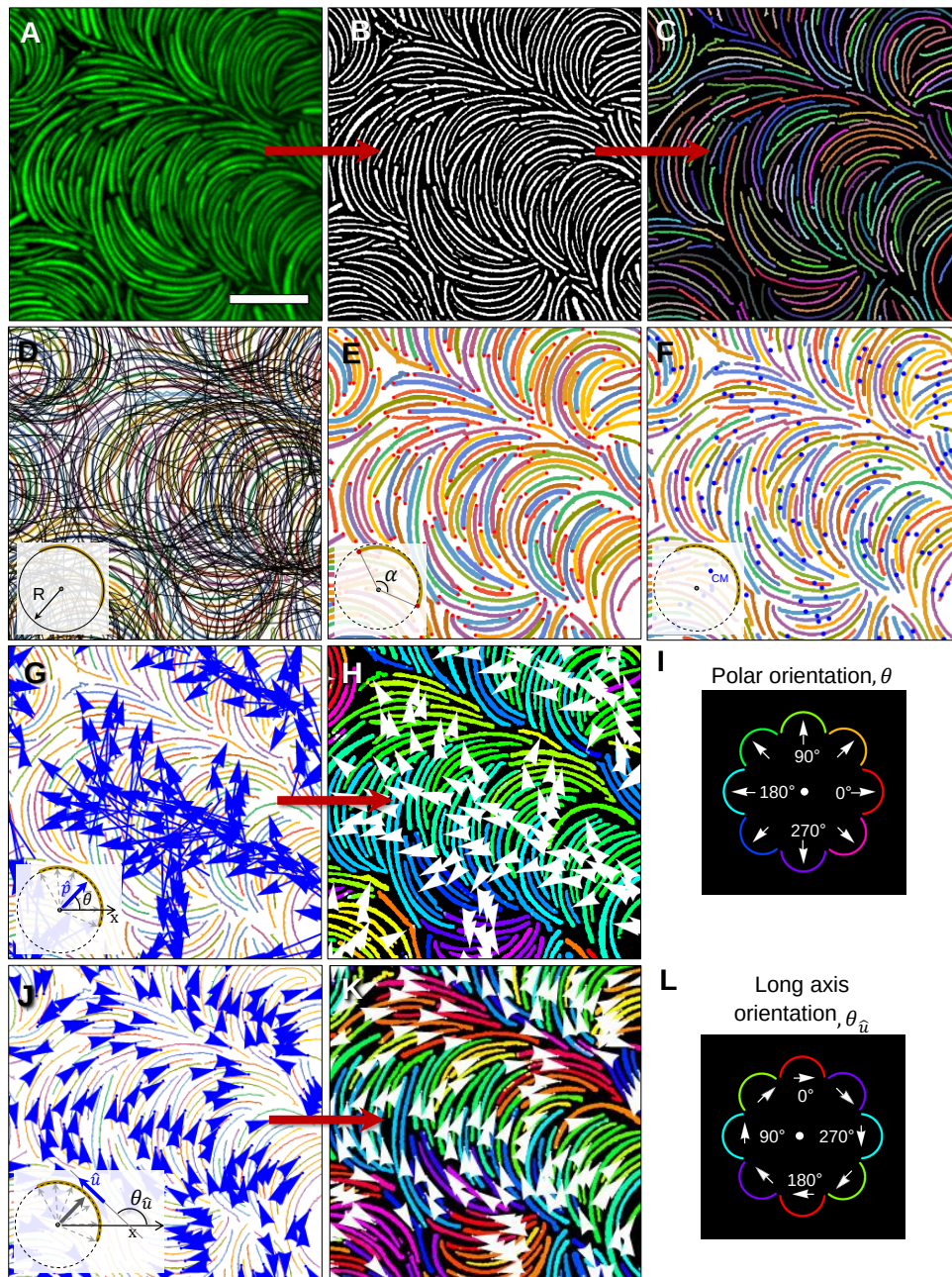


Figure 5.3: Step-wise image analysis procedure to extract the curvature, length, position and orientation of each colloidal banana from confocal microscopy images. (A) Original confocal image, (B) binarized image, (C) segmented image, where the different colors represent different bananas. Segmented image overlaid with (D) the fitting circles, (E) the end points of the particles, (F) the centers of mass, (G) the polar orientation vectors and (J) long axis orientation vectors. In (H, K) the bananas are colored according to their polar orientation and their long axis orientation, respectively, as given by the color codes in I and L. The scale bar is $10 \mu\text{m}$

To determine the positions of the particles, we calculate their centre of mass using the pixel coordinates of each banana (see Figure 5.3F). The orientation of the banana-shaped particles, in two dimensions, is characterised by the polar vector $\hat{\mathbf{p}}$, which is associated to the short axis of the banana (see Figure 5.3G), and the orientation vector $\hat{\mathbf{u}}$ which is associated to the long axis of the banana (see Figure 5.3J). The polar vector, is calculated using the average vector originating from all the vectors starting from the centre of curvature and ending at the backbone of the banana (see Figure 5.3G). The orientation vector is then simply calculated by rotating the polar vector by $\pi/2$ (see Figure 5.3J). Note that we characterise the orientation of these vectors by the angle, θ they form with respect to the horizontal axis, x . A periodic colour map is used to colour the bananas according to their polar, θ , and long axis orientations, $\theta_{\hat{u}}$, as shown in Figure 5.3H, I, K and L. Note that θ is defined to vary between 0 and 2π and $\theta_{\hat{u}}$ between 0 and π . Finally, it is important to note that this analysis is valid as long as the imaging plane is parallel to the long axis of the bananas.

The packing fraction of the samples is determined from the confocal images using $\phi = NA_b/A$, where N is the total number of particles in the field of view of area A , and A_b is the cross-sectional area of a banana-shaped particle, given by $A_b = LD$. Here, L and D are the mean length and diameter of the particles as obtained from the SEM images (see Section 5.2.1).

5.2.4 Identifying the splay-bend nematic phase

While in a standard nematic phase, particles are aligned along a nematic director $\hat{\mathbf{n}}$ [2], in a spatially modulated nematic phase, like the splay-bend nematic phase (N_{SB}), the orientation of the particles varies in space. As a result, the N_{SB} is characterised by a nematic director field $\hat{\mathbf{n}}(r)$ [13, 14] (see Figure 5.4). The splay-bend nematic phase is also characterised by its biaxiality, meaning that both the polar and long axes of the constituent particles are oriented along two mutually orthogonal nematic directors (in Figure 5.4 these are the x and y axes). This type of order forces the nematic director field to be confined to a plane, for example the xy plane, as also shown in Figure 5.4. If we define the y -axis to be parallel to the nematic director, the theoretical expression of the nematic director field of a splay-bend nematic phase [13] is given by:

$$\hat{\mathbf{n}}(y) = \left\{ \sin \left(\theta_0 \sin \left(\frac{2\pi}{p} y \right) \right), \cos \left(\theta_0 \sin \left(\frac{2\pi}{p} y \right) \right) \right\}, \quad (5.1)$$

where θ_0 and p are the amplitude and pitch-length of the modulation, respectively [13] (see Figure 5.4). In terms of positional order, a weak, if not absent spacial modulation of the particles positions is expected in the splay-bend nematic phase [14]. This is a typical characteristic for nematic phases [2], which distinguishes smectic (with positional order) from nematic phases.

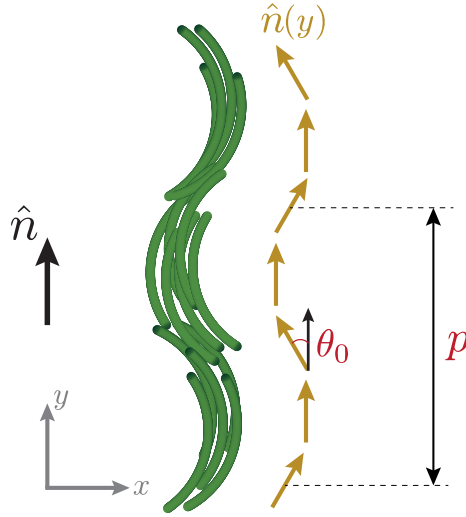


Figure 5.4: Schematic of the splay-bend nematic phase, in the xy -plane, and its corresponding nematic director field, $\hat{\mathbf{n}}(y)$, along the nematic director $\hat{\mathbf{n}}$, with amplitude θ_0 and pitch-length p .

Since a unique order parameter to identify the nematic splay-bend phase does not exist in literature, we measure the spatial modulation of (i) the particles positions $\rho(y)$, to distinguish nematic from smectic phases, and (ii) the nematic director field $\hat{\mathbf{n}}(y)$ along the nematic director of the phase $\hat{\mathbf{n}}$, to distinguish the splay-bend nematic ordering from other nematic phases. First we determine the center of mass positions and the particle orientations $\hat{\mathbf{u}}_{\mathbf{i}}$ of all the particles as explained in Section 5.2.3 and shown in Figure 5.5A and B, respectively. Next, we calculate the nematic director $\hat{\mathbf{n}}$, which is defined as the average orientation of all the particles, is by diagonalising the nematic order parameter tensor [14, 60]

$$Q_{\alpha\beta} = \frac{1}{N} \sum_{i=1}^N \left[\frac{3}{2} \hat{\mathbf{u}}_{i\alpha} \hat{\mathbf{u}}_{i\beta} - \frac{\delta_{\alpha\beta}}{2} \right], \quad (5.2)$$

where $\hat{\mathbf{u}}_{i\alpha}$ is the α -th component of the unit vector describing the orientation of the long axis of a banana-shaped particle i , N is the number of particles and $\delta_{\alpha\beta}$ the Kronecker delta. The global nematic order parameter (NOP) or S_2 (see Section 2.1.4) is defined as the largest eigenvalue of $Q_{\alpha\beta}$ and the corresponding eigenvector is the nematic director $\hat{\mathbf{n}}$.

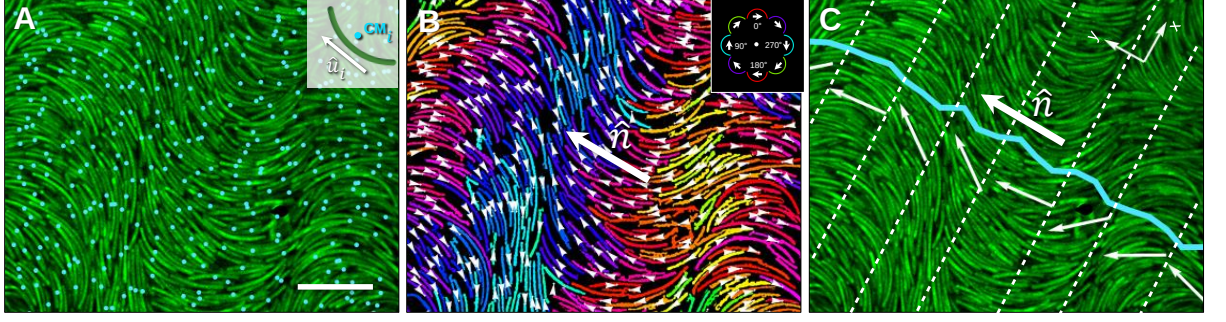


Figure 5.5: (A) Center of mass positions of all the bananas. (B) Bananas coloured according to the particle orientation (see white arrows and inset). (C) Modulation of the density, $\rho(y)$ (blue line) and the nematic director field, $\hat{n}(y)$ (white arrows) along the nematic director, $\hat{n}$ for bananas with average curvature of $\kappa = 0.07 \mu\text{m}^{-1}$ and $\phi = 0.67$. Note that the y -axis is parallel to $\hat{n}$. Scale bars are $10 \mu\text{m}$.

After aligning the y -axis to $\hat{n}$, we then divide the image into bins that are perpendicular to the y -axis and calculate the main local particle orientation and the local number density in each bin (see Figure 5.5C). From these we extract the number density profile and the nematic director field $\hat{n}(y)$ along the nematic director $\hat{n}$, which are shown as the blue line and the white arrows in Figure 5.5C, respectively. If no significant density modulations are found and the director field follows the theoretical expression of $\hat{n}(y)$ (see equation 5.1), the phase is considered to be a splay-bend nematic phase.

As an additional characterisation, we calculate the typical nematic and smectic order parameters used for rod-like systems [14, 117]. As introduced at the beginning of this section, the global nematic order parameter (NOP) is calculated as the largest eigenvalue of $Q_{\alpha\beta}$ (see Equation 5.2). The global smectic order parameter (SmOP) is calculated using [14, 117]

$$\text{SmOP} = \max_l \left| \sum_{j=1}^N e^{2\pi i \mathbf{r}_j \cdot \mathbf{n} / l} \right|, \quad (5.3)$$

where the value of $l \in \mathbb{R}$ that maximized the above expression is identified as the layer spacing.

5.3 Results and discussion

5.3.1 Phase behaviour of differently curved colloidal bananas

We study the phase behaviour of banana-shaped particles, and how this is affected by curvature, by preparing concentrated samples of three differently-curved colloidal bananas and imaging them using confocal microscopy. Whilst the three-dimensional samples are typically $\sim 50 \mu\text{m}$

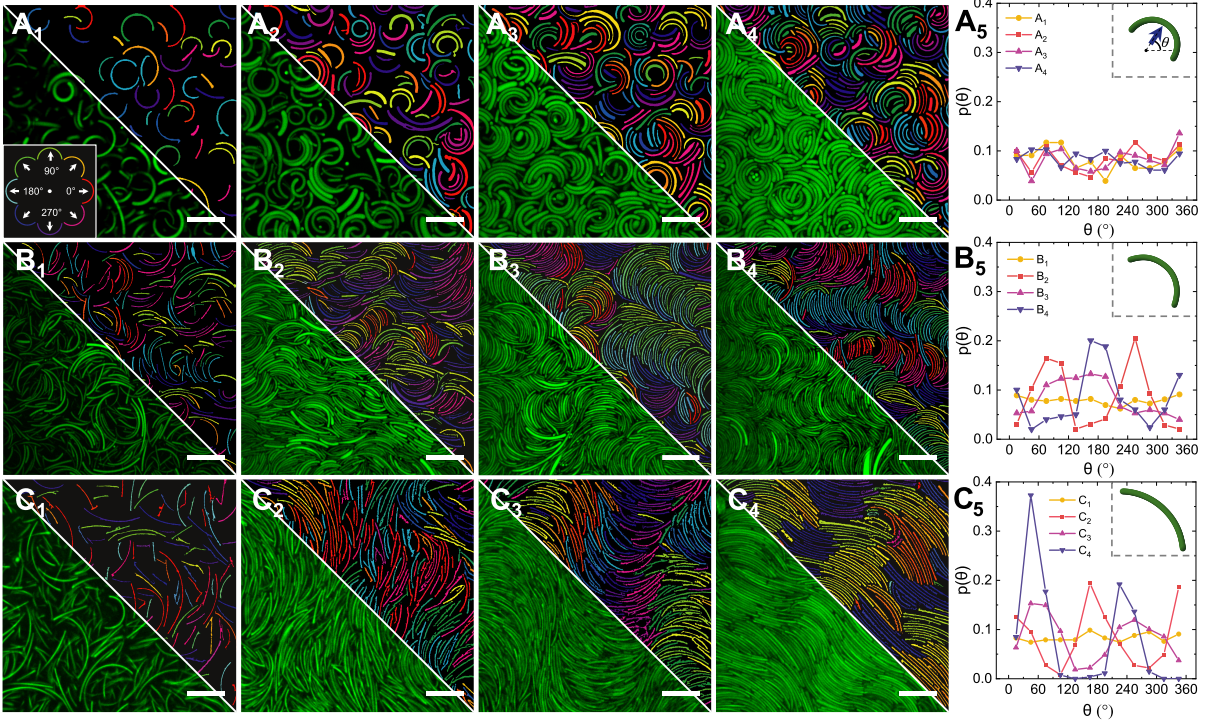


Figure 5.6: Phase behaviour of banana-shaped colloidal particles with different curvatures. Confocal microscopy images of colloidal bananas with an average curvature of (A₁-A₄) $\kappa = 0.25 \mu\text{m}^{-1}$ and packing fractions $\phi = 0.12, 0.26, 0.61$ and 0.84 , respectively; (B₁-B₄) $\kappa = 0.10 \mu\text{m}^{-1}$ and $\phi = 0.27, 0.63, 0.79$ and 0.82 , respectively; and (C₁-C₄) $\kappa = 0.07 \mu\text{m}^{-1}$ and $\phi = 0.29, 0.60, 0.67$ and 0.79 , respectively. The top-right overlays on the images show the bananas coloured according to their polar orientation as defined in panel A₅ and the legend in panel A₁. Panels A₅ - C₅ show the polar angle distributions of the corresponding confocal microscopy images. Scale bars are $10 \mu\text{m}$.

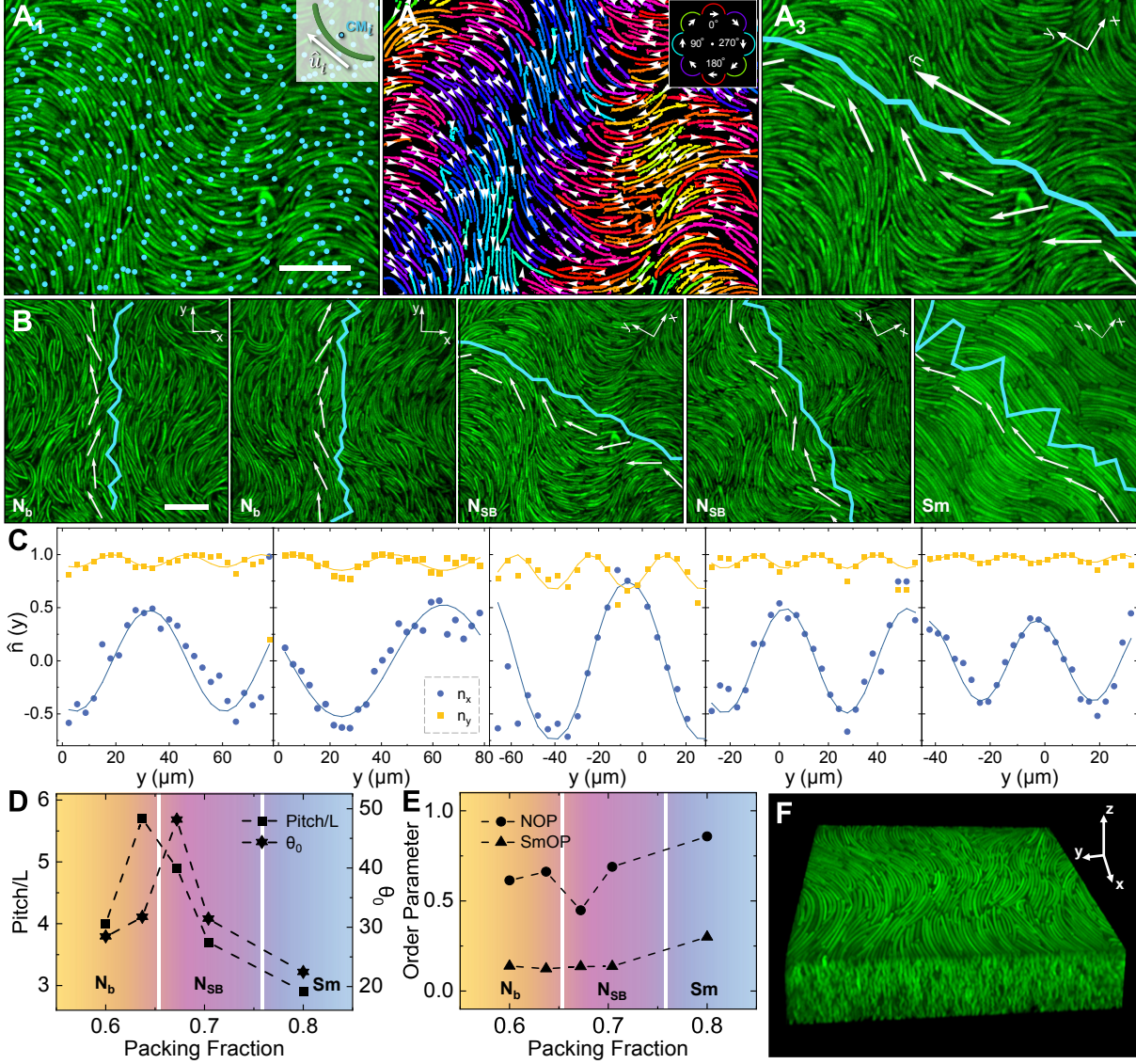
thick, we image the system relatively close to the bottom wall of the sample container to which the bananas align, as this facilitates a quantitative two-dimensional structural analysis at the particle level (see Section 5.2.4). In Figure 5.6, we present confocal microscopy images of the structures formed by the three differently curved colloidal bananas at different packing fractions ϕ . The most curved bananas ($\kappa = 0.25 \mu\text{m}^{-1}$) only display isotropic phases (*I*) at all packing fractions, as shown in Fig. 5.6A (see Fig. A.10 in the Appendix for confocal images of the system at all packing fractions studied). Although small smectic domains are observed at high packing fractions, the combination of polydispersity and small opening angles of these bananas suppresses the formation of any ordering at larger length scales. This is corroborated by the flat distribution of polar orientation θ (see inset in Fig. 5.6A₅) of the bananas, $p(\theta)$, in Fig. 5.6A₅, and the lack of orientational correlations over space in the overlays in Fig. 4A₁-A₄, where the bananas are coloured according to their polar orientation. Note that due to the alignment of the bananas to the wall, the orientation of the long axis is directly related to the polar orientation via a $\pi/2$ rotation.

The bananas with intermediate curvature, $\kappa = 0.10 \mu\text{m}^{-1}$, also exhibit isotropic ordering at low packing fractions (Fig. 5.6B₁), but self-assemble into biaxial nematic and polar and antipolar smectic-like phases at higher packing fractions as shown in Fig. 5.6B₂-B₄ (see Fig. A.11 in the Appendix for images at all packing fractions). The onset of orientational ordering in the nematic and smectic phases manifests itself as the emergence of peaks in $p(\theta)$ above $\phi = 0.63$, as shown in Fig. 5.6B₅. The biaxial nature of this ordering is inherent to the orthogonality between the long and polar axes of the bananas due to their alignment to the wall. In particular, the biaxial nematic phase (N_b) observed at $\phi = 0.63$ (Fig. 5.6B₂) is characterized by two peaks in $p(\theta)$, which correspond to the two polar orientations the bananas show in this phase. At higher packing fractions, $\phi = 0.79$ (Fig. 5.6B₃), the emergence of smectic domains, with some local polar smectic ordering, is observed [176]. Note that the polydomain structure at this packing fraction results in a single broad peak in $p(\theta)$. Antipolar smectic ordering is observed at $\phi = 0.82$ (Fig. 5.6B₄), which leads to a double peak in $p(\theta)$ due to the neighbouring layers exhibiting alternating polar orientation, as is also evident from the overlay in Fig. 5.6B₄.

Even richer phase behaviour is observed for the least curved bananas ($\kappa = 0.07 \mu\text{m}^{-1}$), as shown in Fig. 5.6C (see Fig. A.12 in the Appendix for images at all packing fractions). As expected, the isotropic phase is observed at low packing fractions. Upon increasing packing fraction, the system starts to exhibit biaxial nematic ordering (Fig. 5.6C₂ and 5.6C₃), as is evident from the development of peaks in $p(\theta)$ (Fig. 5.6C₅), and eventually forms layered antipolar smectic structures at $\phi = 0.79$ (Fig. 5.6C₄). Most interestingly, however, the biaxial nematic phase of bananas with this curvature (Fig. 5.6C₃) clearly exhibits a strong spatial modulation of the particle orientations, which is reminiscent of the elusive biaxial splay-bend nematic phase.

5.3.2 Splay-bend nematic phase in colloidal bananas

To distinguish the splay-bend nematic phase from the biaxial nematic and smectic phases, we measure the spatial modulation of the positional and orientational order of the particles along the nematic director $\hat{\mathbf{n}}$ (see Section 5.2.4). To this end, we determine the center of mass positions and the particle orientations $\hat{\mathbf{u}}_i$ (see inset Fig. 5.7A₁) of all the particles as presented in Fig. 5.7A₁ and 5.7A₂, respectively, for the least curved bananas at $\phi = 0.67$ shown in Fig. 5.6C₃. From these, we extract the number density profile and the nematic director field along the nematic director $\hat{\mathbf{n}}$, which are shown as the blue line and the white arrows in Fig. 5.7A₃, respectively. Note that the y -axis is defined to be parallel to $\hat{\mathbf{n}}$. In Fig. 5.7B



we present these measurements for the five highest packing fractions ($\phi = 0.60 - 0.79$) for the bananas with the lowest curvature ($\kappa = 0.07 \mu\text{m}^{-1}$). Firstly, we observe that the number density profiles are mostly flat, characteristic for nematic phases, except for the highest packing fraction ($\phi = 0.79$), where clear peaks develop due to the organisation of the bananas into smectic layers. Consistently, the global smectic order parameter only increases at $\phi = 0.79$, as shown in Fig. 5.7E, confirming the smectic nature of this phase. Secondly, we observe a clear modulation of the nematic director field, $\hat{\mathbf{n}}(y)$, for all five packing fractions as is evident from the periodic fluctuations in the orientations of the white arrows in Fig. 5B.

A detailed characterisation of the measured $\hat{\mathbf{n}}(y)$ is shown in Fig. 5.7C, where the spatial modulations of its components parallel (n_y) and perpendicular (n_x) to the nematic director are shown for all five packing fractions. To unambiguously identify the splay-bend nature of these phases, we fit the measured nematic director field with the theoretical expression for the director field of a splay-bend nematic phase [13], given by $\hat{\mathbf{n}}(y) = \left\{ \sin \left(\theta_0 \sin \left(\frac{2\pi}{p} y \right) \right), \cos \left(\theta_0 \sin \left(\frac{2\pi}{p} y \right) \right) \right\}$, where θ_0 and p are the amplitude and pitch-length of the modulation, respectively (see Section 5.2.4) [13]. As shown in Fig. 5.7C, we find that our experimental data for n_x and n_y are remarkably well described by the expression for $\hat{\mathbf{n}}(y)$ for all packing fractions in the range $\phi = 0.60 - 0.79$, confirming the splay-bend nature of the director field. However, for $\phi < 0.67$, the amplitude θ_0 and pitch-length p , obtained from these fits, increase with increasing ϕ (see Fig. 5.7D), in contrast to what is expected for the splay-bend nematic phase [14]. Only for $\phi \geq 0.67$, θ_0 and p are directly proportional to each other and decrease with increasing ϕ (see Fig. 5.7D), in agreement with computer simulations of the splay-bend nematic phase [14], suggesting that the splay-bend nematic phase forms at $\phi \geq 0.67$. This is corroborated by the decrease in the global nematic order parameter at $\phi = 0.67$, consistent with the onset of significant splay-bend modulations of the particle orientations, resulting in a decrease of the global alignment of particles (see Fig. 5.7E). For our least curved colloidal bananas ($\kappa = 0.07 \mu\text{m}^{-1}$) it is thus clear that they undergo a transition from the biaxial nematic phase to the modulated splay-bend nematic phase at $\phi \approx 0.67$, before going into the smectic phase at $\phi \simeq 0.79$. As far as we are aware, this is the first experimental observation of the splay-bend nematic phase, which was predicted in 1976 [66]. Finally, we demonstrate the 3D nature of the splay-bend nematic phase in Fig. 5.7F, where a 3D confocal microscopy image shows the splay-bend deformations up to fifteen particle diameters into the bulk of our sample (see Fig.A.13 in the Appendix for confocal images at different heights).

5.3.3 Experimental phase diagram

From our experimental results the following picture of the phase behaviour for our differently curved colloidal bananas emerges. For the most curved bananas ($\kappa = 0.25 \mu\text{m}^{-1}$) only the isotropic phase is observed, for the bananas with intermediate curvature ($\kappa = 0.10 \mu\text{m}^{-1}$) a phase sequence of I - N_b - Sm is found and the least curved bananas ($\kappa = 0.07 \mu\text{m}^{-1}$) exhibit a I - N_b - N_{SB} - Sm phase sequence as a function of the packing fraction (see Figure 5.8). While our results for the least curved bananas are largely consistent with the phase behaviour found in computer simulations of similar banana-shaped particles [14], we do not observe the twist-bend nematic phase, which is predicted to occur between the nematic and splay-bend nematic phases [14]. We attribute the absence of the N_{TB} phase in the experimental phase behaviour to a combination of the effect of gravity and the presence of a flat bottom wall in our sample cell. An external field like a gravitational or electric field may transform the N_{TB} phase into a N_{SB} phase in the case the nematic director is perpendicular to the external field [175]. In addition, the presence of a flat wall favors biaxial order, and hence the N_{SB} rather than the N_{TB} phase may form close to the wall. The direct observation of the colloidal analogue of the N_{TB} phase therefore still remains an exciting experimental challenge.

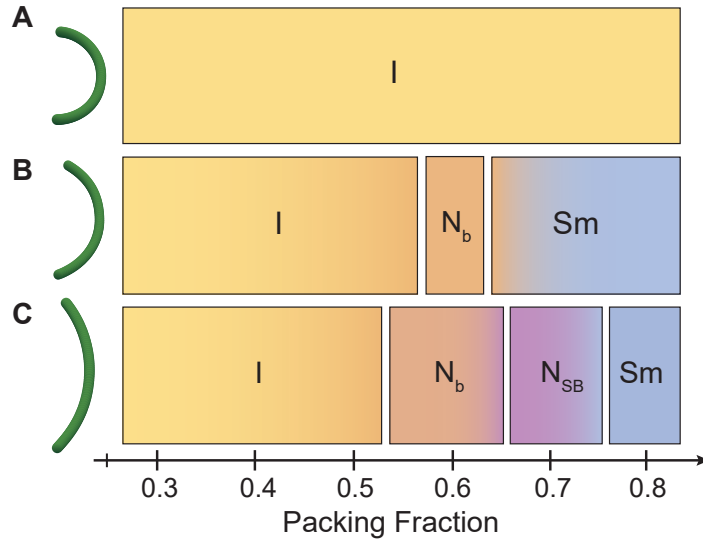


Figure 5.8: Experimental phase diagram for banana-shaped particles with average curvatures of (A) $\kappa = 0.25 \mu\text{m}^{-1}$, showing isotropic phases (I), (B) $\kappa = 0.10 \mu\text{m}^{-1}$, showing I , biaxial nematic (N_b) and smectic (Sm) phases, and (C) $\kappa = 0.07 \mu\text{m}^{-1}$, showing I , N_b , splay-bend nematic N_{SB} , and Sm phases at increasing packing fraction ϕ .

5.4 Conclusions

In summary, we have experimentally established the phase behaviour of three differently curved colloidal banana-shaped particles at the particle level. A range of exotic liquid crystalline structures including biaxial, splay-bend nematic phases and polar and antipolar smectic-like phases have been observed depending on the particle curvature. The experimental observation of the splay-bend nematic phase in the system of slightly bent bananas confirms the importance of a smooth particle curvature and polydispersity for the stability of this phase [14], and it also suggests that the typical sharp kink and purity of bent-core molecules could be one of the reasons as to why this phase has not yet been observed in molecular systems.

Acknowledgments

This work was done in collaboration with Massimiliano Chiappini and Marjolein Dijkstra from the University of Utrecht. Adam Edwards is thanked for useful discussions.

Chapter 6

Hierarchical self-assembly of polydisperse colloidal bananas a into vortex phase

ABSTRACT

Hierarchically self-assembled materials – structures with order at multiple length scales – are ubiquitous in nature and found at all length scales. Examples range from collagen structures in human bones to engineered photonic materials. These structures usually assemble from monodisperse microscopic building blocks that interact via complex directional interactions. In this chapter, we show that polydisperse colloidal bananas can, in fact, self-assemble into a complex hierarchical structure, called the vortex phase, only due to entropic interactions and polydispersity in the particle curvature. Using confocal microscopy, we uncover the formation mechanism of the vortex phase and characterise its exotic structure and dynamics at the single-particle level. These results open up new avenues towards rationally exploiting the often undesired polydispersity of colloidal building blocks for programming entropy-driven self-assembly of hierarchical materials.

6.1 Introduction

Self-assembly of microscopic building blocks is a powerful route for preparing materials with pre-designed structure and engineered properties [17, 25, 177–181]. Nature provides a fascinating range of self-assembled architectures offering insight into how structural organisation can emerge at different length scales [182–187]. In the biological world, for instance, TMV coat proteins self-organise into sophisticated capsids around viral RNA strands [185, 188]. In molecular systems, lipid molecules form a range of self-assembled structures such as cell membranes [189, 190]. At the colloidal scale, a rich variety of crystals with remarkable optical properties, such as opal and other gemstones, also assemble from a range of colloidal constituents [28, 34, 186, 191, 192]. The structural complexity of self-assembled materials is typically dictated by the type of interactions between the constituent building blocks and their shape [17, 179, 180]. Colloids are ideal systems to independently study the role of these key parameters, as their shape and interactions can be systematically tuned and rationally designed [17, 28, 193–195].

In colloidal systems interacting solely via excluded volume interactions, the shape of the particles can already lead to the assembly of complex structures [94, 95, 196, 197]. For instance, binary colloidal crystals [196] are obtained from spherical particles, complex dodecagonal quasicrystals are formed by tetrahedrons [94], and exotic banana-shaped liquid crystals are assembled from colloidal bananas [197]. Introducing complex interactions between the colloidal building blocks - on the top of their shape - leads to their assembly into hierarchical materials with structural order at multiple length scales [179, 198–200]. Examples include colloidal diamond structures assembled by patchy tetrahedrons functionalised with DNA strands [34] and superlattice structures formed by octapod-like particles functionalised with hydrophobic molecules [201]. The successful hierarchical self-assembly of these structures not only relies on the directionality of the particle interactions, but also on the uniformity in size of the constituent building blocks, as polydispersity typically disrupts ordering via the formation of defects [82, 202].

In this Chapter, however, we show that a colloidal suspension of polydisperse banana-shaped particles interacting only via simple excluded volume interactions [197] self-assembles into remarkably ordered concentric structures, which we term *colloidal vortices*. At high packing fractions, these structures form a hierarchical material, which we term the *vortex phase*. Using confocal microscopy, we uncover the formation mechanism of this tightly packed phase and characterise its exotic structure and dynamics at the single particle level.

6.2 Experimental methods

6.2.1 Size distributions of banana-shaped particles

In this work, we use two main populations of colloidal bananas (A and B) with a similar mean length L and diameter D , but a different mean radius of curvature R , and opening angle α . The corresponding radius of curvature, length and opening angle distributions are shown in Fig. 6.1, and the mean values and polydispersities are summarised in Table 6.1.

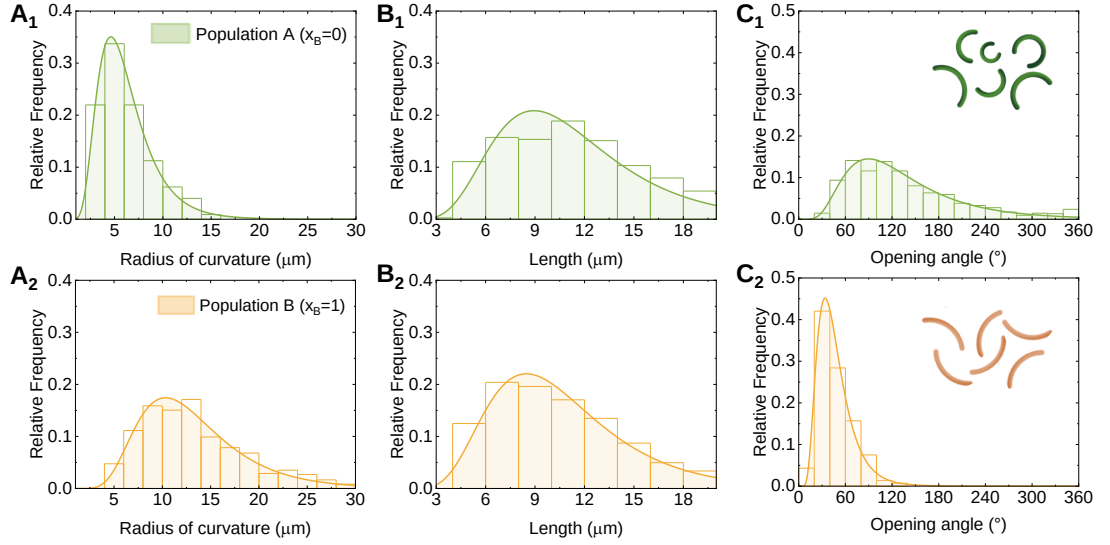


Figure 6.1: Histograms of the radius of curvature, length and opening angle of (A₁-C₁) bananas in population A and (A₂-C₂) bananas of population B.

Table 6.1: Mean length (L), diameter (D), radius of curvature (R), opening angle (α), and polydispersity (%) of the SU-8 banana-shaped particles in populations A and B. The polydispersity (%) is defined as $\sigma_i = \delta_i / \langle i \rangle$, where δ_i is the standard deviation of the mean value $\langle i \rangle$.

Population	L (μm)	D (μm)	R (μm)	α ($^\circ$)
Pop A	12.0 (40.7%)	0.85 (16.7%)	6.1 (44.4%)	140 (54.2%)
Pop B	11.7 (37.2%)	0.79 (18.4%)	12.9 (40.5%)	70 (48.0%)

6.2.2 Sample preparation and confocal imaging

Confocal microscopy images with a 16-bit pixel depth are acquired using a 12 kHz resonant scanner head (Thorlabs) and a 532 nm laser, coupled to an Olympus IX73 inverted microscope equipped with a 60 $\times$ (NA = 1.42) oil immersion objective (Olympus).

To study the assembly of polydisperse bananas into a vortex phase, we prepare thin samples of dense particle suspensions by filling home-made sample cells (see Section 2.4.2) with colloidal suspensions with an initial volume fraction of $\phi \approx 0.1$. Next, we let the colloidal bananas sediment towards the bottom of the sample cell, where they form a two dimensional monolayer

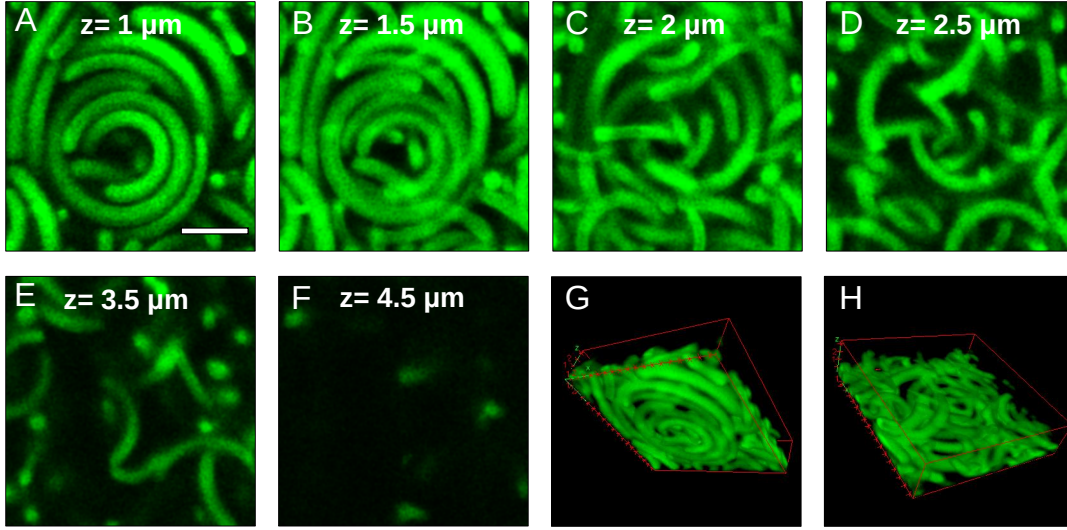


Figure 6.2: (A-F) Confocal microscopy images of the vortex phase at different imaging depths, z , with respect to the bottom of the sample cell. (G-H) 3D snapshots of the confocal images of the sediment at two different perspectives. Scale bars are $4 \mu\text{m}$ for (A-F).

with just few particles above it where the imaging is done (see Fig. 6.2). For the phase behaviour studies, a small tilt angle a small angle ($2 - 3^\circ$) is used during the equilibration of the sample to induce a packing fraction gradient in the same sample (see Section 2.4.2).

The gravitational length (L_g) of our colloidal bananas in water is $L_g \approx 0.22\mu\text{m}$. We have used $L=12.0 \mu\text{m}$ and $D=0.85\mu\text{m}$ as the average dimensions of the particles (see Table 6.1). Note that the value of L_g is an approximation as the bananas are very polydisperse in size.

6.2.3 Image analysis of confocal images

Position and orientation of the bananas

The positions and orientation of the colloidal bananas from confocal images are obtained using similar Mathematica routines to those described in Section 2.4.3. In particular, we determine the positions of the particles in two different manners: (i) using their centre of mass, which is measured from the pixel coordinates of the skeletons of each banana (see Fig. 6.3B), by using their centre of curvature, which is obtained from the coordinates of the centres of the fitting circles (see Fig. 6.3C). We characterise the orientation of the colloidal bananas, in two dimensions, using the polar vector, $\hat{\mathbf{p}}$, which is associated to the short axis of the bananas, as illustrated in Fig. 6.3D. Note that in two dimensions the orientation vector, which is related to the long axis of the bananas is related to the short axis by a $\pi/2$ rotation.

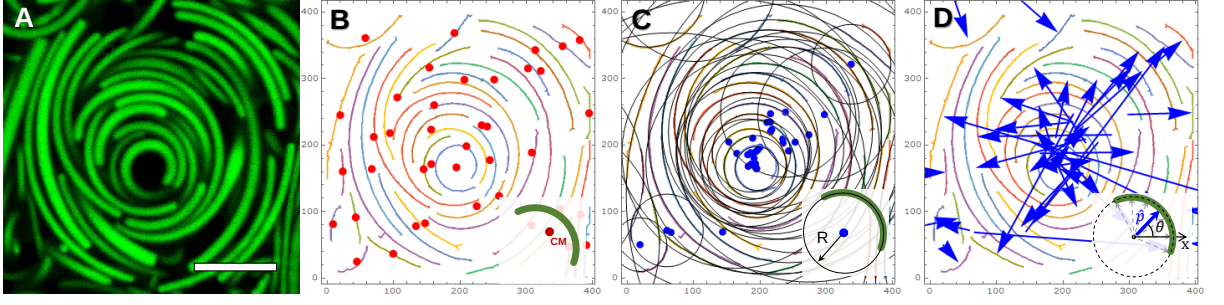


Figure 6.3: Image analysis steps to determine the position and orientation of the colloidal bananas from confocal images. (A) Original confocal image, segmented image (where the different colours represent different bananas) overlaid with the (B) centres of mass, (C) fitting circles and centres of curvature and (D) the polar orientation vectors of the colloidal bananas in a colloidal vortex. The scale bar is $5\ \mu\text{m}$.

Vortex identification and size

To identify the assembly of the bananas into vortices we use the centre of curvature coordinates of the particles, as they are very close together when bananas self-assemble into a vortex. This is shown in Fig. 6.4A₁ for a single vortex and Fig. 6.4A₂ for many vortices. Then, we apply the 'FindCluster' built-in cluster algorithm with the 'Agglomerate' method to these coordinates, in order to group them into different clusters (see Fig. 6.4B₁₋₂ where the different colours represent different clusters). Note that our cluster method is based on distance minimisation of the considered points. Next, we select the clusters with a number of constituent particles larger than 4, and consider them as vortices. From the identified vortices, we can measure a range of features, such as their centre of mass, which we calculate using the median of the centre of curvature coordinates of the constituent bananas, and the number of particles per vortex.

Finally, we determine the size of the vortices, R_V , by measuring the average distance between the centre of the vortex and the centre of mass of the bananas located at the outer edge of the vortices (see Fig. 6.4D₁₋₂). Note that when samples show mixtures of liquid crystalline ordering and vortices, we use a more sophisticated cluster algorithm which also considers the orientation of the particles: we distinguish nematic domains from vortices as nematic domains show a global nematic director [197] and vortices do not.

Dynamics of the colloidal vortices

To characterise the dynamics of the vortices we track the centre of mass of the vortices over time using confocal microscopy (see Figure 6.5A). To this end, we use a custom-written image

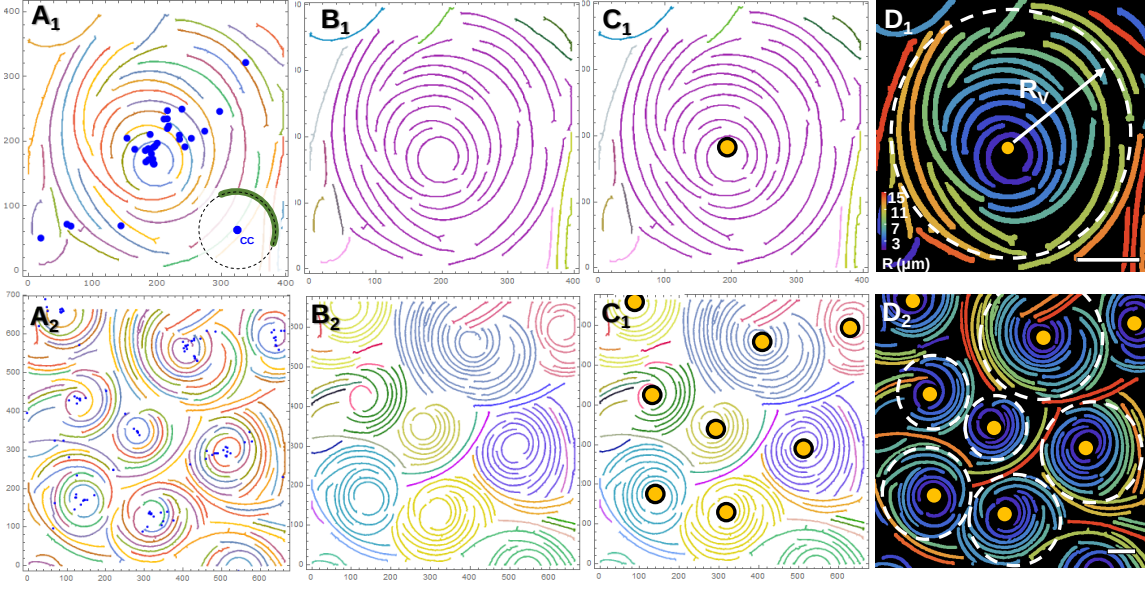


Figure 6.4: Step-wise image analysis procedure to detect the assembly of bananas into vortices. (A_{1-2}) Skeletons of the bananas and their centre of curvature. (B_{1-2}) Bananas coloured according to their cluster index. (C_{1-2}) Bananas coloured according to their cluster index and overlaid with the centres of mass of the vortices (yellow dots). (D_{1-2}) Bananas coloured according to their curvature. The radius of the vortices is indicated as R_V . Scale bars are $5 \mu\text{m}$.

analysis routine in Mathematica based on the Crocker and Grier algorithm [203]. From the vortex trajectories (see Figure 6.5B) we calculate their mean square displacement (MSD), and then extract approximate coefficients of diffusion [21]. To qualitatively characterise the dynamics of single bananas in a vortex, we track their centres of mass and polar orientations over time. We typically record time series of the vortices for 2 hours with an acquisition rate of 1 frame every 30 seconds.

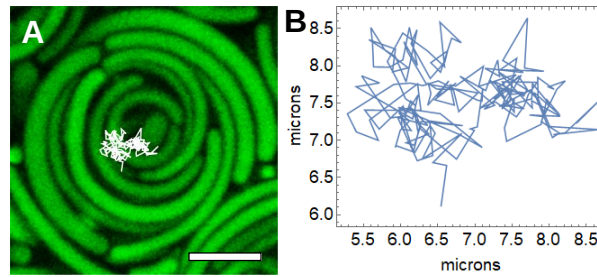


Figure 6.5: (A) Snapshot of colloidal vortex overlaid with the trajectory of its centre of mass over the course of 1.7 hours. (B) Trajectory of the centre of mass of the vortex. The scale bar is $5 \mu\text{m}$.

Packing fraction

The packing fraction, ϕ of the samples is calculated from binarised images as $\phi = N_b/N$, where N_b is the number of bright pixels corresponding to the colloidal bananas and N is the total number of pixels in the field of view.

6.3 Results and discussion

6.3.1 Vortex phase from polydisperse bananas

In Figure 6.6 we present confocal microscopy images of polydisperse SU-8 colloidal bananas in water [197] with a radius of curvature R , length L and opening angle α (see schematic in Fig. 6.6A) at low and high packing fractions ϕ . These images are taken close to the bottom wall of the sample container, where the particles have sedimented into monolayer with only few particles above it (see Fig. 6.2). Whilst at low ϕ the bananas form an isotropic phase (see Fig. 6.6B), at high ϕ bananas self-assemble into a vortex phase (see Fig. 6.6C). This phase

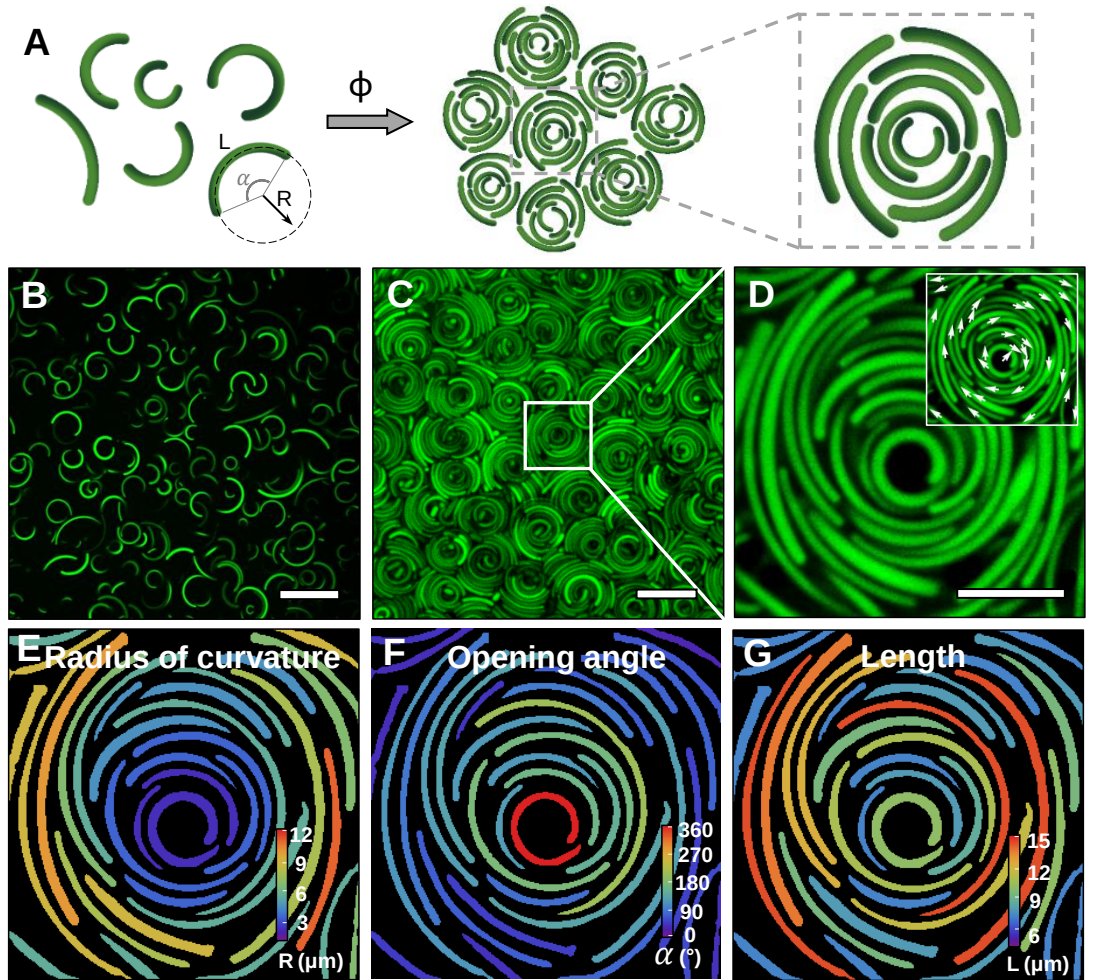


Figure 6.6: Colloidal vortices from polydisperse banana-shaped particles. (A) Schematic showing the formation of colloidal vortices from polydisperse banana-shaped particles with a radius of curvature R , length L , opening angle α and packing fraction ϕ . Confocal microscopy images of (B) a dilute sample ($\phi=0.05$) and (C) a concentrated sample of polydisperse bananas ($\phi=0.70$) showing the hierarchical assembly of colloidal vortices. (D) Zoom of a single colloidal vortex. The inset shows the orientational field (white arrows) of the long axes of the bananas. (E-G) Image of a colloidal vortex where the bananas are coloured according to their (E) radius of curvature (F) opening angle and (G) length as indicated in the legend bars in each panel. Scale bars are 10 μm for (B,C) and 5 μm for (D).

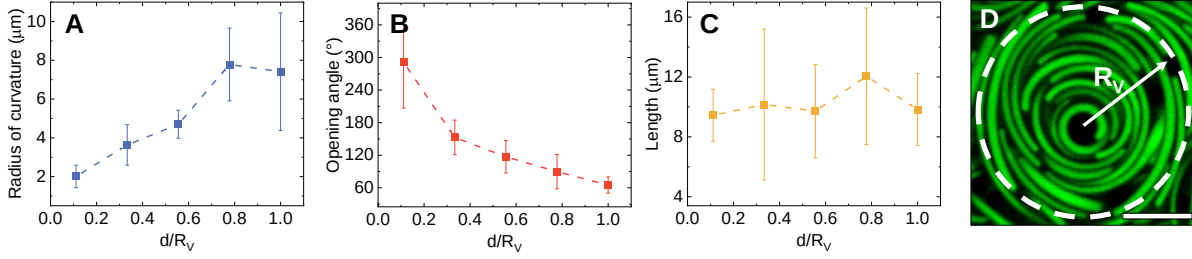


Figure 6.7: Relation between the (A) radius of curvature, (B) opening angle and (C) length of the colloidal bananas and their radial position in a vortex. (D) Confocal microscopy image of a single vortex, where its size R_V is indicated by the white arrow. The scale bar is 5 μm .

has a quasi two-dimensional nature and a two-level hierarchical structure where the individual bananas first self-organise into colloidal vortices (Fig. 6.6D), which then further assemble into a colloidal vortex phase (Fig. 6.6C). Note that our colloidal vortex phase shows a structural resemblance to vortex matter seen in liquid crystals [204, 205] and magnetic materials [206, 207] (see the vortex-like orientational field formed by the long axes of the bananas in the inset of Fig. 1D), but it does not have rotational flow properties.

As seen in Fig. 6.6D, colloidal bananas within a vortex show concentric assembly where the radius of curvature of the particles increases with their radial position from the centre of the vortex. This is quantified in Fig. 6.7A and is also evident from Fig. 6.6E, where the particles are coloured according to their radius of curvature. A strong radial dependence is also observed in the opening angle (see Fig. 6.6F and Fig. 6.7B), as bananas with a high α tend to be located closer to the centre of the vortex, however, no substantial relation is found between the particle length and the radial position, as shown in Fig. 6.6G and Fig. 6.7C.

6.3.2 Role of curvature and opening angle

To unravel the effect of curvature and opening angle on the structural formation of the colloidal vortices and the vortex phase, we prepare mixtures of two populations of polydisperse bananas with similar average lengths ($L \approx 12 \mu\text{m}$) but significantly different curvatures and opening angles, as shown in the schematics in Fig. 6.8. Then, we systematically change the compositions of the mixtures in order to carefully tune their distributions of R and α . Population *A* has a mean radius of curvature of $R_A = 6.1 \mu\text{m}$ with a mean opening angle of $\alpha_A = 140^\circ$ and population *B* has $R_B = 12.9 \mu\text{m}$ with $\alpha_B = 70^\circ$ (see the distributions in Fig. 6.8F, G and Section 6.2.1). Note that the polydispersities in curvature, opening angle and length are, respectively, $\sigma_R \approx 40\%$,

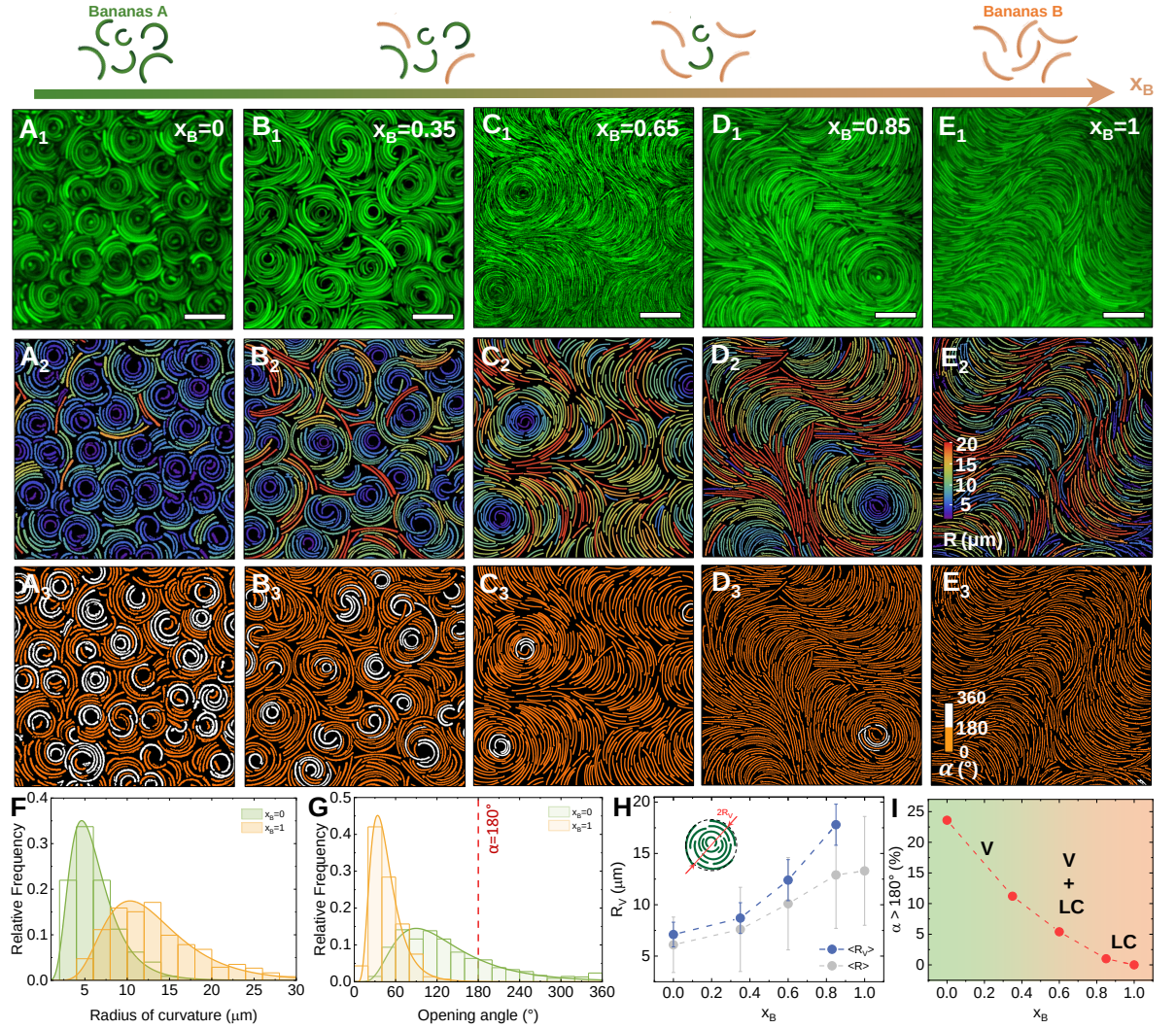


Figure 6.8: Role of curvature and opening angle in the formation of vortex phases. (A₁-E₁) Confocal microscopy images of mixtures of polydisperse bananas at a packing fraction $\phi \approx 0.7$ with a number fraction $x_B = 0, 0.35, 0.65, 0.85$ and 1, respectively. (A₂-E₂) Bananas coloured according to their radius of curvature R . (A₃-E₃) Bananas coloured according to their opening angle α being larger (white) or smaller (orange) than 180° . (F) and (G) show the distributions of the radius of curvature and opening angle of the original populations. (H) Mean vortex radius R_V , mean R of all bananas and (I) percentage of bananas with $\alpha > 180^\circ$ as a function of the mixture number fraction x_B . Scale bars are $15 \mu\text{m}$.

$\sigma_\alpha \approx 50\%$ and $\sigma_L \approx 40\%$ for both populations. In Fig. 6.8A₁ to E₁ we show confocal images of mixtures at similar overall packing fractions of $\phi \approx 0.7$, but different compositions, expressed as the number fractions of bananas from population B, x_B . Notably, we observe that while vortex phases form at low x_B (Fig. 6.8A₁ and B₁), mixtures of vortices and liquid crystalline (LC) order form at intermediate x_B (Fig. 6.8C₁ and D₁) and only liquid crystalline structures, in this case the splay-bend nematic phase [197], form as x_B approaches unity (Fig. 6.8E₁).

We next address the role of the particle curvature on the structural formation of these phases by measuring the overall curvature distributions of the bananas in all the mixtures

and by characterising their local arrangement via colouring the bananas according to their curvature (see Fig. 6.8A₂-E₂). Firstly, we observe the characteristic assembly of the bananas into curvature sorted concentric structures in those samples with $x_B=0-0.85$ (see Fig. 6.8A₂ and D₂). Interestingly, we find that the size of the vortices, R_V , increases from $7.1\mu\text{m}$ to $17.2\mu\text{m}$ as x_B increases from 0 to 0.85, as shown in Fig. 6.8H (see Section 6.2.3 for details of R_V measurements). This is consistent with the fact that the fraction of bananas with large average radii of curvature (R_B), and hence those that are typically located at the outer part of the vortices delineating their size, also increases with x_B . Accordingly, we find that R_V is roughly proportional to the mean curvature of all the bananas in the mixture, R , especially at low x_B (see Fig. 6.8H). However, the discrepancy between R_V and R increases at higher x_B as R_V seems to be highly sensitive to the fraction of particles with large radius of curvature. Remarkably, the size polydispersity of the vortices ($\sim 15\%$) is approximately 60% lower than that of the individual bananas ($\sim 40\%$), which is inherent to the single vortices being able to accommodate multiple particle curvatures. Similar size polydispersity reductions have been seen in other polydisperse systems as a result of self-assembly processes, see e.g. [208, 209]. We also note that high x_B (see Fig. 6.8D₂ and E₂), where the bananas mostly self-assemble into a splay-bend nematic phase [197], the particles with larger radius of curvature tend to be located in the inflexion point between neighbouring layers of the LC phase.

While polydispersity in the radii of curvature is clearly at the heart of the assembly of the vortices and their size, it does not fully explain the transition between the vortex and the liquid crystalline phase at increasing x_B . To this end, we consider the role of the opening angle in this transition by measuring the opening angle distributions of the bananas at all x_B , and characterising the fraction of bananas with high opening angles, which we consider to be $\alpha > 180^\circ$, i.e. of bananas taking up more than half of a full circle. Next, we produce binarised images according to high or low α , as shown in Fig. 6.8A₃ to E₃. From these images we observe that bananas with high α are predominantly found at the centre of each vortex, and crucially, that no vortices are formed around bananas with $\alpha < 180^\circ$. This clearly suggests that the presence of bananas with high opening angles is key for the formation of the vortices. We measure the percentage of bananas with high α , at all compositions (see Fig. 6.8I), and find that it decreases from 25% to 0% as x_B approaches unity. When this percentage is smaller than 10%, the system transitions from a vortex phase to a mixture of vortices and LC ordering.

Combining our results on the role of curvature and opening angle, we conclude that vortex phases form when there is a large range of radius of curvatures with a polydispersity of $\sim 40\%$ –allowing for the radial concentric ordering according to R – and a minimum of 10% of bananas with high opening angles and small radius of curvature –which act as the nuclei of the vortices. Note that at high x_B , i.e. in the absence of bananas with high opening angle but still with a large curvature polydispersity, the system does not longer find the most efficient packing by forming vortices, which can be also seen as $+1$ defects [210], but via the formation of $\pm 1/2$ defects in a liquid crystalline environment, as shown in Fig. A.14 in the Appendix.

6.3.3 Formation of the vortex phase and phase behaviour of polydisperse bananas

Next, we follow the formation dynamics of the colloidal vortices in real time using confocal microscopy. We prepare samples of bananas at a composition of $x_B=0.35$ (where the vortex phase forms) that sediment towards the bottom of the sample cell, forming a quasi-2D monolayer (see Fig. 6.2, which we image over time as shown in Fig. 6.9A and B. The formation of the colloidal vortices is a complex and dynamic process where bananas with different curvatures constantly try to form different concentric configurations in order to optimise their packing [87, 88, 211]

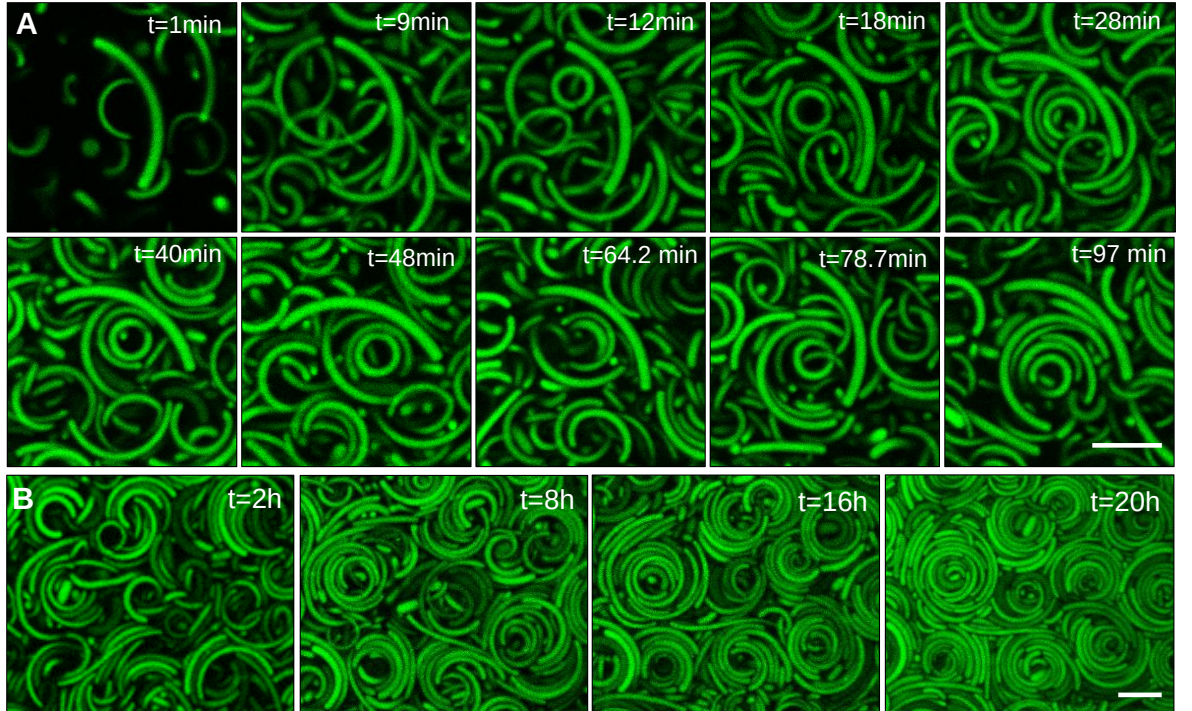


Figure 6.9: Formation of colloidal vortices and vortex phase. Confocal images of (A) the formation of a single colloidal vortex and (B) the hierarchical self-assembly of vortices into the vortex phase at different times, t , after the sample preparation at $x_B=0.35$. Scale bars are (A,B) 10 μm .

as the particle concentration increases with time (see Fig. 6.9A). The out-of-plane motion of the bananas is crucial for allowing the particles to reconfigure and find the right curvature that match the one of the already formed vortex (see typical L_g values in the section 6.2.2). As the packing fraction increases, new vortices continue to form and simultaneously self-assemble into the vortex phase (see Fig. 6.9B). We observe that the typical time scale associated with the formation of single vortices is on the order of few hours, whereas their hierarchical self-assembly into a vortex phase takes place over tens of hours, clearly showing the two-step hierarchical nature of the formation of a vortex phase.

To systematically study the phase behaviour of the colloidal vortices as a function of the packing fraction ϕ , we prepare concentrated samples at a fixed composition of $x_B=0.35$ and equilibrate them using a small tilt angle to induce a gradient in ϕ and hence access multiple packing fractions using a single sample. In Fig. 6.10C, we show confocal microscopy images of the system at different ϕ , where the bananas are coloured according to their curvature. While

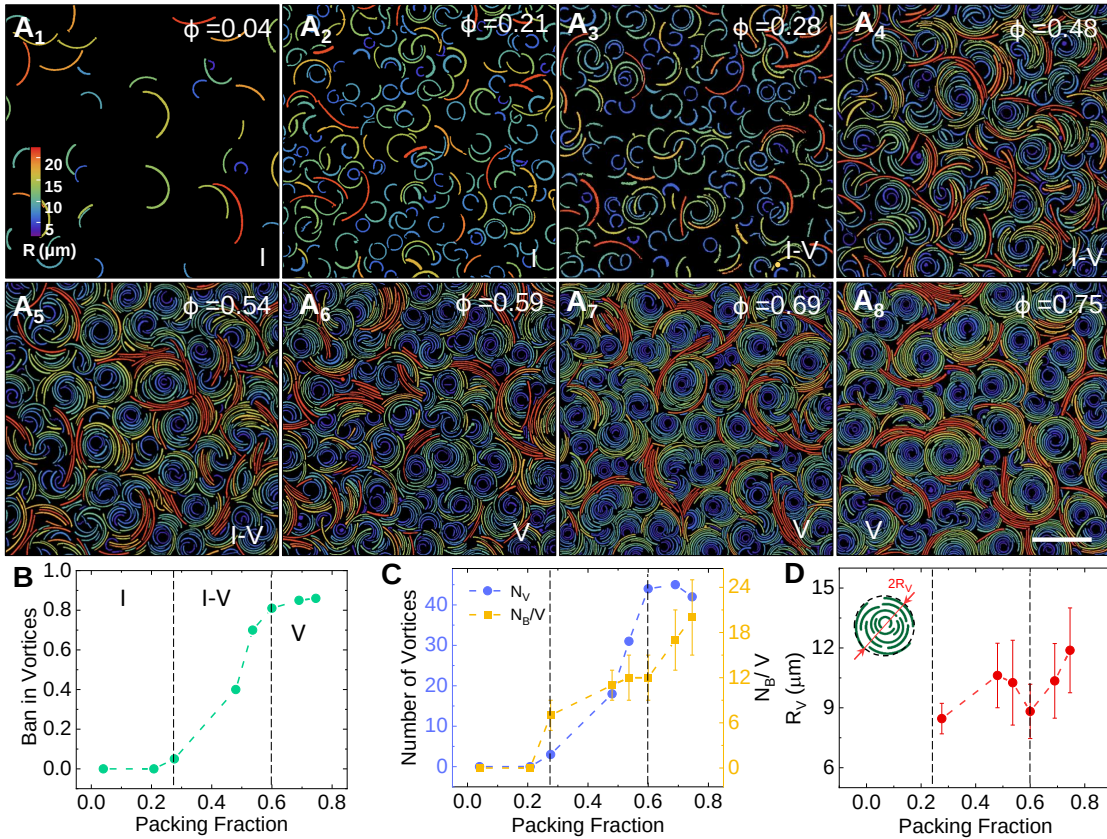


Figure 6.10: Phase behaviour of polydisperse colloidal bananas. (A) Confocal images coloured according to curvature at packing fractions ranging from $\phi=0.28$ -0.75. (B) Fraction of bananas in vortices as function of ϕ . (C) Number of vortices, N_v and number of bananas per vortex, N_B/V as function of ϕ . (D) Average inner and outer radius of curvature of the vortices as function of ϕ . Scale bars are 20 μm .

the bananas show isotropic ordering (I) at low packing fractions (see Fig. 6.9A₁₋₂), above $\phi=0.28$ they start to locally self-assemble into colloidal vortices exhibiting isotropic-vortex coexistence ($I - V$), as shown in Fig. 6.9A₃₋₅. Around $\phi=0.59$, the majority of the bananas self-assemble into vortices, forming the vortex phase (V) (see Fig. 6.9A₆₋₈). This is corroborated by the increase of the fraction of bananas in vortices as a function of ϕ (see Fig. 6.10B), clearly showing the two main phases observed in this system. To further characterise these, we quantify the number of vortices, N_V , number of bananas per vortex N_B/V and their radii, R_V , as a function of the packing fraction, as shown in Fig. 6.10B,C and D (see analysis in Section 6.2.3). In the coexistence region ($\phi \approx 0.28-0.59$), the number of vortices increases proportionally with ϕ , while the number of bananas per vortex plateaus (see Fig. 6.10C), which suggests that bananas self-assemble into vortices but still have space to reconfigure. We also measure an initial increase of the size of the vortices with ϕ , followed by a slight decrease, as the vortices are simply being compressed by the increasing density of vortices in the sample. In the vortex phase ($\phi > 0.59$), most of the bananas are forming vortices and these just grow in size with increasing ϕ . This is shown by the roughly constant number of vortices ($N_V \approx 40$) and the increase of number of bananas per vortex up to $N_B/V \approx 20$ (see Fig. 6.10C) and vortex size up to $12 \mu\text{m}$ (see Fig. 6.10D) as ϕ reaches 0.75.

6.3.4 Structure and dynamics of the vortex phase

Finally, we characterise the structure and dynamics of the vortex phase at the vortex and single-particle level as shown in Fig. 6.11. Firstly, we demonstrate that vortex phases form over large length scales as shown in the large field of view confocal microscopy image in Fig. 6.11A. From

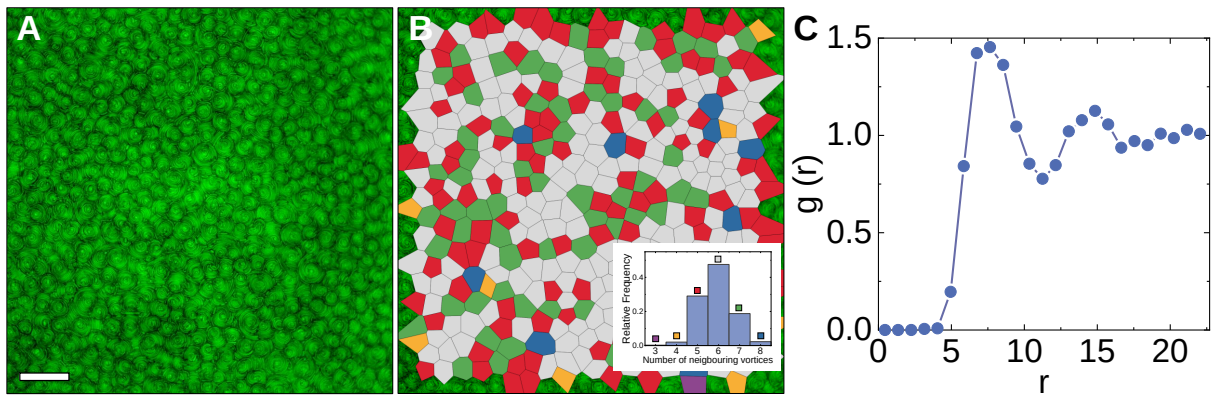


Figure 6.11: Structural characterisation of the colloidal vortex phase. (A) Large field of view confocal microscopy image of the vortex phase and (B) its corresponding voronoi plot where cells are coloured according to the number of neighbouring particles. Inset of (B) shows the histogram of the number of neighbouring vortices in the voronoid construction. (C) Pair distribution function $g(r)$ of the vortex phase. The scale bar is $25 \mu\text{m}$

this image, we calculate the voronoi construction (see Fig. 6.11B), and the radial distribution function, $g(r)$ (see Fig. 6.11C) of the vortex phase using the centre of mass coordinates of the constituent vortices. The appearance of the $g(r)$ is characteristic of that of a liquid-like structure with short-range correlations only, which is consistent with the absence of significant long-range ordering of the vortices shown by voronoi plot and a broad distribution of nearest neighbours (see inset Fig. 6.11B). We also note that the liquid-like structure of the vortex phase is consistent with the fact that the vortices are polydisperse in size ($\sim 15\%$) [212].

Lastly, we characterise the dynamics of the vortex phase by taking snapshots of its structure over time. Fig. 6.12A shows an average image of the vortex phase over 60 minutes and qualitatively reveals that the vortices are not very mobile in the vortex phase as their structure can still be fairly well resolved after a relatively long time. This is quantified by tracking the centre of mass of a single vortex in the vortex phase (see Fig. 6.12B₁ and Section 6.2.3), from which we extract an approximate diffusion coefficient of $D_V \sim 0.3 \text{ nm}^2/\text{s}$. The small D_V value is not surprising as vortices are large and complex ‘compound particles’ moving in a highly packed environment ($\phi \sim 0.7$). Also, we note that the measured mean square displacement (see Fig. 6.12C) appears sub-diffusive at larger lag times, which could suggest a glassy nature of the vortex phase [77]. Interestingly, we find that while individual bananas are radially confined in the vortices, these are actually mobile in the azimuthal direction as inferred from the large span of coloured the arrows representing the orientation of the short axis of the bananas (see Fig. 6.12B₂). In other words, this qualitatively confirms that the assembly of the colloidal

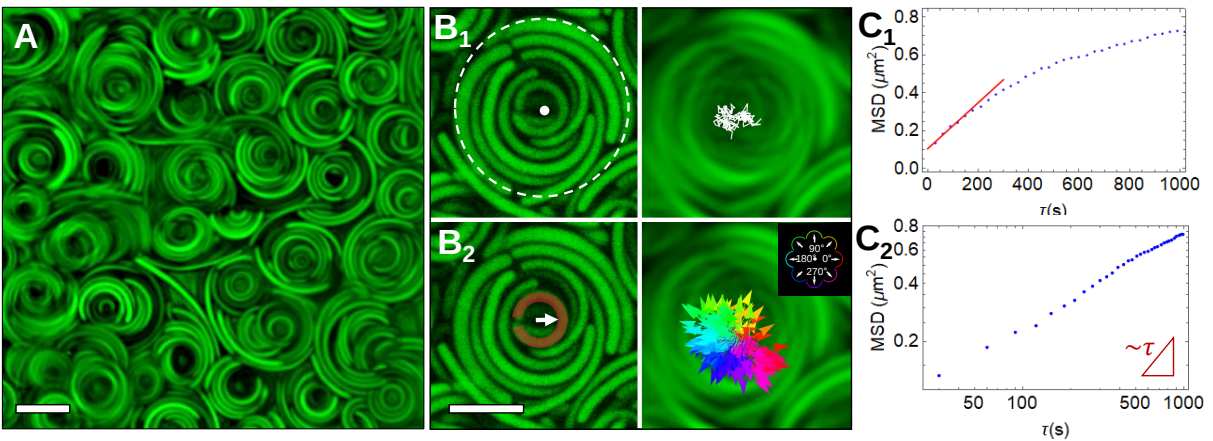


Figure 6.12: Dynamical characterisation of the colloidal vortex phase. (A) Time average of confocal snapshots taken over 60 minutes. (B₁) Tracking of the centre of mass of a single vortex in the vortex phase and (B₂) tracking of the short axis orientation (coloured arrows) of a single single banana in a vortex. (C₁) MSD plot as a function of the lag time τ , of the vortices with a linear fit up to 120 seconds. (C₂) Log-log of MSD plot shown in C₁. The slope of the red triangle is one. Scale bars are (A) 10 μm and (B) 5 μm .

bananas into vortices at high packing fractions is driven by entropy as the bananas seem to maximise their azimuthal degrees of freedom at the expense of their radial free volume [86,211].

6.4 Conclusions

In summary, we have shown that polydisperse colloidal bananas interacting only via simple excluded volume interactions can lead to the hierarchical self-assembly of banana particles into colloidal vortices which then further assemble into a vortex phase with liquid-like structure. We demonstrate that both the size and number of vortices can be controlled by tuning the geometrical features of the constituent colloidal bananas, such as its curvature and opening angle. These results provide a stimulating example as to how polydispersity can be actually crucial for generating ordering across multiple length scales. As such, with our results we open new avenues towards rationally exploiting the often undesired polydispersity of colloidal building blocks for programming entropy-driven self-assembly of novel functional materials with pre-designed structure. In addition, we foresee many opportunities for further studies including, for instance, the extension of the vortex phase into the third dimension, the effect of the particle size distributions on the structure of the phases and the nucleation of vortices using spherical particles. All of these studies will provide further insight into the self-assembly of complex structures at the colloidal scale.

Acknowledgments

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Chapter 7

Synthesis of rough colloidal SU-8 rods and bananas via nanoprecipitation

ABSTRACT

Surface roughness plays an important role in determining the mechanical properties, wettability and self-assembly in colloidal systems. In this chapter, we describe the development of a simple and fast method to produce rough colloidal SU-8 rods, bananas and spheres, via the nanoprecipitation of SU-8 in water. During this process, SU-8 nanospheres are absorbed onto the surface of the colloidal SU-8 particles and then cross-linked using UV-light. The size of the spherical asperities and the asperity density is controlled by the concentration of SU-8 used during the nanoprecipitation reaction. Fluorescent labelling of the rough SU-8 colloidal particles allows for their confocal imaging and demonstrates their stability at high packing fractions. With these newly developed rough particles, we provide a colloidal model system that allows for studies addressing the impact of surface roughness on materials composed of anisotropic particles.

7.1 Introduction

Controlling the surface roughness of colloidal particles is a powerful tool for designing materials with engineered rheological, wetting and self-assembly properties [213]. For instance, dense suspensions of rough colloidal spheres show shear thickening, i.e. a viscosity increase upon increasing shear rate, at lower shear rates than suspensions of colloidal spheres with a smooth surface [214, 215]. This mechanical effect is explained in terms of inter-particle frictional forces [215] and finds applications in shock-absorbing materials [216]. Surface roughness also plays an important role in the wetting behaviour of colloidal particles at liquid-liquid interfaces [217]. This is particularly important for Pickering emulsions, in which droplets of water-in-oil (w/o) or oil-in-water (o/w) are stabilised by particles adsorbed at the oil-water interface. Interestingly, it has been shown that using rough particles, as opposed to smooth ones, increases the stability of Pickering emulsions [218] and also allows to stabilise o/w and w/o emulsions without changing their chemical properties [217].

Another fascinating example of the impact of surface roughness at the colloidal scale is the directed self-assembly processes via depletion interactions [219]. The presence of surface asperities with a typical size larger than that of the depletant reduces the depletion attraction between particles [220] or parts of the particles [219], leading, for example, to the selective formation of clusters depending on the particle roughness [219]. To date, most of the studies addressing the relationship between microscopic surface roughness and macroscopic properties of soft matter systems have been performed with colloidal spheres [213, 221]. However, the impact of surface roughness on materials formed by anisotropic colloidal particles, and therefore the interplay between surface roughness and shape, remains unexplored due to the lack of rough anisotropic colloidal particles.

In this Chapter, we develop a simple, fast and scalable method to produce rough colloidal SU-8 rods and banana-shaped particles with tunable asperity size and asperity density. Using the nanoprecipitation of SU-8 – a photoresist consisting of an epoxy-based oligomer, a solvent, and a photoacid initiator – we coat the surface of colloidal SU-8 particles [27, 197] with SU-8 nanospheres. The resulting spherical asperities are subsequently cross-linked onto the SU-8 colloidal particles using UV-light exposure. We characterise the morphology of the resulting rough colloidal particles using scanning electron microscopy and show that they form stable

suspensions which can be imaged at the single-particle level with confocal microscopy. With our work, we provide a colloidal model system that can be used to address surface roughness related phenomena in materials formed by anisotropic colloidal particles.

7.2 Experimental methods

7.2.1 Synthesis of ‘bare’ colloidal SU-8 particles

The syntheses of colloidal SU-8 rods, spheres and bananas are described in [27] and [197], and Chapter 3 and 4. The key steps of both procedures are briefly recapped here. For the synthesis of the colloidal SU-8 rods, approximately 0.1g of SU-8 50 is injected into 110mL of glycerol, which is subsequently mixed under high-shear at 1500rpm for 10 min. The resulting long SU-8 rods are then exposed to sonication (VWR ultrasonic cleaner, 45 kHz, 80 W) for 3 hours to break them into smaller colloidal rods [27]. These rods are subsequently photo-crosslinked by exposing them to UV-light (365nm, Spectroline 14A/FB) for 30 min. Finally, to remove the glycerol, the colloidal SU-8 rods are washed by repeated centrifugation and redispersion cycles using water containing 0.5 wt% Pluronic F-108.

For the synthesis of colloidal SU-8 spheres and bananas, the long SU-8 rods obtained after the high-shear mixing are heated, instead of sonicated, in a pre-heated oven at 95°C for 30 min, which induces a shape deformation [197]. While colloidal SU-8 spheres are obtained when the rods are heated directly after their synthesis, the colloidal bananas are obtained when the rods are partially cross-linked with weak UV-light [197] during 45 minutes prior to the heating stage. After 30 min at 95°C, the resulting SU-8 particles are fully cross-linked with strong UV-light exposure for 30 min and cleaned in a similar fashion as described for the colloidal SU-8 rods.

7.2.2 Synthesis of SU-8 nanoparticles via nanoprecipitation

SU-8 nanopsheres are produced via the nanoprecipitation of SU-8 in water. In a typical synthesis, 100μL of a solution of SU-8 50 with concentrations ranging from 0.5-10 wt% of SU-8 in GBL is added to 5 mL of water. After the addition of the SU-8 solution, SU-8 nanoparticles are immediately formed and the resulting dispersion is subsequently hand-shaken for 4-6 seconds. Next, 1 mL of Pluronic F-108 5wt% in water is added to avoid coalescence of the formed spheres.

The resulting SU-8 nanoparticles are then exposed to UV-light for 30 minutes and kept in water containing 1 wt% Pluronic F-108. For the synthesis of fluorescent SU-8 nanospheres, Cy3 (the fluorescent dye) was simply mixed with the SU-8 50 at a mass ratio of 10 mg dye/g SU-8 50.

7.2.3 Synthesis of rough colloidal SU-8 particles

The synthesis of rough colloidal SU-8 particles is based on the adsorption of the nanoprecipitated SU-8 nanospheres onto larger SU-8 colloidal particles via physisorption. To synthesise rough particles, we follow the same protocol as described in section 7.2.2 but now the water phase contains colloidal SU-8 particles, i.e. rods, spheres or bananas. In a typical reaction, the SU-8 particles are dispersed in 5 mL of pure water at an approximate particle concentration of 0.02 v/v%. Note that prior to this, the surfactant, which is typically present in particle suspensions in water, is removed via centrifugation and redispersion cycles in pure water. Next, we add 100 μ L of a SU-8 solution with concentration ranging from 0.5-10wt% of SU-8 50 in GBL to the aqueous dispersion of colloidal SU-8 particles. After hand-shaking the mixture for 4-6 seconds, 1 mL of 5wt% Pluronic F-108 in water is added. The resulting dispersion is subsequently sonicated and vortexed for ten seconds. The sample is subsequently UV-cured for 30 min to cross-link the SU-8 spherical asperities onto the surface of the colloidal particles. Finally, the bulk nanoparticles that did not adsorb onto the SU-8 colloidal particles are removed by means of centrifugation and redispersion cycles in water containing 1wt% of Pluronic F-108.

7.2.4 Scanning electron microscopy and particle dimensions

The size distributions the colloidal SU-8 particles are determined from scanning electron microscopy (SEM) images by measuring the length and diameter of at least 400 particles the custom-written image analysis routines in Mathematica described in Section 2.4.3. The dimensions of the SU-8 asperities are determined by measuring the asperity diameter of at least 100 rough particles from SEM images using ImageJ. The polydispersity (%) of the particles is defined as $\sigma_i = \delta_i / \langle i \rangle$, where δ_i is the standard deviation and $\langle i \rangle$ the mean value.

7.2.5 Confocal imaging of dense samples of rough colloidal SU-8 particles

For the confocal imaging of dense suspensions of rough colloidal SU-8 particles, we fill rectangular VitroCom capillaries ($0.1\text{mm} \times 0.2\text{ mm} \times 5\text{ cm}$) with aqueous particle dispersions with an initial particle concentration of approximately $0.20\text{ v/v\%}$ and subsequently sealed them using epoxy glue. After filling the sample cells, the colloidal particles slowly sediment towards the bottom of the sample cell, where the imaging is performed. Confocal microscopy images with a 16-bit pixel depth were acquired using a 12 kHz resonant scanner head (Thorlabs) and a 532nm laser, coupled to an Olympus IX73 inverted microscope equipped with a $60\times$ ($\text{NA} = 1.42$) oil immersion objective (Olympus).

7.3 Results and discussion

In this work, we exploit the nanoprecipitation method to rapidly produce rough colloidal SU-8 particles (rods, spheres and bananas) via the adsorption of SU-8 spheres onto the surface of the larger SU-8 colloidal particles. As an example, we show SEM images of the resulting rough SU-8 rods in Figure 1. We will describe our findings using rough colloidal SU-8 rods, but the same methods are used to fabricate rough colloidal SU-8 bananas and spheres. Firstly, we will study the typical dimensions of the SU-8 nanospheres obtained via nanoprecipitation. Next, we will describe how nanoprecipitation is used to produce rough colloidal SU-8 particles with tunable asperity size and asperity density. Finally, we will present confocal images of dense suspensions of rough rods and bananas and discuss their potential as colloidal model systems of rough anisotropic particles.

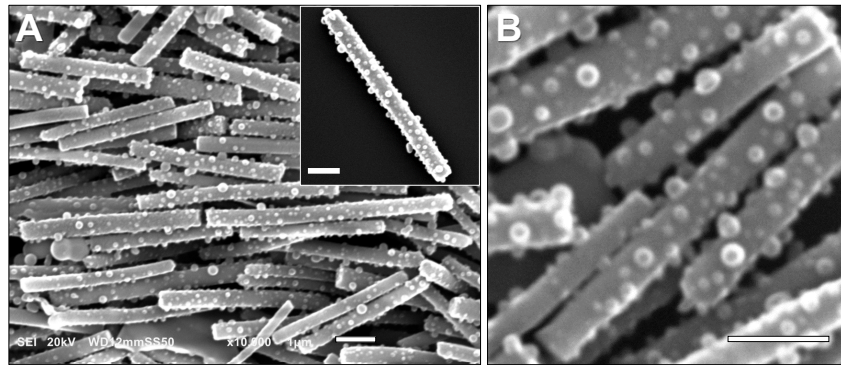


Figure 7.1: (A,B) Scanning electron microscopy images of the rough SU-8 colloidal rods obtain via the nanoprecipitation of SU-8 in water. Scale bars are $1\text{ }\mu\text{m}$.

7.3.1 Synthesis of SU-8 nanospheres via nanoprecipitation

Nanoprecipitation is a simple and scalable method used for producing polymeric nanoparticles in an extremely fast fashion [222–225]. This method requires three main ingredients, a polymer, an organic solvent and an aqueous solvent. The polymer is typically dissolved in the organic solvent, resulting in a polymer solution. It is essential that the organic and aqueous solvents are miscible with each other and that the polymer is insoluble in water. When these prerequisites are satisfied, the mixing of the polymer solution and the aqueous phase results in the instantaneous formation of polymer nanoparticles. This immediate process stems from the rapid mixing of the organic and aqueous solvent, which leads to the instantaneous precipitation of the water-insoluble polymer and hence the formation of polymer nanoparticles in water [226]. The resulting dispersion is typically stabilised by the presence of a surfactant in the aqueous phase.

In our nanoprecipitation experiments, SU-8 is the polymer and GBL is the organic solvent. In particular, we study the effect of the SU-8 concentration, $[\text{SU-8}]$, on the diameter of the resulting SU-8 nanospheres, as this determines the dimensions of the asperities of the resulting rough particles. Figure 7.2 shows SEM images of the SU-8 nanospheres obtained in water using SU-8 concentrations ranging from 0.5wt% to 10wt%. From these images, we measure

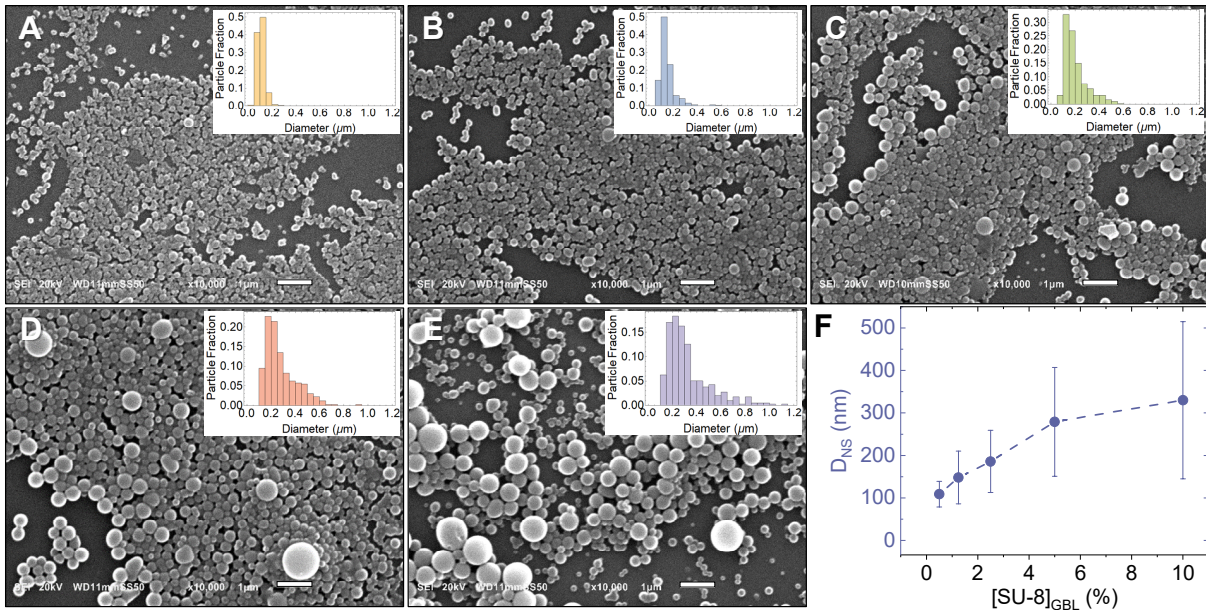


Figure 7.2: SEM images of the SU-8 nanospheres obtained at (A) 0.5, (B) 1.25, (C) 2.5, (D) 5 and (E) 10 wt% of SU-8 polymer solutions in GBL. Insets show the size distributions of each sample. (F) Mean diameter of the SU-8 nanospheres (D_{NS}) as a function of the concentration of SU-8 in GBL. Error bars are the standard deviation of the size distributions. Scale bars are 1 μm .

the diameter of the nanospheres and extract the size distributions and mean diameter (D_{NS}) at each SU-8 concentration, as shown in the insets of Figure 7.2A-E and the plot in Figure 7.2F, respectively. We observe that the mean diameter of the SU-8 nanospheres increases with increasing SU-8 concentration, from a mean diameter of $109nm$ for $[SU-8]=0.5\text{ wt}\%$ to $330nm$ for $[SU-8]=10wt\%$. Similar trends are reported for the nanoprecipitation in water of other hydrophobic polymers [227, 228]. We note that while the size distributions are relatively narrow at low SU-8 concentrations with typical polydispersity values around 25%, they become skewed towards larger particles diameters as the SU-8 concentration increases. We attribute this effect to the coalescence of multiple nanoparticles during the nanoprecipitation at high SU-8 concentrations [223, 227, 228].

7.3.2 Synthesis of rough colloidal SU-8 rods

Next, we synthesise rough colloidal SU-8 particles by exploiting the nanoprecipitation of SU-8 in water in the presence of colloidal SU-8 particles. As shown in the schematic in Figure 7.3A, the coating procedure consists of two key steps. In the first step, small SU-8 nanospheres are synthesised and physisorbed onto the surface of the larger colloidal rods dispersed in the aqueous

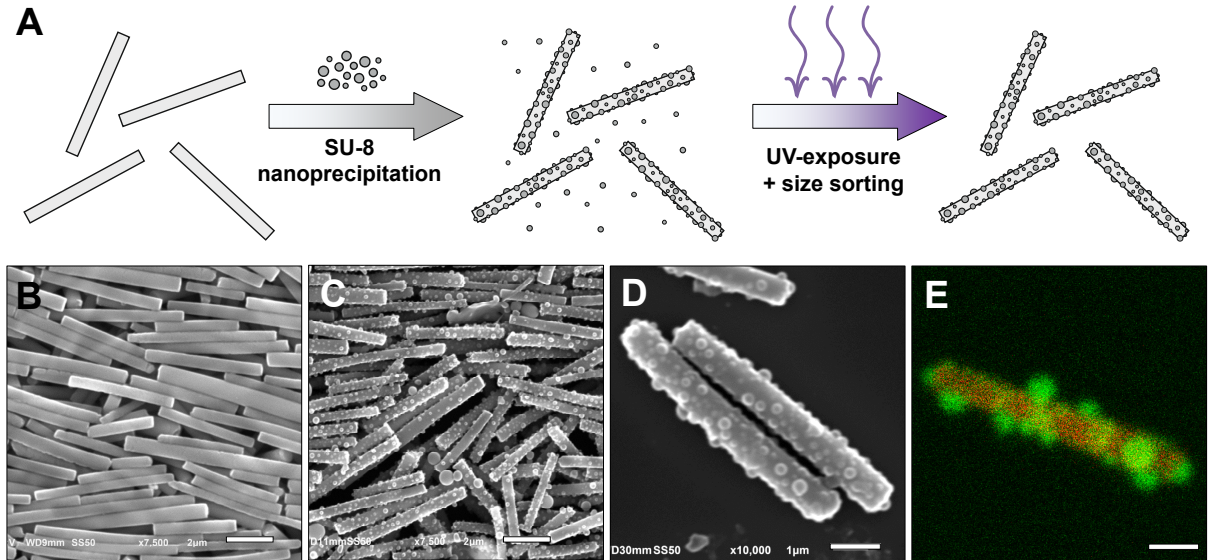


Figure 7.3: (A) Schematic showing the synthesis of rough colloidal SU-8 rods. In the first step, the SU-8 rods are coated with SU-8 nanoparticles formed during the nanoprecipitation of SU-8. In the second step, the adsorbed SU-8 nanospheres are cross-linked to the surface of the rods via UV-light exposure. Finally, the rough rods are separated from the unabsorbed SU-8 nanoparticles via centrifugation. SEM images of (B) the bare SU-8 rods, (C,D) rough rods. (E) Confocal microscopy image of a rough SU-8 rods with the body (red) and asperities (green) labelled with two fluorescent dyes. Scale bars are $2\text{ }\mu\text{m}$ for (B,C) and $1\text{ }\mu\text{m}$ for (D,E).

phase presumably via Van der Waals interactions. The resulting rough rods are stabilised using Pluronic F-108, a water soluble surfactant. In the second step, the adsorbed spherical asperities are cross-linked to the surface of the rod particles via UV-light exposure, as SU-8 is a photo-sensitive material. Finally, the remaining unabsorbed SU-8 nanospheres dispersed in water are removed via centrifugation and redispersion cycles. Figure 7.3B-D show SEM images of the rough rods obtained after the coating procedure. Figure 2E confirms the composite nature of the particles by labelling the spherical asperities and colloidal rods with different fluorescent dyes and imaging them with confocal microscopy.

We note that it is particularly important to ensure that the surface of the SU-8 rods is completely surfactant-free when performing the nanoprecipitation step. The presence of surfactant on the surface of the rods dramatically reduces the physisorption of the SU-8 nanospheres onto the surface of the rods. This is demonstrated in Figure 7.4A, where no asperities are visible on the surface of the rods as 0.5wt% of Pluronic was present during the nanoprecipitation step. We speculate that this is due to steric repulsions mediated by the surfactant molecules which adsorb onto the surface of the rods and/or nanoprecipitated particles [229]. Finally, we also address the role of the UV-light exposure, i.e. cross-linking, on the mechanical stability of the spherical asperities adsorbed to the surface of the rods. To this end, we subjected cross-linked and uncross-linked rough rods to sonication and vortex mixing for 20 minutes. The SEM images shown in Figure 7.4B and C reveal that a significant part of the adsorbed nanospheres of the uncross-linked rough rods is lost after sonication and vortex mixing (see Figure 7.4B). This suggests that, despite the fact we start with cross-linked SU-8 rods [27], these still have some

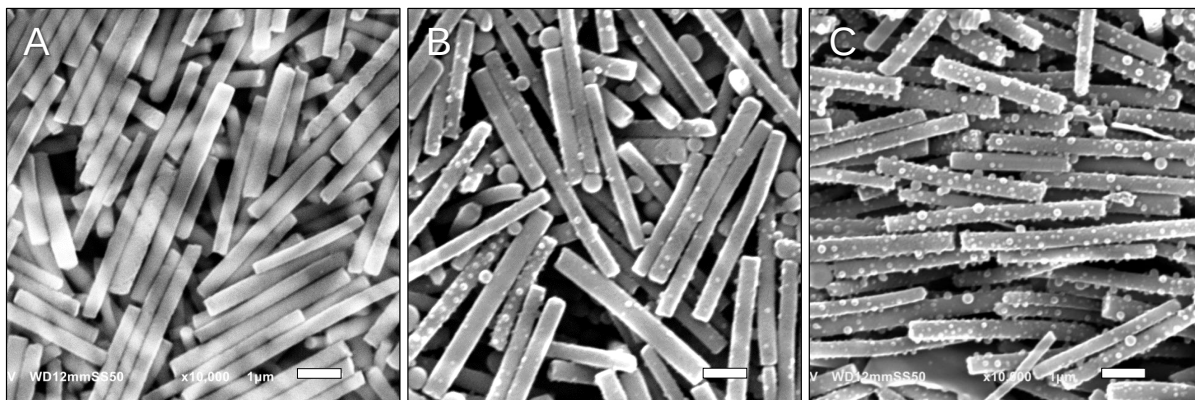


Figure 7.4: (A) Bare SU-8 rods obtained after the nanoprecipitation step in the presence of 0.5 wt% Pluronic in water. (B) Uncross-linked and (C) Cross-linked SU-8 rough obtained after 20 minutes of sonication and vortex mixing. For all samples, a concentration of SU-8 of 1.25wt% was used in the nanoprecipitation step. Scale bars are 1 μm .

residual epoxy groups on their surface, which enable their chemical bonding with the adsorbed SU-8 nanospheres upon UV-exposure. The cross-linking of the rough rods is therefore necessary to ensure proper linkage between the asperities and the rods (see Figure 7.4C), which is of crucial importance for applications where the particles are subjected to moderately large forces, such as in rheology experiments.

7.3.3 Tunability of the asperity size and asperity density

Next, we study the effect of the SU-8 concentration on the size of the asperities and asperity density on the rods. We start with an aqueous dispersion of colloidal rods with typical dimensions of $0.4\ \mu\text{m}$ in diameter and $6\ \mu\text{m}$ in length. To induce the nanoprecipitation of SU-8 nanospheres, we add a SU-8 solution with SU-8 concentrations ranging from 0.5 to 10wt% as previously reported in section 7.3.1 and shown in Figure 7.2. By analysing SEM images as the ones shown in the insets of Figure 7.5, we measure both the size and the number of spherical asperities per rod at each SU-8 concentration. As shown in Figure 7.5G, the average asperity diameter increases with increasing SU-8 concentration, which is consistent with Figure 7.2, though we note that it differs from the average diameter of the nanoprecipitated spheres (see the grey line), especially at high SU-8 concentrations. This disparity is presumably due to the fact that large nanoparticles are less likely to adsorb onto the surface of the rods.

We also characterise both the number density of asperities (ρ_A) and surface coverage (θ) of the rods. These two parameters are calculated as $\rho_A = N_A/A_{rod}$ and $\theta = \rho_A A_A$, where N_A is the number of asperities, A_{rod} is the average area of the cylindrical rods and A_A is the average cross-sectional area of the asperities. In our calculations, we use that $A_A = \pi(D_A/2)^2$. Note that we measure the size and number of asperities from a half of the rod surface using SEM images and assume that is the same for the other half when calculating ρ_A and θ . The plot shown in Figure 7.5H shows the evolution of the asperity number density and surface coverage with SU-8 concentration. Starting from bare rods, we observe that the asperity number density first increases from 4 to 20 asperities/ μm^2 for $0.5 < [\text{SU-8}] < 1.25\text{wt}\%$ and then gradually decreases to 5 asperities/ μm^2 upon increasing concentration of SU-8. On the other hand, the surface coverage increases from 2% to 20% between SU-8 concentrations of 0.5 and 1.25wt% and above 1.25wt% the surface coverage remains roughly constant as the average asperity diameter increases with increasing [SU-8]. From both the asperity number density measurements and the SEM images

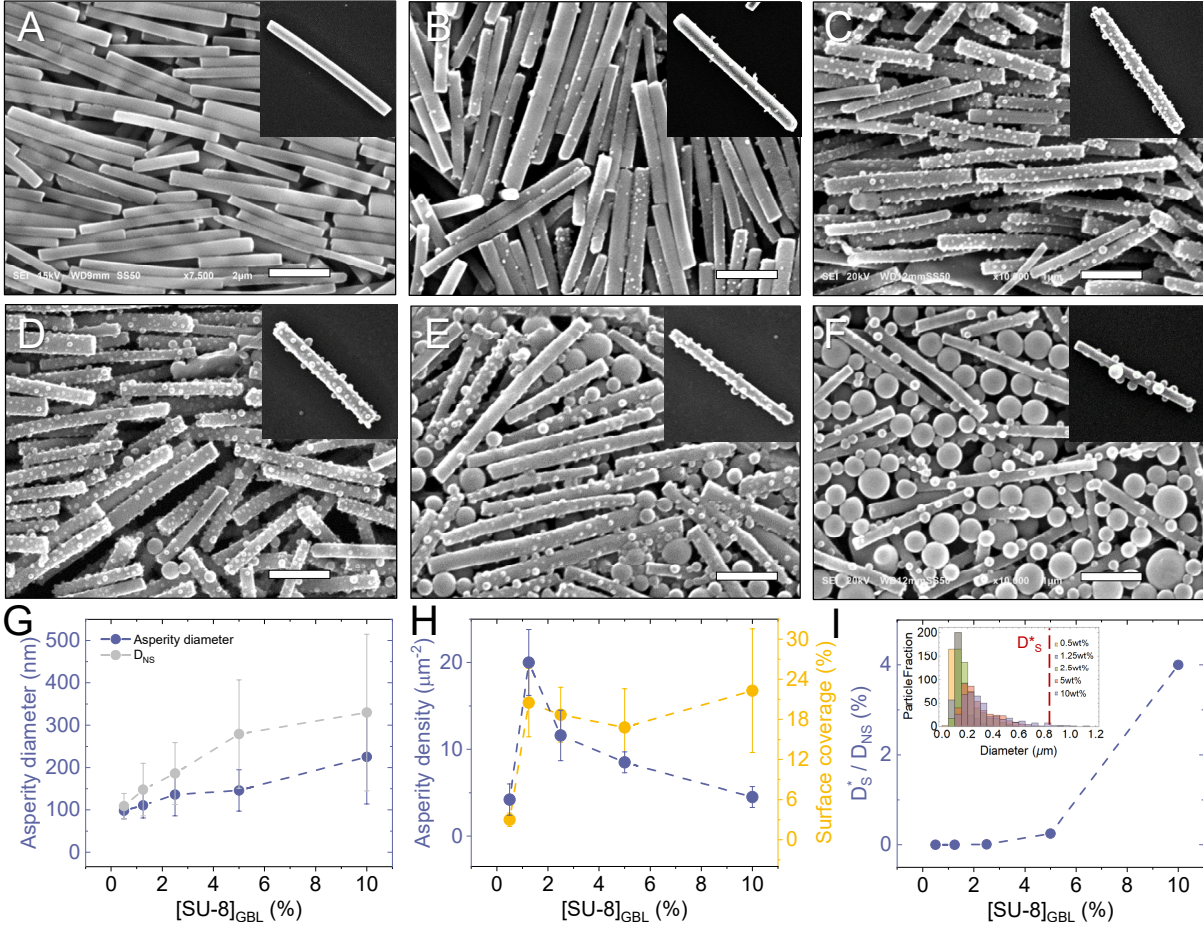


Figure 7.5: SEM images of rough SU-8 colloidal rods obtained at (A) 0, (B) 0.5, (C) 1.25, (D) 2.5, (E) 5 and (F) 10 wt% of SU-8 in GBL. Insets show SEM images of single rough rods. (G) Mean diameter of the asperities (blue) and SU-8 nanospheres (grey) as a function of [SU-8]. (H) Asperity number density (blue) and surface coverage (yellow) on the rods as a function of [SU-8]. (I) Percentage of SU-8 nanospheres with a diameter larger than $D_S^* = 80\text{nm}$ as a function of [SU-8]. Error bars are the standard deviations. Scale bars are 1 μm .

shown in Figure 7.5A-F, we can infer that the most dense and homogeneous coating is obtained in the SU-8 concentration range of 1.25-2.5wt%.

Finally, we discuss the separation of the rough rods from the unadsorbed SU-8 nanospheres via centrifugation. In general, it is easy to separate small spheres from larger rod-like particles via centrifugation because they sediment at different velocities [230]. However, as the diameter of the nanoprecipitated spheres increases, their separation from the rods becomes more challenging. By equating the sedimentation velocities of rods [231] and spheres, we find that D_S^* , the diameter of a sphere sedimenting at the same speed as a rod with diameter D_{rod} and length L_{rod} , is given by $D_S^* = \sqrt{\frac{3}{2}} D_{rod} \left[\ln \left(\frac{L_{rod}}{D_{rod}} \right) + c \right]^{1/2}$. Note that c accounts for end-effects in the sedimentation of cylindrical rods with aspect ratio between 2 and 30 [232]. In our system, we typically use rods with average dimensions of $L_{rod} = 6\mu\text{m}$ and $D_{rod} = 0.4\mu\text{m}$, which corresponds to $c=0.312$,

a small value compared to that of the logarithmic term, and a $D_S^* = 800nm$. This suggests that unadsorbed SU-8 nanospheres with $D_{NS} > 800nm$ are not easily separated from the rough SU-8 rods. This is indeed confirmed by the SEM images shown in Figure 7.5E and F, where not only rough rods but also SU-8 nanospheres with $D_{NS} > 800nm$ are observed. On the other hand, Figure 7.5B-D show samples of mainly rough rods, consistent with the fact that the diameters of the nanoprecipitated SU-8 nanospheres for $[SU-8] < 5wt\%$ were smaller than $800nm$ (see Figure 7.2). In Figure 7.5I we quantify this effect by showing the percentage of nanoparticles with a diameter larger than $800nm$ obtained during the nanoprecipitation of SU-8 nanospheres (see Figure 7.2). Indeed, only for SU-8 concentrations larger than $5wt\%$ there is a significant fraction of particles with a diameter larger than $800nm$, which makes their separation from the rough rods via centrifugation very cumbersome. However, an easier separation of the rough rods and the unadsorbed nanospheres obtained for $[SU-8] > 5wt\%$ should be facilitated by using rods with a larger diameter [27], or by adding salt or polymers [233].

7.3.4 Beyond colloidal rods: rough colloidal SU-8 bananas and spheres

We can directly apply the coating method described for the colloidal SU-8 rods (see Section 7.3.2), to the recently developed library of SU-8 colloidal particles, including colloidal bananas and spheres [197]. This is indeed confirmed by the SEM images shown in Figure 7.6, where both

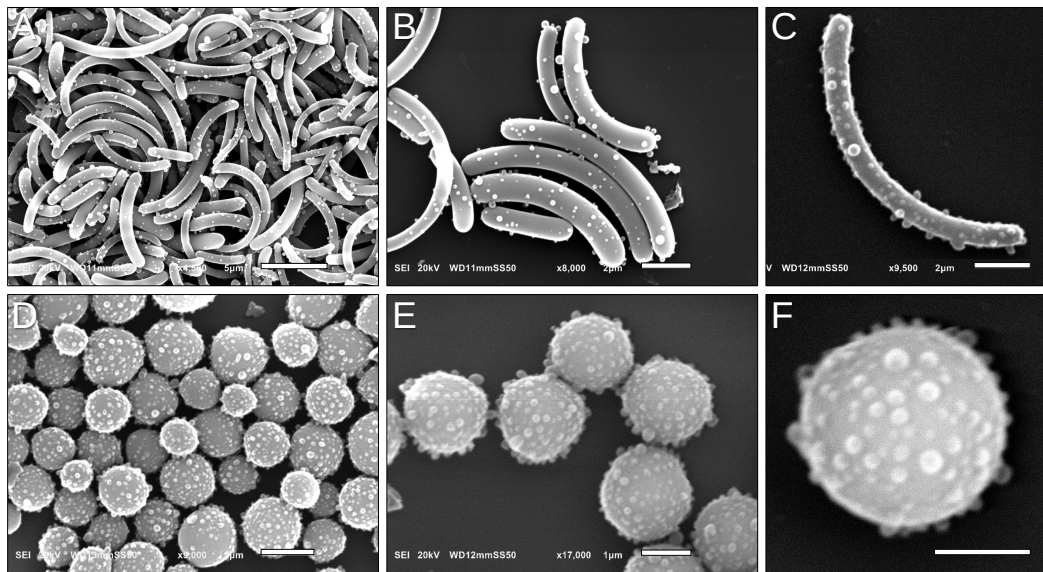


Figure 7.6: SEM images of rough colloidal SU-8 bananas and spheres obtained using $2.5wt\%$ [SU8]. Scale bars are $5\mu m$ for (A), $2\mu m$ for (B-D) and $1\mu m$ for (E,F)

rough colloidal SU-8 bananas and spheres are obtained via the nanoprecipitation of SU-8 in water. The rough bananas are particularly interesting as they provide a colloidal model system where the interplay between surface roughness phenomena and shape anisotropy can be studied as a function of the particle curvature.

7.3.5 Confocal microscopy imaging of concentrated samples of rough colloidal SU-8 particles

To enable the imaging of suspensions of rough colloidal SU-8 particles using confocal microscopy, we label both the asperities and the body of the colloidal SU-8 particles with a fluorescent dye. In Figure 7.7, we show confocal microscopy images of dense samples of rough and fluorescent SU-8 rods and bananas, where nematic ordering is observed for the rough rods (see Figure 7.7A) and an isotropic structure is observed for the rough bananas (see Figure 7.7B). The fact that they show similar phase behaviour as that of the corresponding to smooth particles (see Chapter 4 and 5) [27, 197] illustrates the stability of our newly developed rough colloidal SU-8 particles. Also, it facilitates further studies to address the impact of surface roughness on both the structure and timescales involved in the formation of orientally ordered phases of rough particles, such as the formation of nematic glasses [234, 235].

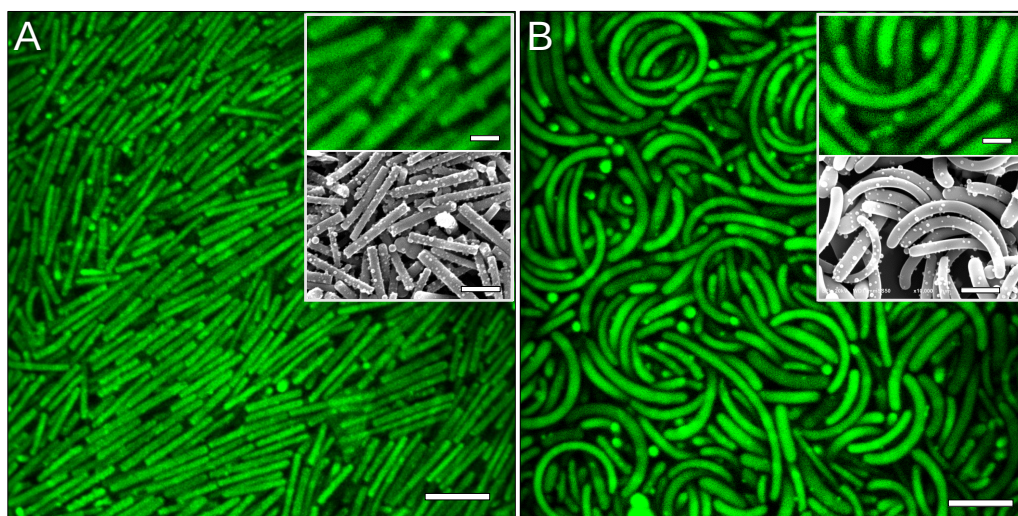


Figure 7.7: Confocal microscopy images of (A) a nematic phase of rough colloidal SU-8 rods and (B) an dense isotropic phase of rough bananas. The insets a show zoom of the confocal image and SEM images of the corresponding particles, where their surface roughness can be clearly observed. Scale bars are 5 μm for the main panels and 1 μm for the insets.

7.4 Conclusions

In summary, we have successfully developed a method for the rapid fabrication of rough anisotropic colloidal SU-8 particles, including rough colloidal rods and bananas, with tuneable asperity size and asperity density. The ease of synthesis combined with the stability and tunability of the colloidal SU-8 system [27, 197] creates a range of unique possibilities to address surface roughness related phenomena in colloidal systems of anisotropic particles. These features are particularly interesting for exploring the role of surface roughness in the rheological properties of liquid crystalline materials, which already show substantially different behaviour than spherical particles due to their characteristic flow-alignment [236]. Also, the characterisation of the structure and dynamics of these ‘rough’ liquid crystalline phases, might lead to a deeper understanding of the formation of nematic glasses [234, 235]. Moreover, direct imaging of suspensions of fluorescently labelled rough particles under shear could be used to elucidate the role of inter-particle friction during shear thickening, which for rods, is observed at much lower volume fractions than for spheres [237], and is associated with complex fluctuations in orientational order [238]. Controlling the surface roughness of the colloidal SU-8 rods could be also used to study the effect of roughness on the depletion-driven formation of nematic tactoids [149] and on their performance as foam-stabilisers [110], where anisotropic particles have already shown outstanding stability efficiencies [110, 239]. Finally, the rough colloidal bananas promise an even richer behaviour as they will allow addressing the effect of particle curvature on the rheological, wetting or self-assembly properties of rough anisotropic particles.

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Appendix

A1. Effect of sonication parameters in the synthesis of colloidal SU-8 rods

We quantify the effect of the sonication power and frequency of the ultrasonic bath on the efficiency of the sonication-induced breakage of the SU-8 rods. As shown in Figure A.1, similar final rod-lengths are achieved at shorter sonication times using higher powers or lower frequencies. The observed very weak dependence of the terminal rod-length on the sonication parameters has also been previously reported for carbon nanotubes and silver nanowires [137].

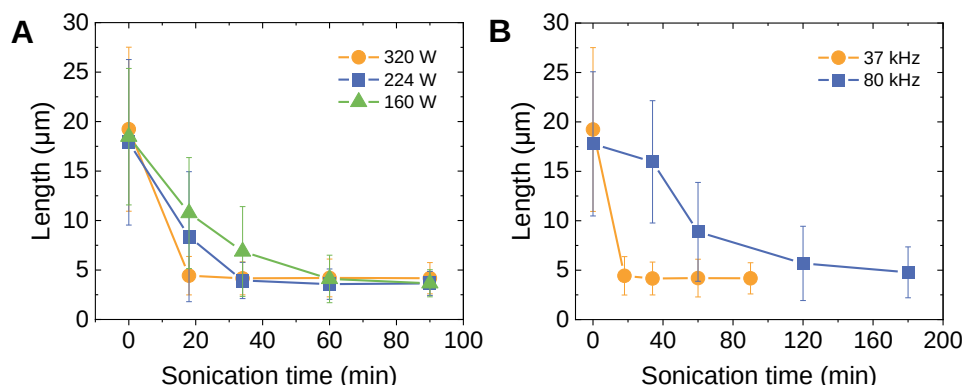


Figure A.1: (A) Evolution of the average length of the SU-8 rods as a function of the sonication time at a frequency of 37 kHz for different powers: 320 W (orange circles), 224 W (blue squares) and 160 W (green triangles). (B) Evolution of the average length of the SU-8 rods as a function of the sonication time at a sonication power of 320 W and a frequency of 37 kHz (orange circles) and 80 kHz (blue squares). An Elmasonic P30H Ultrasonic Cleaner was used for these specific experiments.

We also find that the volume of sonicated sample, thickness of the glass vessel and the position of the vessel relative to the transducer in the ultrasonic bath also affect the time at which the final rod-length is reached. A qualitative summary of our observations is given in Table 1. In our experiments, we typically use a sonication frequency of 45 kHz at a power of 80 W. Experiments are performed at a fixed volume (100 mL of glycerol containing the rods), using the same container (250 mL glass beaker) placed approximately 5 cm from the transducer.

Table 1: Qualitative summary of the effect of experimental parameters on the sonication time required to reach terminal SU-8 rod-size.

Parameter	If the parameter increases
Volume of the sonicated sample	Sonication time increases
Thickness of the glass vessel	Sonication time increases
Distance vessel-transducer	Sonication time increases

A2. Sorting of the colloidal SU-8 rods

The synthesised colloidal SU-8 rods have typical polydispersities of $\sim 40\%$ in length, $\sim 30\%$ in diameter and $\sim 30\%$ in aspect ratio (when 100% glycerol as a dispersion media and 1500 rpm are used). However, cycles of centrifugation and redispersion in water (containing surfactant) can be used to reduce the size polydispersity to 20% in length and 15% in diameter. Figure A.2 shows the dependence of the average rod length, diameter and aspect ratio collected in the supernatant for different centrifugation time and speed combinations.

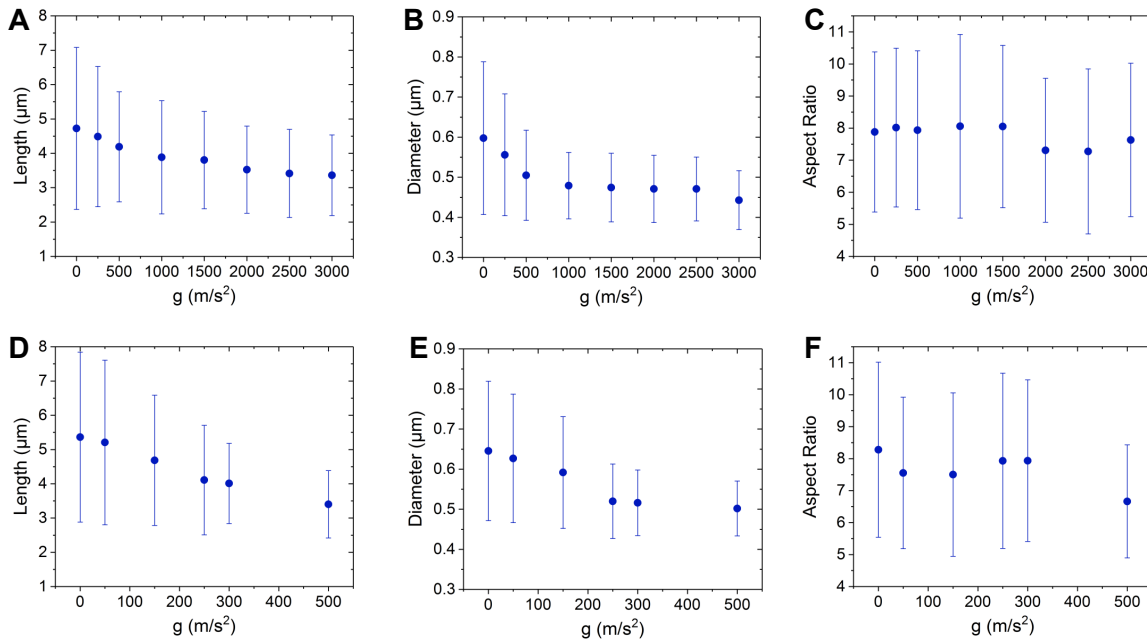


Figure A.2: Dependence of the average length, diameter and aspect ratio of the colloidal SU-8 rods in the supernatant after centrifugation at different speeds for (A-C) 10 min and (D-F) 60 min.

The optimal time-speed combination for the centrifugation-redispersion cycles will depend on the size of the original rods. For colloidal SU-8 rods synthesised at a shear stress of 518 Pa using 100% glycerol, the optimal time-speed combination is found to be 15 min at 600g. This combination results in a sufficiently high yield, while significantly reducing the polydispersities of the rods in the supernatant to $\sigma_L \approx 25\%$, $\sigma_D \approx 15\%$ and $\sigma_{L/D} \approx 30\%$. The process is repeated at least 6 times by re-dispersing the particles in the sediment to maximize the yield. SEM images of the particles collected from the supernatant and those from the sediment are shown in Figure A.3, where a clear size difference is observed. The corresponding size distributions are plotted in Figure A.4. While the aspect ratio distribution does not significantly change, the length and diameter distributions of the rods from the supernatant are much narrower after the sorting procedure. As expected, longer and thicker rods are found in the sediment. The rods from the supernatant are typically used for further experiments.

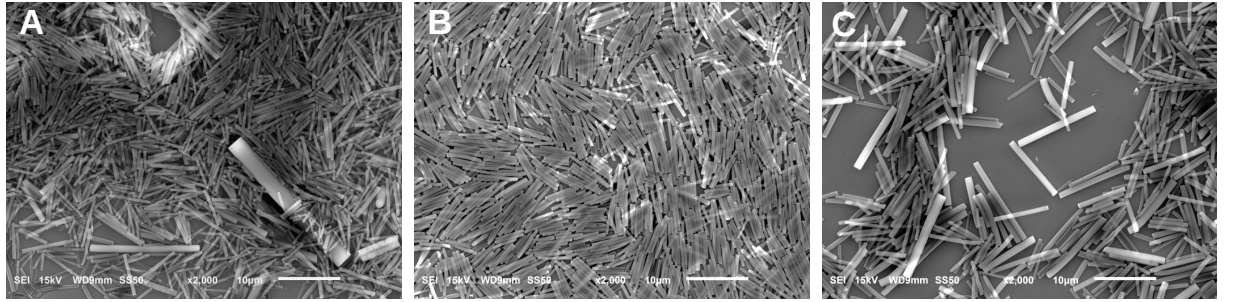


Figure A.3: Scanning electron microscopy (SEM) images of the (A) unsorted rods, (B) rods from the supernatant and (C) rods from the sediment after repeated cycles of centrifugation and re-dispersion at 600g for 15 min. Scale bars are 10 μm .

Table 2: Mean length (L), diameter (D), aspect ratio (L/D) and respective polydispersities (σ_L , σ_D , $\sigma_{D/L}$) of the SU-8 rods before and after the sorting procedure. The polydispersity (%) of the rods was defined as $\sigma_i = \delta_i / \langle i \rangle$.

Sample ID	L (μm)	σ_L (%)	D (μm)	σ_D (%)	L/D	$\sigma_{D/L}$ (%)
Unsorted rods	4.6	47.8	0.57	30.9	8.1	29.9
Supernatant	4.2	25.2	0.52	16.9	7.9	28.1
Sediment	6.4	39.2	0.70	32.1	8.2	31.1

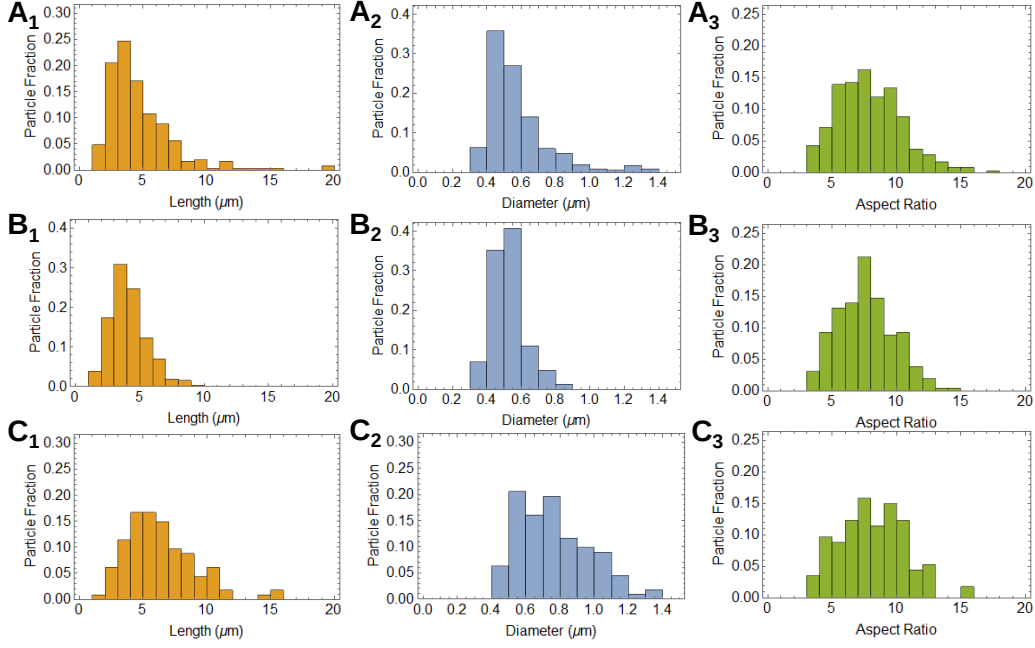


Figure A.4: Length, diameter and aspect ratio distributions of the (A_{1-3}) unsorted rods, (B_{1-3}) supernatant and (C_{1-3}) sediment of repeated centrifugation cycles at 600g for 15 min.

A3. Estimation of the isotropic-nematic phase transition point

To estimate the volume fraction at which the isotropic-nematic phase transition observed in Figure 3.6f occurs, we analyse a 3D confocal z-stack ($157.8 \times 157.8 \times 8 \mu m^3$) across the isotropic-nematic interface of the same sample, from which we determine the number density and nematic order parameter profiles, as shown in Figure A.5. The number density profile is obtained from the positions of the detected fluorescent particles by binning the data in 8 vertical bins with a well-defined volume of $157.8 \times 19.7 \times 8 \mu m^3$. Using the number ratio between fluorescent and non-fluorescent rods (1:30) and the average particle dimensions measured from SEM ($L = 5.0 \mu m$, $D = 0.65 \mu m$, $L/D = 7.7$), we obtain the volume fraction profile across the isotropic-nematic interface. From the orientations of the rods, we calculate the in-plane (2D) nematic order parameter S_2 (see Section 2.1.4) per bin according to

$$S_2 = \langle 2 \cos^2(\theta) \rangle - 1, \quad (1)$$

where θ is the angle between the orientation of the rods and the director, defined as the mean orientation of the rods in each bin. This allows us to locate the position of the isotropic-nematic phase transition, which we estimate to occur at an approximate volume fraction of 0.25.

We emphasize that this value is a rough estimate, because (i) we assume there is no fractionation, (ii) we use the average dimension of the rods as measured from the SEM images which might differ from the dimensions of the rods in solution. Nevertheless, this value is comparable to the value reported in the work of Kuijk et al. [83], and is also consistent with the value reported for hard spherocylinders at the appropriate aspect ratio (about 0.3 for aspect ratio of 7.7 [92]). Note, however, that we do not quantitatively confirm that our particle interactions are indeed hard-core like. We expect that higher resolution 3D-confocal z-stacks with refined particle tracking methods will allow us to obtain more precise measurements for the location of the isotropic-nematic transition.

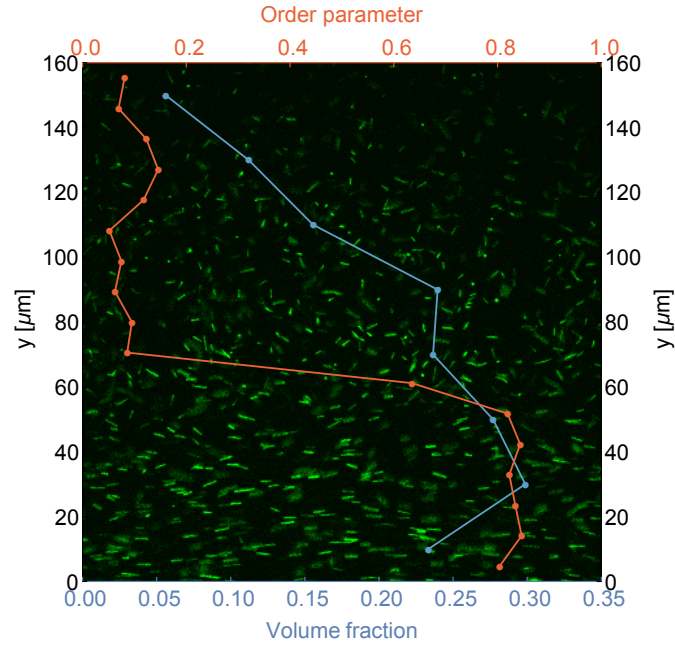


Figure A.5: Plot of the volume fraction and nematic order parameter S_2 profiles as a function of the sample height, y , in a system of colloidal SU-8 rods under a gravity.

A4. Birefringence of in systems of colloidal SU-8 particles

In this section, we qualitatively study the birefringence exhibited by the liquid crystal phases formed by our colloidal SU-8 rods and bananas. Birefringence is the optical property of a material having a refractive index that depends on the polarization and propagation direction of light [2, 240]. Liquid crystals are birefringent materials because light travels at different velocities when it propagates parallel or perpendicular to the nematic director of the phase [2, 240].

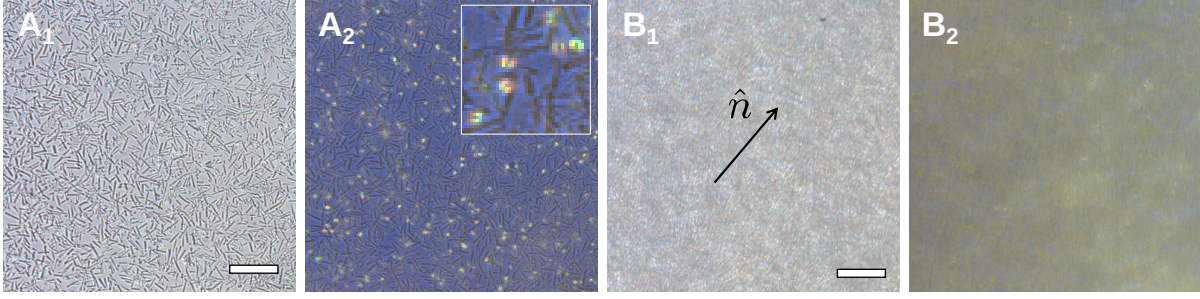


Figure A.6: Optical microscopy images of SU-8 rods sample dispersed in water (A_1 and B_1) in bright field and (A_2 and B_2) between crossed polarisers in the (A) isotropic phase and (B) nematic phase. Bright spots are observed when rods are oriented vertically. The scale bars are $20 \mu m$.

To study the birefringence of our colloidal liquid crystals, we use polarised optical microscopy (POM). This is a frequently used technique to characterise the anisotropic optical properties of liquid crystals, as they typically transform linearly polarised light into elliptically polarised light, allowing for the formation of beautiful images when using crossed polarisers [2, 240]. Firstly, we find that the nematic phases formed by our colloidal rods show a weak, yet observable birefringent signal (see Figure A.6B₂). A stronger birefringent signal might be achieved using thinner samples [2, 240]. We also note that when an isotropic phase of rods is imaged between crossed polarisers, bright spots appear when rods orient vertically to the imaging plane (see Figure A.6A₂). This effect could be related to the fact that SU-8 rods can act as optical waveguides [241], which depolarise light as it travels through the rods.

Similar results are observed for samples of colloidal SU-8 bananas. This is shown in Figure A.7, where polarised optical microscopy images of colloidal bananas at different packing fractions are presented. At low packing fractions (see Fig. A.7A-B), we again observe the appearance of bright spots, which arise from the bananas standing vertically. At intermediate and high packing fractions (see Fig. A.7C-H), bananas self-assemble into liquid crystal phases, and as a result, a beautiful and pronounced structural birefringent signal is exhibited. Note that in this case, we image a very thin sample consisting of quasi two-dimensional monolayer. This could explain the stronger birefringent signal compared to the rods [2]. Finally, in Figure A.8, we show POM images of the rotation of the birefringent signal exhibited by banana-shaped liquid crystals according to the rotation of the crossed polarisers.

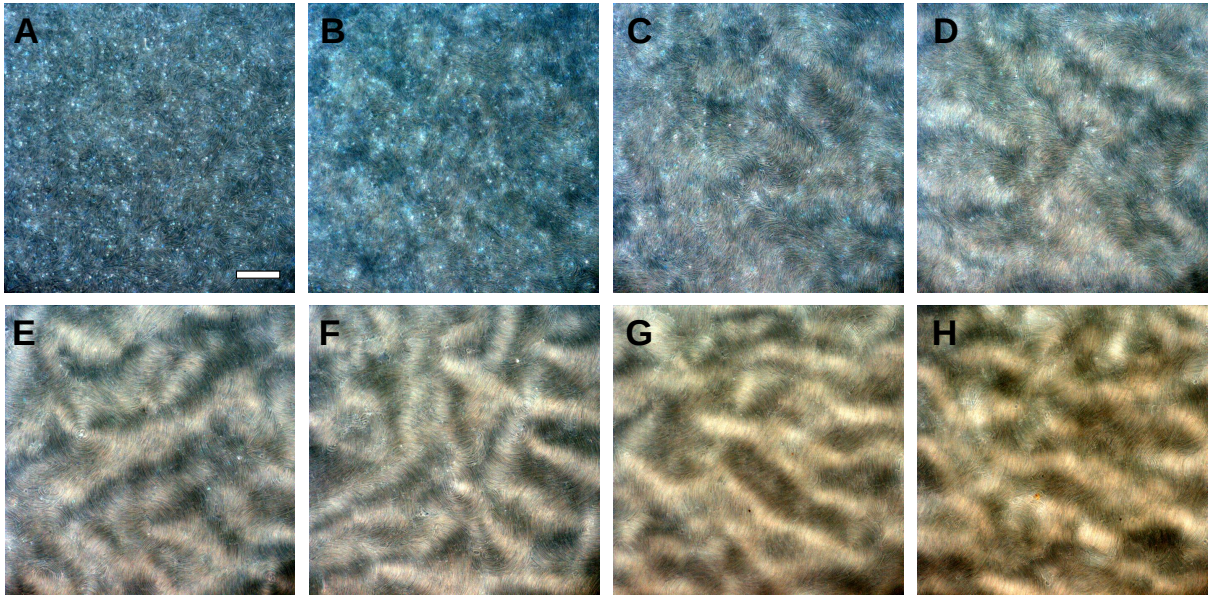


Figure A.7: Polarised optical microscopy images of a system of colloidal SU-8 bananas in water at increasing packing fractions from A to H. Bright spots are observed when bananas orient vertically. Birefringence is observed when bananas form liquid crystal phases (D-H) The scale bar is $20\ \mu\text{m}$.

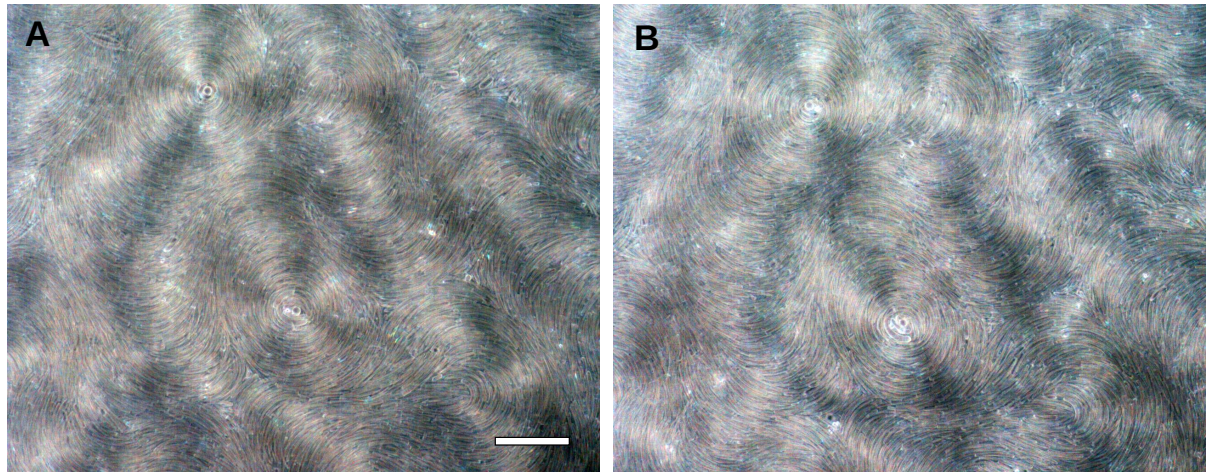


Figure A.8: Polarised optical microscopy images of defects in banana-shaped liquid crystals (A) prior to and (B) after a 45° rotation of the polarisers. The scale bar is $10\ \mu\text{m}$.

A5. Confocal images of colloidal SU-8 particles with different shapes

Figure A.9 shows confocal microscopy images of concentrated samples of colloidal SU-8 particles with different shapes obtained after 30 minutes of heating at increasing UV-exposure time.

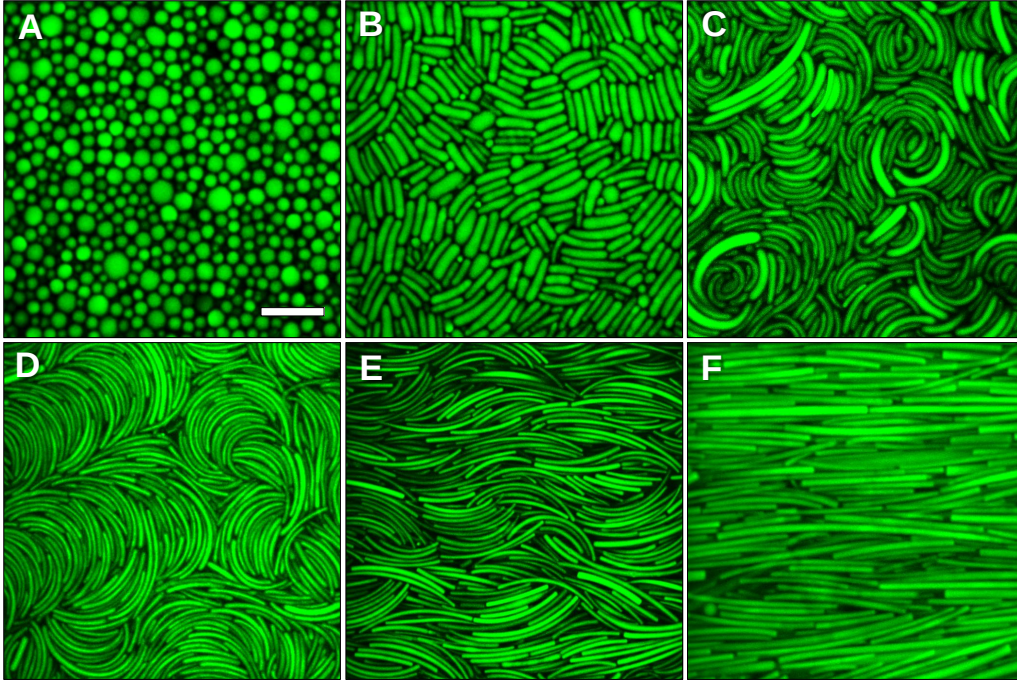


Figure A.9: Confocal microscopy images of concentrated samples of fluorescent SU-8 (A) spheres, (B) spherocylinders, (C-E) banana-shaped particles with decreasing curvature and (F) straight rods obtained after 30 min of heating 95°C for $t_{UV}=1, 5, 15, 25, 45$ and 120 min, respectively. Scale bars are 10 μm .

A6. Confocal images of colloidal bananas with different curvatures

In this section, we present the confocal images for the three differently curved bananas discussed in Chapter 5 at multiple packing fractions, ϕ .

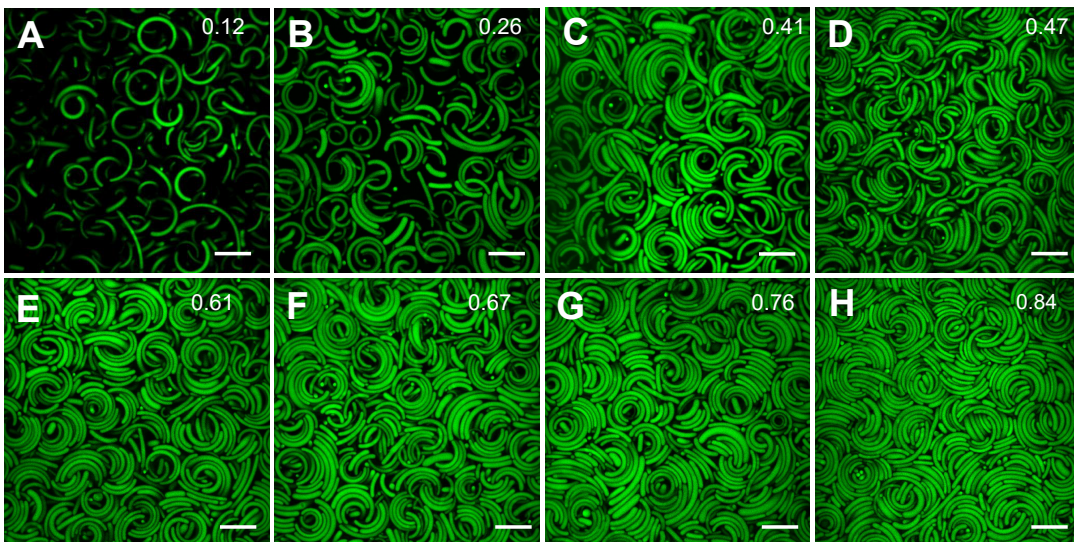


Figure A.10: Confocal microscopy images of colloidal bananas with an average curvature of $\kappa = 0.25 \mu\text{m}^{-1}$ and packing fractions $\phi = 0.12, 0.26, 0.41, 0.47, 0.61, 0.67, 0.76$ and 0.84. Scale bars are 10 μm .

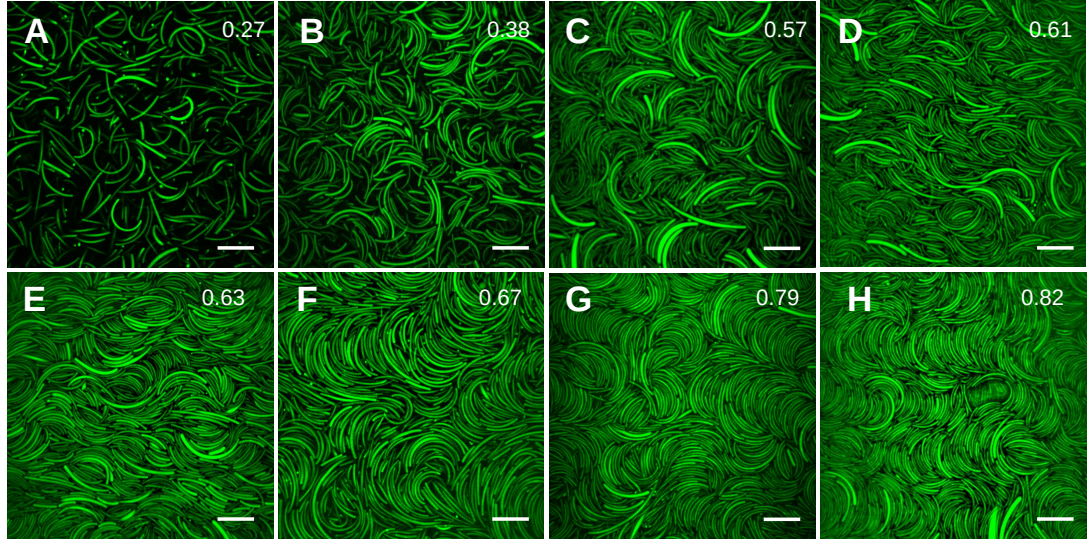


Figure A.11: Confocal microscopy images of colloidal bananas with an average curvature of $\kappa = 0.10 \mu\text{m}^{-1}$ and packing fractions $\phi = 0.27, 0.38, 0.57, 0.61, 0.63, 0.67, 0.79$ and 0.82 . Scale bars are $10 \mu\text{m}$.

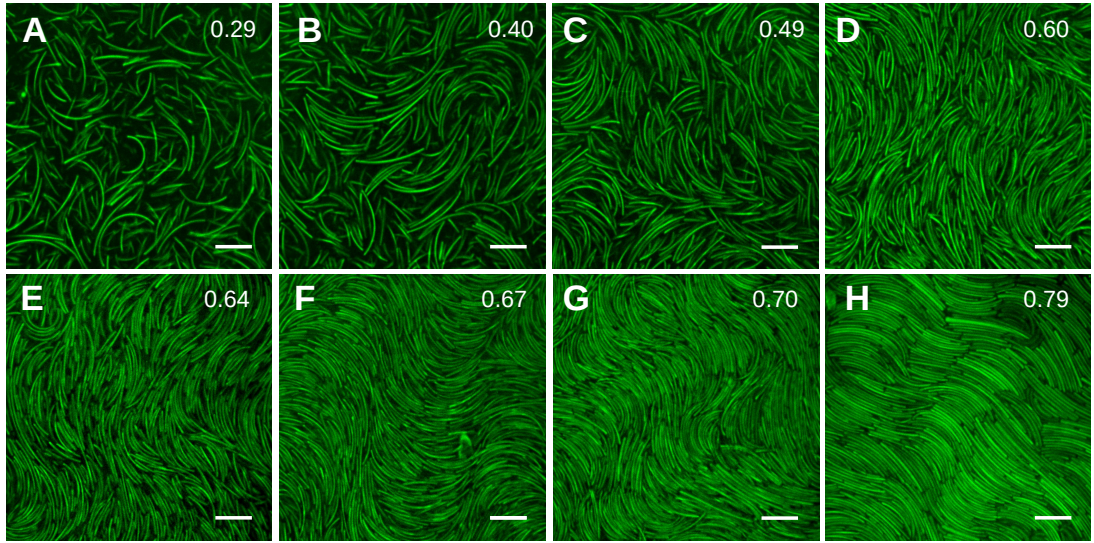


Figure A.12: Confocal microscopy images of colloidal bananas with an average curvature of $\kappa = 0.07 \mu\text{m}^{-1}$ and packing fractions $\phi = 0.29, 0.40, 0.49, 0.60, 0.64, 0.67, 0.70$ and 0.79 . Scale bars are $10 \mu\text{m}$.

A7. Confocal microscopy images of the splay-bend nematic phase at different z -positions

In Figure A.13 shows confocal microscopy images at different imaging depths of the splay-bend nematic phase formed by colloidal bananas with an average curvature of $0.07 \mu\text{m}^{-1}$. The particles are dispersed in tetralin containing 4wt% of OLOA 11000.

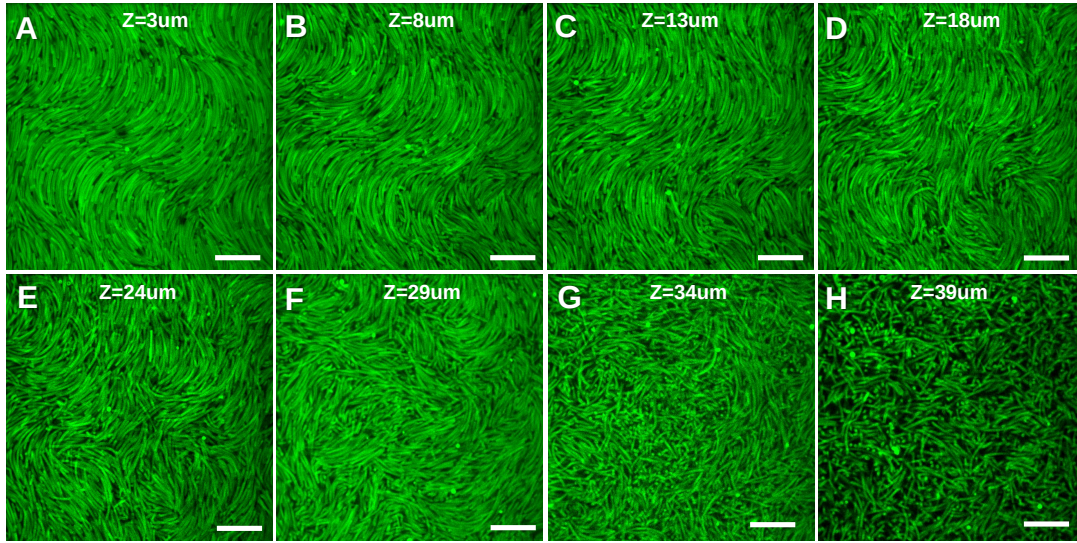


Figure A.13: Confocal images of the splay-bend nematic (A, B, C), nematic (D, E, F) and isotropic (G, H) phases at different imaging depths with respect to the bottom of the sample cell: (A) $3\ \mu\text{m}$, (B) $8\ \mu\text{m}$, (C) $13\ \mu\text{m}$, (D) $18\ \mu\text{m}$, (E) $24\ \mu\text{m}$, (F) $29\ \mu\text{m}$, (G) $34\ \mu\text{m}$ and (H) $39\ \mu\text{m}$ for bananas with the lowest curvature $\kappa = 0.07\ \mu\text{m}^{-1}$. Scale bars are $10\ \mu\text{m}$.

A8. Structural defects in systems of polydisperse bananas with low curvature

At high number fraction of bananas from population B, x_B , i.e. in the absence of bananas with high opening angle but still with a large curvature polydispersity, the system does not longer find the most efficient packing by forming vortices, but via the formation of $\pm 1/2$ defects in the liquid crystalline environment as shown in Fig. A.14.

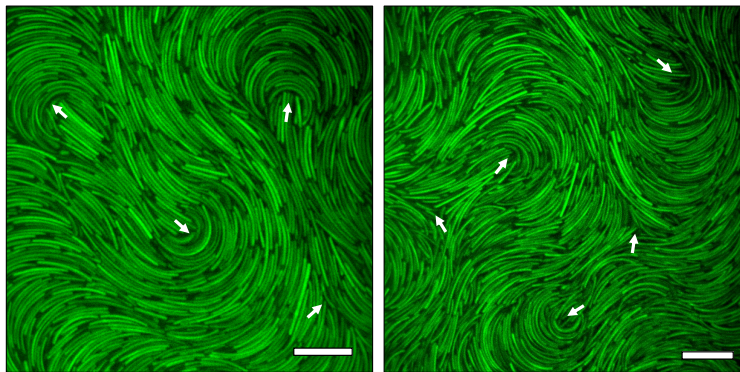


Figure A.14: Structural $\pm 1/2$ defects observed in samples with $x_B=1$. Scale bars are $15\ \mu\text{m}$.

Bibliography

- [1] P. G. de Gennes and J. Prost. *The Physics of Liquid Crystals* (1995).
- [2] P. J. Collings. *Liquid crystals: Nature's delicate phase of matter* (Princeton University Press, 2002), second edi edition.
- [3] F. Mark. *Optical properties of Solids* (Oxford University Press, 2001).
- [4] D. Andrienko. Introduction to liquid crystals. *Journal of Molecular Liquids* **267**, 520 (2018).
- [5] D. Quéré, F. Brochard-Wyart, and P. G. de Gennes. *Capillarity and Wetting Phenomena: Drops, Bubbles, Pearls, Waves* (Springer, 2003).
- [6] D. Dunmur and T. Sluckin. *Soap, Science, and Flat-Screen TVs A History of Liquid Crystals* (Oxford University Press, 2011).
- [7] R. A. Reddy and C. Tschierske. Bent-core liquid crystals: Polar order, superstructural chirality and spontaneous desymmetrisation in soft matter systems. *Journal of Materials Chemistry* **16**, 907 (2006).
- [8] A. Jákli, O. D. Lavrentovich, and J. V. Selinger. Physics of liquid crystals of bent-shaped molecules. *Reviews of Modern Physics* **90**, 45004 (2018).
- [9] H. Takezoe and A. Eremin. *Bent-shaped liquid crystals* (CRC Press, 2017).
- [10] H. Takezoe and Y. Takanishi. Bent-core liquid crystals: Their mysterious and attractive world. *Japanese Journal of Applied Physics, Part 1: Regular Papers and Short Notes and Review Papers* **45**, 597 (2006).
- [11] C. Tschierske and D. J. Photinos. Biaxial nematic phases. *Journal of Materials Chemistry* **20**, 4263 (2010).
- [12] J. Matraszek, J. Mieczkowski, J. Szydłowska, and E. Gorecka. Nematic phase formed by banana-shaped molecules. *Liquid Crystals* **27**, 429 (2000).
- [13] I. Dozov. On the spontaneous symmetry breaking in the mesophases of achiral banana-shaped molecules. *Europhysics Letters* **56**, 247 (2001).

- [14] M. Chiappini, T. Drwenski, R. van Roij, and M. Dijkstra. Biaxial, Twist-bend, and Splay-bend Nematic Phases of Banana-shaped Particles Revealed by Lifting the “Smectic Blanket”. *Physical Review Letters* **123**, 068001 (2019).
- [15] D. F. Evans and H. Wennerstrom. *Colloidal domain* (Wiley-Vch, 1999).
- [16] W. C. Poon. Colloidal suspensions. *The Oxford Handbook of Soft Condensed Matter* 1–50 (2017).
- [17] V. N. Manoharan. Colloidal matter: Packing, geometry, and entropy. *Science* **349**, 1253751 (2015).
- [18] W. Poon. Colloids as Big Atoms. *Science* **304**, 830 (2004).
- [19] V. N. Manoharan. Colloidal matter: Packing, geometry, and entropy. *Science* **349** (2015).
- [20] J. Perrin. Mouvement brownien et realite moleculaire. In *Annales de Chimie et de Physique* **18**, 5 (1909).
- [21] A. Einstein. The theory of the brownian movement. *Annalen der Physik* **17:549** (1905).
- [22] B. J. Alder and T. E. Wainwright. Phase transition for a hard sphere system. *The Journal of Chemical Physics* **27**, 1208 (1957).
- [23] W. W. Wood and J. D. Jacobson. Preliminary results from a recalculation of the Monte Carlo equation of state of hard spheres. *The Journal of Chemical Physics* **27**, 1207 (1957).
- [24] P. N. Pusey and W. Van Megen. Phase behaviour of concentrated suspensions of nearly hard colloidal spheres. *Nature* **320**, 340 (1986).
- [25] S. C. Glotzer and M. J. Solomon. Anisotropy of building blocks and their assembly into complex structures. *Nature Materials* **6**, 557 (2007).
- [26] L. Rossi, S. Sacanna, W. T. M. Irvine, P. M. Chaikin, D. J. Pine, and A. P. Philipse. Cubic crystals from cubic colloids. *Soft Matter* **7**, 4139 (2011).
- [27] C. Fernández-Rico, T. Yanagishima, A. Curran, D. G. A. L. Aarts, and R. P. A. Dullens. Synthesis of Colloidal SU-8 Polymer Rods Using Sonication. *Advanced Materials* **31**, 1807514 (2019).
- [28] N. Vogel, M. Retsch, C. A. Fustin, A. Del Campo, and U. Jonas. Advances in Colloidal Assembly: The Design of Structure and Hierarchy in Two and Three Dimensions. *Chemical Reviews* **115**, 6265 (2015).
- [29] A. L. Thornewyck, J. L. Abbott, D. G. Aarts, and R. P. Dullens. Two-Dimensional Melting of Colloidal Hard Spheres. *Physical Review Letters* **118**, 1 (2017).
- [30] D. G. A. L. Aarts, M. Schmidt, and H. N. W. Lekkerkerker. Direct Visual Observation of Thermal Capillary Waves. *Science* **304**, 847 (2004).

- [31] A. A. Verhoeff, F. A. Lavergne, D. Bartolo, D. G. Aarts, and R. P. Dullens. Optical trapping of interfaces at ultra-low interfacial tension. *Soft Matter* **11**, 3100 (2015).
- [32] V. W. De Villeneuve, R. P. Dullens, D. G. Aarts, E. Groeneveld, J. H. Scherff, W. K. Kegel, and H. N. Lekkerkerker. Chemistry: Colloidal hard-sphere crystal growth frustrated by large spherical impurities. *Science* **309**, 1231 (2005).
- [33] W. T. M. Irvine, M. J. Bowick, and P. M. Chaikin. Fractionalization of interstitials in curved colloidal crystals. *Nature Materials* **11**, 948 (2012).
- [34] M. He, J. P. Gales, É. Ducrot, Z. Gong, G. R. Yi, S. Sacanna, and D. J. Pine. Colloidal diamond. *Nature* **585**, 524 (2020).
- [35] F. M. Van Der Kooij and H. N. Lekkerkerker. Liquid-crystal phase transitions in suspensions of plate-like particles. *Nature* **406**, 868 (2000).
- [36] A. Kuijk, A. V. Blaaderen, and A. Imhof. Rodlike Silica Colloids with Tunable Aspect Ratio. *J. Am. Chem. Soc.* **133**, 2346 (2011).
- [37] Z. Dogic and S. Fraden. Smectic phase in a colloidal suspension of semiflexible virus particles. *Physical review letters* **78**, 2417 (1997).
- [38] C. C. Ho, A. Keller, J. A. Odell, and R. H. Ottewill. Preparation of monodisperse ellipsoidal polystyrene particles. *Colloid & Polymer Science* **271**, 469 (1993).
- [39] C. M. Care and D. J. Cleaver. Computer simulation of liquid crystals. *Reports on Progress in Physics* **68**, 2665 (2005).
- [40] A. V. Blaaderen and P. Wiltzius. Real-Space Structure of Colloidal Hard-Sphere Glasses. *Science* **270**, 1177 (1995).
- [41] W. K. Kegel and V. A. Blaaderen. Direct Observation of Dynamical Heterogeneities in Colloidal Hard-Sphere Suspensions. *Science* **287**, 290 (2000).
- [42] F. Reinitzer. Beitrage zur Kenntniss des Cholesterins. *Monatsh Chem.* **9**, 421 (1888).
- [43] O. Lehmann. Über fließende krystalle. *Zeitschrift für Physikalische Chemie* **1889**.
- [44] D. Demus, J. Goodby, G. W. Gray, and H.-W. Spiess. *Handbook of Liquid Crystals: Fundamentals* (1998).
- [45] D. Vorlander. *Kristallinisch-flüssige substanzen*. Stuttgart: Enke (1905).
- [46] D. Vorlander. Einfluss der molekularen Gestalt auf den krystallinisch-flüssigen Zustand. *Ber Dtsch Chem Ges* **40**, 1970 (1907).
- [47] C. W. Oseen. The theory of liquid crystals,. *Trans. Faraday Soc.* **29**, 883 (1933).
- [48] F. C. Frank. Liquid crystals. on the theory of liquid crystals. *Discuss. Faraday Soc.* **25**, 19 (1958).

- [49] M. J. Stephen and J. P. Straley. Physics of liquid crystals. *Reviews of Modern Physics* **46**, 617 (1974).
- [50] V. D, F. K, and E. Katscher. Über die Einwirkung von Chlorsulfonsäure auf Aldehyde. *Ber Dtsch Chem Ges* **62**, 2381 (1926).
- [51] S. Chandrasekhar, B. Sadashiva, and K. Suresh. Liquid crystals of disc-like molecules. *Pramana* **9**, 471 (1977).
- [52] C. Imrie and P. A. Henderson. Liquid crystal dimers and oligomers. *Current Opinion in Colloid and Interface Science* **7**, 298 (2002).
- [53] F. T. Niori, T. Sekine, T. Watanabe, J. and T. H. Distinct ferroelectric smectic liquid crystals consisting of banana shaped achiral molecules. *J. Mater. Chem.* **6**, 1231 (1996).
- [54] R. J. Mandle, M. P. Stevens, and J. W. Goodby. Developments in liquid-crystalline dimers and oligomers. *Liquid Crystals* **44**, 2046 (2017).
- [55] G. Friedel. Etude sur les groupements cristallins. Societe de l'Imprimerie Theolier (1904).
- [56] S. Kumar and A. N. Gowda. The chemistry of bent-core molecules forming nematic liquid crystals. *Liquid Crystals Reviews* **3**, 99 (2015).
- [57] D. Chen, M. Nakata, R. Shao, M. R. Tuchband, M. Shuai, U. Baumeister, W. Weissflog, D. M. Walba, M. A. Glaser, J. E. MacLennan, and N. A. Clark. Twist-bend heliconical chiral nematic liquid crystal phase of an achiral rigid bent-core mesogen. *Physical Review E - Statistical, Nonlinear, and Soft Matter Physics* **89**, 022506 (2014).
- [58] V. H. Zocher. Über freiwillige Strukturbildung in Solen: eine neue Art anisotrop flüssiger Medien. *Zeitschrift für anorganische und allgemeine Chemie* **147**, 91 (1925).
- [59] H. N. W. Lekkerkerker and G. J. Vroege. Liquid crystal phase transitions in suspensions of mineral colloids: new life from old roots. *Philos. Trans. R. Soc., A* **371** (2013).
- [60] M. Doi. *Soft matter physics* (Oxford University Press, 2013).
- [61] Z. Tu, O.-Y. Zhongcan, L. Jixing, and Y. Xie. *Geometric Methods in Elastic Theory of Membranes in Liquid Crystal Phases* (World Scientific, 2018).
- [62] S. Dussi and M. Dijkstra. Entropy-driven formation of chiral nematic phases by computer simulations. *Nature Communications* **7**, 1 (2016).
- [63] H. E. Bakker, S. Dussi, B. L. Droste, T. H. Besseling, C. L. Kennedy, E. I. Wiegant, B. Liu, A. Imhof, M. Dijkstra, and A. Van Blaaderen. Phase diagram of binary colloidal rod-sphere mixtures from a 3D real-space analysis of sedimentation-diffusion equilibria. *Soft Matter* **12**, 9238 (2016).
- [64] O. J. Dammone, I. Zacharoudiou, R. P. A. Dullens, J. M. Yeomans, M. P. Lettinga, and D. G. A. L. Aarts. Confinement induced splay-to-bend transition of colloidal rods. *Phys. Rev. Lett.* **109**, 1 (2012).

- [65] M. Kleman and O. D. Lavrentovich. Topological point defects in nematic liquid crystals. *Philosophical Magazine* **86**, 4117 (2006).
- [66] R. B. Meyer. in *Molecular Fluids*. edited by R. Balian and G. Weil, 271–343 (1976).
- [67] J. L. Bitter, Y. Yang, G. Duncan, H. Fairbrother, and M. A. Bevan. Interfacial and Confined Colloidal Rod Diffusion. *Langmuir* **33**, 9034 (2017).
- [68] D. J. Kraft, R. Wittkowski, B. Ten Hagen, K. V. Edmond, D. J. Pine, and H. Löwen. Brownian motion and the hydrodynamic friction tensor for colloidal particles of complex shape. *Physical Review E - Statistical, Nonlinear, and Soft Matter Physics* **88**, 2 (2013).
- [69] A. Chakrabarty, A. Konya, F. Wang, J. V. Selinger, K. Sun, and Q. H. Wei. Brownian motion of boomerang colloidal particles. *Physical Review Letters* **111**, 1 (2013).
- [70] J. Fung and V. N. Manoharan. Holographic measurements of anisotropic three-dimensional diffusion of colloidal clusters. *Physical Review E - Statistical, Nonlinear, and Soft Matter Physics* **88**, 1 (2013).
- [71] A. Chakrabarty, A. Konya, F. Wang, J. V. Selinger, K. Sun, and Q. H. Wei. Brownian motion of arbitrarily shaped particles in two dimensions. *Langmuir* **30**, 13844 (2014).
- [72] Y. Han, A. M. Alsayed, M. Nobili, J. Zhang, T. C. Lubensky, and A. G. Yodh. Brownian motion of an ellipsoid. *Optics InfoBase Conference Papers* 626–631 (2006).
- [73] J. P. Simonin. Calculation of equilibrium sedimentation profiles of screened charged colloids. *Journal of Physical Chemistry* **99**, 1577 (1995).
- [74] J. D. Weeks, D. Chandler, and H. C. Andersen. Role of repulsive forces in determining the equilibrium structure of simple liquids. *The Journal of Chemical Physics* **54**, 5237 (1971).
- [75] A. Van Blaaderen and A. Vrij. Synthesis and characterization of colloidal dispersions of fluorescent, monodisperse silica spheres. *Langmuir* **8**, 2921 (1992).
- [76] R. P. A. Dullens, M. Claesson, D. Derks, A. V. Blaaderen, and W. K. Kegel. Monodisperse Core-Shell Poly(methyl methacrylate) Latex Colloids **19**, 13 (2003).
- [77] W. K. Kegel. Direct observation of dynamical heterogeneities in colloidal hard-sphere suspensions. *Science* **287**, 290 (2000).
- [78] Y. Wang, Y. Wang, D. R. Breed, V. N. Manoharan, L. Feng, A. D. Hollingsworth, M. Weck, D. J. Pine, S. Figure, Y. Wang, D. R. Breed, V. N. Manoharan, L. Feng, A. D. Hollingsworth, M. Weck, and D. J. Pine. Colloids with valence and specific directional bonding. *Nature* **491**, 51 (2012).
- [79] J. Zhang, E. Luijten, and S. Granick. Toward design rules of directional janus colloidal assembly. *Annual Review of Physical Chemistry* **66**, 581 (2015).

- [80] S. Sacanna and D. J. Pine. Shape-anisotropic colloids: Building blocks for complex assemblies. *Current Opinion in Colloid and Interface Science* **16**, 96 (2011).
- [81] S. Sacanna, M. Korpics, K. Rodriguez, L. Colón-Meléndez, S. H. Kim, D. J. Pine, and G. R. Yi. Shaping colloids for self-assembly. *Nature Communications* **4**, 2 (2013).
- [82] B. Li, D. Zhou, and Y. Han. Assembly and phase transitions of colloidal crystals (2016).
- [83] A. Kuijk, D. V. Byelov, A. V. Petukhov, A. van Blaaderen, and A. Imhof. Phase behavior of colloidal silica rods. *Faraday Discuss.* **159**, 181 (2012).
- [84] W. Li, H. Palis, R. Méridol, J. Majimel, S. Ravaine, and E. Duguet. Colloidal molecules and patchy particles: Complementary concepts, synthesis and self-assembly. *Chemical Society Reviews* **49**, 1955 (2020).
- [85] D. J. Kraft, W. S. Vlug, C. M. Van Kats, A. Van Blaaderen, A. Imhof, and W. K. Kegel. Self-assembly of colloids with liquid protrusions. *Journal of the American Chemical Society* **131**, 1182 (2009).
- [86] L. Onsager. The effects of shape on the interaction of colloidal particles. *Ann. N. Y. Acad. Sci.* **51**, 627 (1949).
- [87] F. Sciortino. Entropy in self-assembly. *Rivista del Nuovo Cimento* **42**, 511 (2019).
- [88] G. Van Anders, D. Klotsa, N. K. Ahmed, M. Engel, and S. C. Glotzer. Understanding shape entropy through local dense packing. *Proceedings of the National Academy of Sciences of the United States of America* **111**, E4812 (2014).
- [89] D. Frenkel. Order through entropy. *Nature Materials* **14**, 9 (2015).
- [90] A. V. Petukhov, R. Tuinier, and G. J. Vroege. Entropic patchiness: Effects of colloid shape and depletion. *Current Opinion in Colloid and Interface Science* **30**, 54 (2017).
- [91] G. J. Vroege and H. N. Lekkerkerker. Phase transitions in lyotropic colloidal and polymer liquid crystals. *Reports on Progress in Physics* **55**, 1241 (1992).
- [92] P. Bolhuis and D. Frenkel. Tracing the phase boundaries of hard spherocylinders. *J. Chem. Phys.* **106**, 666 (1997).
- [93] P. A. Buining, C. Pathmamanoharan, J. B. H. Jansen, and H. N. W. Lekkerkerker. Preparation of Colloidal Boehmite Needles by Hydrothermal Treatment of Aluminum Alkoxide Precursors. *J. Am. Ceram. Soc.* **74**, 1303 (1991).
- [94] A. Haji-Akbari, M. Engel, A. S. Keys, X. Zheng, R. G. Petschek, P. Palffy-Muhoray, and S. C. Glotzer. Disordered, quasicrystalline and crystalline phases of densely packed tetrahedra. *Nature* **462**, 773 (2009).
- [95] P. F. Damasceno, M. Engel, and S. C. Glotzer. Predictive self-assembly of polyhedra into complex structures. *Science* **337**, 453 (2012).

- [96] R. G. Alargova, K. H. Bhatt, V. N. Paunov, and O. D. Velev. Scalable synthesis of a new class of polymer microrods by a liquid-liquid dispersion technique. *Advanced Materials* **16**, 1653 (2004).
- [97] R. G. Alargova, V. N. Paunov, and O. D. Velev. Formation of polymer microrods in shear flow by emulsification-solvent attrition mechanism. *Langmuir* **22**, 765 (2006).
- [98] R. Martinez-Duarte and M. J. Madou. *SU-8 Photolithography and its impact on Microfluidics* (2010).
- [99] R. Agarwal, K. Ladavac, Y. Roichman, C. M. Lieber, and D. G. Grier. Manipulation and assembly of nanowires with holographic optical traps. *Opt. Express* **13**, 1135 (2005).
- [100] A. del Campo and C. Greiner. SU-8: a photoresist for high-aspect-ratio and 3D submicron lithography. *Journal of micromechanics and microengineering* **17**, 960 (2007).
- [101] D. MicroChem Corp. Negative Tone Photoresist Formulations 5-10. (www.microchem.com) .
- [102] R. Daunton, A. J. Gallant, and D. Wood. Manipulation of exposure dose parameters to improve production of high aspect ratio structures using SU-8. *Journal of Micromechanics and Microengineering* **22**, 4 (2012).
- [103] J. V. Crivello and J. H. Lam. Photoinitiated cationic polymerization with triarylsulfonium salts. *Journal of Polymer Science, Part A: Polymer Chemistry* **34**, 3231 (1996).
- [104] S. Keller, G. Blagoi, M. Lillemose, D. Haeffiger, and A. Boisen. Processing of thin SU-8 films. *Journal of Micromechanics and Microengineering* **18** (2008).
- [105] F. Ru and J. F. Richard. Influence of processing conditions on the thermal and mechanical properties of SU8 negative photoresist coatings. *Journal of Micromechanics and Microengineering* **13**, 80 (2003).
- [106] V. Prasad, D. Semwogerere, and E. R. Weeks. Confocal microscopy of colloids. *J. Phys.: Cond. Matt.* **19**, 113102 (2007).
- [107] S. Tottori, L. Zhang, F. Qiu, K. K. Krawczyk, A. Franco-Obregón, and B. J. Nelson. Magnetic helical micromachines: Fabrication, controlled swimming, and cargo transport. *Advanced Materials* **24**, 811 (2012).
- [108] C. Wyatt Shields Iv, S. Zhu, Y. Yang, B. Bharti, J. Liu, B. B. Yellen, O. D. Velev, and G. P. López. Field-directed assembly of patchy anisotropic microparticles with defined shape. *Soft Matter* **9**, 9219 (2013).
- [109] J. H. Moon, A. J. Kim, J. C. Crocker, and S. Yang. High-throughput synthesis of anisotropic colloids via holographic lithography. *Adv. Mater.* **19**, 2508 (2007).
- [110] R. G. Alargova, D. S. Warhadpande, V. N. Paunov, and O. D. Velev. Foam superstabilization by polymer microrods. *Langmuir* **20**, 10371 (2004).

- [111] M. Minsky. Memoir on inventing the confocal scanning microscope. *Scanning* **4**, 128 (1998).
- [112] R. P. A. Dullens. Colloidal hard spheres: cooking and looking. *Soft Matter* **2**, 805 (2006).
- [113] M. C. Jenkins and S. U. Egelhaaf. Confocal microscopy of colloidal particles: Towards reliable, optimum coordinates. *Advances in Colloid and Interface Science* **136**, 65 (2008).
- [114] A. Mohraz and M. J. Solomon. Direct visualization of colloidal rod assembly by confocal microscopy. *Langmuir* **21**, 5298 (2005).
- [115] D. Mukhija and M. J. Solomon. Nematic order in suspensions of colloidal rods by application of a centrifugal field. *Soft Matter* **7**, 540 (2011).
- [116] T. H. Besseling, M. Hermes, A. Kuijk, B. de Nijs, T. S. Deng, M. Dijkstra, A. Imhof, and A. van Blaaderen. Determination of the positions and orientations of concentrated rod-like colloids from 3D microscopy data. *J. Phys.: Condens. Matter* (2014).
- [117] H. E. Bakker, S. Dussi, B. L. Droste, T. H. Besseling, C. L. Kennedy, E. I. Wiegant, B. Liu, A. Imhof, M. Dijkstra, and A. van Blaaderen. Phase diagram of binary colloidal rod-sphere mixtures from a 3D real-space analysis of sedimentation–diffusion equilibria. *Soft Matter* **12**, 9238 (2016).
- [118] I. D. Morrison. Electrical charges in nonaqueous media. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **71**, 1 (1993).
- [119] Y. Liu, T. Yanagishima, A. Curran, K. V. Edmond, S. Sacanna, and R. P. Dullens. Colloidal Organosilica Spheres for Three-Dimensional Confocal Microscopy. *Langmuir* **35**, 7962 (2019).
- [120] S. K. Sainis, V. Germain, C. O. Mejean, and E. R. Dufresne. Electrostatic interactions of colloidal particles in nonpolar solvents: Role of surface chemistry and charge control agents. *Langmuir* **24**, 1160 (2008).
- [121] D. Frenkel, H. N. W. Lekkerkerker, and A. Stroobants. Thermodynamic stability of a smectic phase in a system of hard rods. *Nature* **332**, 822 (1988).
- [122] A. Stroobants. Columnar versus Smectic Order in Binary Mixtures of Hard Parallel Spherocylinders. *Phys. Rev. Lett.* **69**, 2388 (1992).
- [123] M. A. Bates and D. Frenkel. Influence of polydispersity on the phase behavior of colloidal liquid crystals: A Monte Carlo simulation study. *J. Chem. Phys.* **109**, 6193 (1998).
- [124] Z. Dogic and S. Fraden. Ordered phases of filamentous viruses. *Curr. Opin. Colloid Interface Sci.* **11**, 47 (2006).
- [125] M. P. Lettinga and E. Grelet. Self-diffusion of rodlike viruses through smectic layers. *Phys. Rev. Lett.* **99**, 2 (2007).

- [126] E. Grelet. Hexagonal order in crystalline and columnar phases of hard rods. *Phys. Rev. Lett.* **100**, 1 (2008).
- [127] K. M. Keville, E. I. Franses, and J. M. Caruthers. Preparation and characterization of monodisperse polymer microspheroids. *Journal of Colloid and Interface Science* **144**, 103 (1991).
- [128] A. H. Lewis, I. Garlea, J. Alvarado, O. J. Dammone, P. D. Howell, A. Majumdar, B. M. Mulder, M. P. Lettinga, G. H. Koenderink, and D. G. A. L. Aarts. Colloidal liquid crystals in rectangular confinement: Theory and experiment. *Soft Matter* **10**, 7865 (2014).
- [129] D. Mukhija and M. J. Solomon. Nematic order in suspensions of colloidal rods by application of a centrifugal field. *Soft Matter* **7**, 540 (2011).
- [130] Y. Gao, F. Romano, R. P. A. Dullens, J. K. Doye, and D. G. A. L. Aarts. Directed self-assembly into low-density colloidal liquid crystal phases. *Phys. Rev. Mater.* **2**, 015601 (2018).
- [131] J. Hernández-Guzmán and E. R. Weeks. The equilibrium intrinsic crystal-liquid interface of colloids. *Proc. Natl. Acad. Sci. U. S. A.* (2008).
- [132] U. Gasser. Real-Space Imaging of Nucleation and Growth in Colloidal Crystallization. *Science* **292**, 258 (2001).
- [133] Y. Liu, K. V. Edmond, A. Curran, C. Bryant, B. Peng, D. G. Aarts, S. Sacanna, and R. P. Dullens. Core-Shell Particles for Simultaneous 3D Imaging and Optical Tweezing in Dense Colloidal Materials. *Adv. Mater.* **28**, 8001 (2016).
- [134] J. C. R. Reis, I. M. Lampreia, Â. F. Santos, M. L. C. Moita, and G. Douhéret. Refractive Index of Liquid Mixtures: Theory and Experiment. *ChemPhysChem* **11**, 3722 (2010).
- [135] V. A. Tolpekin, M. H. Duits, D. Van Den Ende, and J. Mellema. Aggregation and breakup of colloidal particle aggregates in shear flow, studied with video microscopy. *Langmuir* **20**, 2614 (2004).
- [136] A. Lucas, C. Zakri, M. Maugey, M. Pasquali, P. Van Der Schoot, and P. Poulin. Kinetics of nanotube and microfiber scission under sonication. *J. Phys. Chem. C* **113**, 20599 (2009).
- [137] Y. Y. Huang, T. P. Knowles, and E. M. Terentjev. Strength of nanotubes, filaments, and nanowires from sonication-induced scission. *Adv. Mater.* **21**, 3945 (2009).
- [138] G. J. Vroege, D. M. Thies-Weesie, A. V. Petukhov, B. J. Lemaire, and P. Davidson. Smectic liquid-crystalline order in suspensions of highly polydisperse goethite nanorods. *Adv. Mater.* **18**, 2565 (2006).
- [139] E. Van Den Pol, D. M. Thies-Weesie, A. V. Petukhov, G. J. Vroege, and K. Kvashnina. Influence of polydispersity on the phase behavior of colloidal goethite. *J. Chem. Phys.* **129**, 164715 (2008).

- [140] A. Curran, S. Tuohy, D. G. A. L. Aarts, M. J. Booth, T. Wilson, and R. P. A. Dullens. Decoupled and simultaneous three-dimensional imaging and optical manipulation through a single objective. *Optica* **1**, 223 (2014).
- [141] J. L. Abbott, J. A. Spiers, Y. Gao, D. G. A. L. Aarts, and R. P. A. Dullens. Colloidal rods in optical potential energy landscapes. *J. Phys. D: Appl. Phys.* **52**, 024002 (2018).
- [142] A. Modlinska, A. M. Alsayed, and T. Gibaud. Condensation and dissolution of nematic droplets in dispersions of colloidal rods with thermo-sensitive depletants. *Sci. Rep.* **5**, 1 (2015).
- [143] K. Shundyak and R. van Rojk. Isotropic-nematic interfaces of hard-rod fluids Isotropic – nematic interfaces of hard-rod fluids. *J. Phys.: Condens. Matter* **13**, 4789 (2001).
- [144] S. Wolfsheimer, C. Tanase, K. Shundyak, R. Van Roij, and T. Schilling. Isotropic-nematic interface in suspensions of hard rods: Mean-field properties and capillary waves. *Phys. Rev. E* **73**, 1 (2006).
- [145] R. L. C. Vink and T. Schilling. Interfacial tension of the isotropic-nematic interface in suspensions of soft spherocylinders. *Phys. Rev. E* **71**, 1 (2005).
- [146] S. K. Smoukov, T. Tian, N. Vitchuli, S. Gangwal, P. Geisen, M. Wright, E. Shim, M. Marquez, J. Fowler, and O. D. Velev. Scalable liquid shear-driven fabrication of polymer nanofibers. *Adv. Mater.* **27**, 2642 (2015).
- [147] S. Jiguet, A. Bertsch, H. Hofmann, and P. Renaud. Conductive SU8 photoresist for microfabrication. *Adv. Func. Mater.* **15**, 1511 (2005).
- [148] L. Chen, G. Chen, and L. Lu. Piezoresistive behavior study on finger-sensing silicone rubber/graphite nanosheet nanocomposites. *Adv. Func. Mater.* **17**, 898 (2007).
- [149] A. Modlinska, A. M. Alsayed, and T. Gibaud. Condensation and dissolution of nematic droplets in dispersions of colloidal rods with thermo-sensitive depletants. *Scientific Reports* **5**, 1 (2015).
- [150] H. N. Lekkerkerker and R. Tuinier. *Book Depletion* (Springer, 2011).
- [151] A. Persat, H. A. Stone, and Z. Gitai. The curved shape of *caulobacter crescentus* enhances surface colonization in flow. *Nature Communications* **5**, 3824 (2014).
- [152] R. Schuech, T. Hoehfurner, D. J. Smith, and S. Humphries. Motile curved bacteria are Pareto-optimal. *Proceedings of the National Academy of Sciences of the United States of America* **116**, 14440 (2019).
- [153] B. Qualmann, D. Koch, and M. M. Kessels. Let’s go bananas: Revisiting the endocytic BAR code. *EMBO Journal* **30**, 3501 (2011).
- [154] Y.-B. Shen and Z. Shen. When physics takes over: BAR proteins and membrane curvature. *Trends in Cell Biology* **25**, 59 (2015).

- [155] Y. Yang, H. Pei, G. Chen, K. T. Webb, L. J. Martinez-Miranda, I. K. Lloyd, Z. Lu, K. Liu, and Z. Nie. Phase behaviors of colloidal analogs of bent-core liquid crystals. *Science Advances* **4**, 3aas8829 (2018).
- [156] M. Caggioni, J. Lenis, A. V. Bayles, E. M. Furst, and P. T. Spicer. Temperature-Induced Collapse, and Arrested Collapse, of Anisotropic Endoskeleton Droplets. *Langmuir* **31**, 8558 (2015).
- [157] R. W. Style, A. Jagota, C.-y. Hui, and E. R. Dufresne. Elastocapillarity : Surface Tension and the Mechanics of Soft Solids. *Annual Review of Fluid Mechanics* **8**, 99 (2017).
- [158] K. Ingolf Schiffmann and B. Carsten. Testing the viscoelastic properties of SU8 photo resist thin films at different stages of processing by nanoindentation creep and stress relaxation. *International Journal of Materials Research* **98**, 397 (2007).
- [159] J. Bico, E. Reyssat, and B. Roman. Elastocapillarity : When Surface Tension Deforms Elastic Solids. *Annual Review of Fluid Mechanics* **50**, 629 (2018).
- [160] B. Senyuk, H. Wonderly, M. Mathews, Q. Li, S. V. Shiyankovskii, and O. D. Lavrentovich. Surface alignment, anchoring transitions, optical properties, and topological defects in the nematic phase of thermotropic bent-core liquid crystal A131. *Physical Review E - Statistical, Nonlinear, and Soft Matter Physics* **82**, 1 (2010).
- [161] C. J. Cesarsky, S. I. Syrovatskii, I. V. Moskalenko, A. Lukasiak, V. Ptuskin, and W. Weber. Spontaneous Ferroelectric Order in a bent-core Smectic Liquid Crystal of Fluid Orthorhombic Layers. *Quantum* **2**, 72 (2011).
- [162] R. W. Perry, M. C. Holmes-Cerfon, M. P. Brenner, and V. N. Manoharan. Two-Dimensional Clusters of Colloidal Spheres: Ground States, Excited States, and Structural Rearrangements. *Physical Review Letters* **114**, 1 (2015).
- [163] V. Berk, J. C. Fong, G. T. Dempsey, O. N. Develioglou, X. Zhuang, J. Liphardt, F. H. Yildiz, and S. Chu. Molecular architecture and assembly principles of *Vibrio cholerae* biofilms. *Science* **337**, 236 (2012).
- [164] M. Duperthuy, B. E. Uhlin, and S. N. Wai. Biofilm recruitment of *vibrio cholerae* by matrix proteolysis. *Trends in Microbiology* **23**, 667 (2015).
- [165] H. T. Spanke, R. W. Style, C. François-Martin, M. Feofilova, M. Eisentraut, H. Kress, J. Agudo-Canalejo, and E. R. Dufresne. Wrapping of Microparticles by Floppy Lipid Vesicles. *Physical Review Letters* **125**, 198102 (2020).
- [166] H. G. Franquelim, A. Khmelinskaia, J. P. Sobczak, H. Dietz, and P. Schwille. Membrane sculpting by curved DNA origami scaffolds. *Nature Communications* **9**, 1 (2018).
- [167] C. Tschierske. Micro-segregation, molecular shape and molecular topology - Partners for the design of liquid crystalline materials with complex mesophase morphologies. *Journal of Materials Chemistry* **11**, 2647 (2001).

- [168] D. R. Link, G. Natale, R. Shao, J. E. MacLennan, N. A. Clark, E. Körblova, and D. M. Walba. Spontaneous formation of macroscopic chiral domains in a fluid smectic phase of achiral molecules. *Science* **278**, 1924 (1997).
- [169] T. Sekine, T. Niori, J. Watanabe, T. Furukawa, S. W. Choi, and H. Takezoe. Spontaneous helix formation in smectic liquid crystals comprising achiral molecules. *Journal of Materials Chemistry* **7**, 1307 (1997).
- [170] C. Greco and A. Ferrarini. Entropy-Driven Chiral Order in a System of Achiral Bent Particles. *Physical Review Letters* **115**, 147801 (2015).
- [171] M. Mathews, S. Kang, S. Kumar, and Q. Li. Designing bent-core nematogens towards biaxial nematic liquid crystals. *Liquid Crystals* **38**, 31 (2011).
- [172] A. Jákli. Liquid crystals of the twenty-first century – nematic phase of bent-core molecules. *Liquid Crystals Reviews* **1**, 65 (2013).
- [173] L. A. Madsen, T. J. Dingemans, M. Nakata, and E. T. Samulski. Thermotropic biaxial nematic liquid crystals. *Physical Review Letters* **92**, 145505 (2004).
- [174] K. Adlem, M. Čopič, G. R. Luckhurst, A. Mertelj, O. Parri, R. M. Richardson, B. D. Snow, B. A. Timimi, R. P. Tuffin, and D. Wilkes. Chemically induced twist-bend nematic liquid crystals, liquid crystal dimers, and negative elastic constants. *Physical Review E - Statistical, Nonlinear, and Soft Matter Physics* **88**, 022503 (2013).
- [175] G. Pająk, L. Longa, and A. Chrzanowska. Nematic twist-bend phase in an external field. *Proceedings of the National Academy of Sciences of the United States of America* **115**, E10303 (2018).
- [176] Y. Lansac, P. K. Maiti, N. A. Clark, and M. A. Glaser. Phase behavior of bent-core molecules. *Physical Review E - Statistical Physics, Plasmas, Fluids, and Related Interdisciplinary Topics* **67**, 011703 (2003).
- [177] G. M. Whitesides and B. Grzybowski. Self-assembly at all scales. *Science* **295**, 2418 (2002).
- [178] B. A. Grzybowski, C. E. Wilmer, J. Kim, K. P. Browne, and K. J. Bishop. Self-assembly: From crystals to cells. *Soft Matter* **5**, 1110 (2009).
- [179] D. Morpew and D. Chakrabarti. Programming hierarchical self-assembly of colloids: matching stability and accessibility. *Nanoscale* **10**, 13875 (2018).
- [180] M. A. Boles, M. Engel, and D. V. Talapin. Self-assembly of colloidal nanocrystals: From intricate structures to functional materials. *Chemical Reviews* **116**, 11220 (2016).
- [181] C. Hamon, S. Novikov, L. Scarabelli, L. Basabe-Desmonts, and L. M. Liz-Marzán. Hierarchical self-assembly of gold nanoparticles into patterned plasmonic nanostructures. *ACS Nano* **8**, 10694 (2014).

- [182] P. Fratzl and R. Weinkamer. Nature's hierarchical materials. *Progress in Materials Science* **52**, 1263 (2007).
- [183] A. R. Studart. Towards high-performance bioinspired composites. *Advanced Materials* **24**, 5024 (2012).
- [184] A. V. Pinheiro, D. Han, W. M. Shih, and H. Yan. Challenges and opportunities for structural DNA nanotechnology. *Nature Nanotechnology* **6**, 763 (2011).
- [185] A. Klug. The tobacco mosaic virus particle: structure and assembly. *Phil. Trans. R. Soc. Lond. B* 1–6 (1999).
- [186] S. H. Kim, S. Y. Lee, S. M. Yang, and G. R. Yi. Self-assembled colloidal structures for photonics. *NPG Asia Materials* **3**, 25 (2011).
- [187] S. Sun, C. B. Murray, D. Weller, L. Folks, and A. Moser. Monodisperse FePt nanoparticles and ferromagnetic FePt nanocrystal superlattices. *Science* **287**, 1989 (2000).
- [188] R. D. Cadena-Nava, M. Comas-Garcia, R. F. Garmann, A. L. N. Rao, C. M. Knobler, and W. M. Gelbart. Self-Assembly of Viral Capsid Protein and RNA Molecules of Different Sizes. *Journal of Virology* **86**, 3318 (2012).
- [189] I. A. Chen and P. Walde. From self-assembled vesicles to protocells. *Cold Spring Harbor perspectives in biology* **2**, 1 (2010).
- [190] et al. Alberts B, Johnson A, Lewis J. *Molecular Biology of the Cell* (New York: Garland Science), 4th editio edition.
- [191] D. J. Norris, E. G. Arlinghaus, L. Meng, R. Heiny, and L. E. Scriven. Opaline photonic crystals: How does self-assembly work? *Advanced Materials* **16**, 1393 (2004).
- [192] T. Hueckel, G. M. Hocky, J. Palacci, and S. Sacanna. Ionic solids from common colloids. *Nature* **580**, 487 (2020).
- [193] F. Li, D. P. Josephson, and A. Stein. Colloidal assembly: The road from particles to colloidal molecules and crystals. *Angewandte Chemie - International Edition* **50**, 360 (2011).
- [194] H. Lin, S. Lee, L. Sun, M. Spellings, M. Engel, S. C. Glotzer, and C. A. Mirkin. Clathrate colloidal crystals. *Science* **355**, 931 (2017).
- [195] Y. Min, M. Akbulut, K. Kristiansen, Y. Golan, and J. Israelachvili. The role of interparticle and external forces in nanoparticle assembly. *Nanoscience and Technology: A Collection of Reviews from Nature Journals* 38–49 (2009).
- [196] K. P. Velikov, C. G. Christova, R. P. A. Dullens, A. Van, S. Science, N. Series, T. Rice, and G. Apr. Layer-by-Layer Growth Growth of of Binary Colloidal Colloidal Crystals *Crystals* **296**, 106 (2020).

- [197] C. Fernández-Rico, M. Chiappini, T. Yanagishima, H. de Sousa, D. G. A. L. Aarts, M. Dijkstra, and R. P. A. Dullens. Shaping colloidal bananas to reveal biaxial, splay-bend nematic, and smectic phases. *Science* **369**, 950 (2020).
- [198] H. Qiu, Z. M. Hudson, M. A. Winnik, and I. Manners. Multidimensional hierarchical self-assembly of amphiphilic cylindrical block comicelles. *Science* **347**, 1329 (2015).
- [199] D. J. Lunn, J. R. Finnegan, and I. Manners. Self-assembly of "patchy" nanoparticles: A versatile approach to functional hierarchical materials. *Chemical Science* **6**, 3663 (2015).
- [200] A. H. Gröschel, A. Walther, T. I. Löbbling, F. H. Schacher, H. Schmalz, and A. H. Müller. Guided hierarchical co-assembly of soft patchy nanoparticles. *Nature* **503**, 247 (2013).
- [201] K. Miszta, J. De Graaf, G. Bertoni, D. Dorfs, R. Brescia, S. Marras, L. Ceseracciu, R. Cingolani, R. Van Roij, M. Dijkstra, and L. Manna. Hierarchical self-assembly of suspended branched colloidal nanocrystals into superlattice structures. *Nature Materials* **10**, 872 (2011).
- [202] S. E. Phan, W. B. Russel, J. Zhu, and P. M. Chaikin. Effects of polydispersity on hard sphere crystals. *Journal of Chemical Physics* **108**, 9789 (1998).
- [203] J. C. Crocker and D. G. Grier. Methods of digital video microscopy for colloidal studies. *Journal of Colloid and Interface Science* **179**, 298 (1996).
- [204] P. J. Ackerman, J. Van De Lagemaat, and I. I. Smalyukh. Self-assembly and electrostriction of arrays and chains of hopfion particles in chiral liquid crystals. *Nature Communications* **6**, 1 (2015).
- [205] G. P. Alexander, B. G. G. Chen, E. A. Matsumoto, and R. D. Kamien. Colloquium: Disclination loops, point defects, and all that in nematic liquid crystals. *Reviews of Modern Physics* **84**, 497 (2012).
- [206] S. Mühlbauer, B. Binz, F. Jonietz, C. Pfleiderer, A. Rosch, A. Neubauer, R. Georgii, and P. Boni. Skyrmion lattice in a chiral magnet. *Science* **323**, 915 (2009).
- [207] A. K. Yadav, C. T. Nelson, S. L. Hsu, Z. Hong, J. D. Clarkson, C. M. Schlepütz, A. R. Damodaran, P. Shafer, E. Arenholz, L. R. Dedon, D. Chen, A. Vishwanath, A. M. Minor, L. Q. Chen, J. F. Scott, L. W. Martin, and R. Ramesh. Observation of polar vortices in oxide superlattices. *Nature* **530**, 198 (2016).
- [208] B. Luo, A. Kim, J. W. Smith, Z. Ou, Z. Wu, J. Kim, and Q. Chen. Hierarchical self-assembly of 3D lattices from polydisperse anisometric colloids. *Nature Communications* **10**, 1 (2019).
- [209] Y. Xia, T. D. Nguyen, M. Yang, B. Lee, A. Santos, P. Podsiadlo, Z. Tang, S. C. Glotzer, and N. A. Kotov. Self-assembly of self-limiting monodisperse supraparticles from polydisperse nanoparticles. *Nature Nanotechnology* **6**, 580 (2011).

- [210] K. U. Deniz. Defects in liquid crystals (II). *Bulletin of Materials Science* **10**, 61 (1988).
- [211] D. Frenkel. Entropy-driven phase transitions. *Physica A* **263**, 26 (1999).
- [212] T. Kawasaki and H. Tanaka. Structural signature of slow dynamics and dynamic heterogeneity in two-dimensional colloidal liquids: Glassy structural order. *Journal of Physics Condensed Matter* **23** (2011).
- [213] M. Hu, C. P. Hsu, and L. Isa. Particle Surface Roughness as a Design Tool for Colloidal Systems. *Langmuir : the ACS journal of surfaces and colloids* **36**, 11171 (2020).
- [214] D. Lootens, H. Van Damme, Y. Hémar, and P. Hébraud. Dilatant flow of concentrated suspensions of rough particles. *Physical Review Letters* **95**, 1 (2005).
- [215] C. P. Hsu, S. N. Ramakrishna, M. Zanini, N. D. Spencer, and L. Isa. Roughness-dependent tribology effects on discontinuous shear thickening. *Proceedings of the National Academy of Sciences of the United States of America* **115**, 5117 (2018).
- [216] O. E. Petel and A. J. Higgins. Shock wave propagation in dense particle suspensions. *Journal of Applied Physics* **108** (2010).
- [217] M. Zanini, C. Marschelke, S. E. Anachkov, E. Marini, A. Synytska, and L. Isa. Universal emulsion stabilization from the arrested adsorption of rough particles at liquid-liquid interfaces. *Nature Communications* **8**, 1 (2017).
- [218] A. San-Miguel and S. H. Behrens. Influence of nanoscale particle roughness on the stability of pickering emulsions. *Langmuir* **28**, 12038 (2012).
- [219] D. J. Kraft, R. Ni, F. Smalenburg, M. Hermes, K. Yoon, D. A. Weitz, A. Van Blaaderen, J. Groenewold, M. Dijkstra, and W. K. Kegel. Surface roughness directed self-assembly of patchy particles into colloidal micelles. *Proceedings of the National Academy of Sciences of the United States of America* **109**, 10787 (2012).
- [220] M. Kamp, M. Hermes, C. M. Van Kats, D. J. Kraft, W. K. Kegel, M. Dijkstra, and A. Van Blaaderen. Selective Depletion Interactions in Mixtures of Rough and Smooth Silica Spheres. *Langmuir* **32**, 1233 (2016).
- [221] M. Zanini, C. P. Hsu, T. Magrini, E. Marini, and L. Isa. Fabrication of rough colloids by heteroaggregation. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **532**, 116 (2017).
- [222] H. Fessi, F. Puisieux, J. P. Devissaguet, N. Ammoury, and S. Benita. Nanocapsule formation by interfacial polymer deposition following solvent displacement. *International Journal of Pharmaceutics* **55**, 1 (1989).
- [223] S. Hornig, T. Heinze, C. R. Becer, and U. S. Schubert. Synthetic polymeric nanoparticles by nanoprecipitation. *Journal of Materials Chemistry* **19**, 3838 (2009).

- [224] Y. Wang, P. Li, T. T. D. Tran, J. Zhang, and L. Kong. Manufacturing techniques and surface engineering of polymer based nanoparticles for targeted drug delivery to cancer. *Nanomaterials* **6** (2016).
- [225] J. Tao, S. F. Chow, and Y. Zheng. Application of flash nanoprecipitation to fabricate poorly water-soluble drug nanoparticles. *Acta Pharmaceutica Sinica B* **9**, 4 (2019).
- [226] C. Zhao, S. Melis, E. P. Hughes, T. Li, X. Zhang, P. D. Olmsted, and E. Van Keuren. Particle Formation Mechanisms in the Nanoprecipitation of Polystyrene. *Langmuir* (2020).
- [227] M. Beck-Broichsitter, E. Rytting, T. Lehardt, X. Wang, and T. Kissel. Preparation of nanoparticles by solvent displacement for drug delivery: A shift in the "ouzo region" upon drug loading. *European Journal of Pharmaceutical Sciences* **41**, 244 (2010).
- [228] S. Galindo-Rodriguez, E. Allémann, H. Fessi, and E. Doelker. Physicochemical parameters associated with nanoparticle formation in the salting-out, emulsification-diffusion, and nanoprecipitation methods. *Pharmaceutical Research* **21**, 1428 (2004).
- [229] J. Opdam, R. Tuinier, T. Hueckel, T. J. Snoeren, and S. Sacanna. Selective colloidal bonds via polymer-mediated interactions. *Soft Matter* **16**, 7438 (2020).
- [230] V. Sharma, K. Park, and M. Srinivasarao. Shape separation of gold nanorods using centrifugation. *Proceedings of the National Academy of Sciences of the United States of America* **106**, 4981 (2009).
- [231] S. Beoemesma. Viscous force constant for a closed cylinder. *The Journal of Chemical Physics* **32**, 1632 (1960).
- [232] M. Mercedes Tirado, C. López Martínez, and J. García De La Torre. Comparison of theories for the translational and rotational diffusion coefficients of rod-like macromolecules. Application to short DNA fragments. *The Journal of Chemical Physics* **81**, 2047 (1984).
- [233] H. Gui, H. Chen, C. Y. Khripin, B. Liu, J. A. Fagan, C. Zhou, and M. Zheng. A facile and low-cost length sorting of single-wall carbon nanotubes by precipitation and applications for thin-film transistors. *Nanoscale* **8**, 3467 (2016).
- [234] M. J. Solomon and P. T. Spicer. Microstructural regimes of colloidal rod suspensions, gels, and glasses. *Soft Matter* **6**, 1391 (2010).
- [235] J. K. Dhont, K. Kang, H. Kriegs, O. Danko, J. Marakis, and D. Vlassopoulos. Nonuniform flow in soft glasses of colloidal rods. *Physical Review Fluids* **2**, 1 (2017).
- [236] Y. Xu, A. Atrens, and J. R. Stokes. A review of nanocrystalline cellulose suspensions: Rheology, liquid crystal ordering and colloidal phase behaviour. *Advances in Colloid and Interface Science* **275**, 102076 (2020).
- [237] N. M. James, H. Xue, M. Goyal, and H. M. Jaeger. Controlling shear jamming in dense suspensions: Via the particle aspect ratio. *Soft Matter* **15**, 3649 (2019).

-
- [238] V. Rathee, S. Arora, D. L. Blair, J. S. Urbach, A. K. Sood, and R. Ganapathy. Role of particle orientational order during shear thickening in suspensions of colloidal rods. *Physical Review E* **101** (2020).
- [239] B. Madivala, S. Vandebril, J. Fransaer, and J. Vermant. Exploiting particle shape in solid stabilized emulsions. *Soft Matter* **5**, 1717 (2009).
- [240] W. L. Born, Max and Wolf, Emil and Bhatia, A. B. and Clemmow, P. C. and Gabor, D. and Stokes, A. R. and Taylor, A. M. and Wayman, P. A. and Wilcock. *Principles of Optics: Electromagnetic Theory of Propagation, Interference and Diffraction of Light* (Cambridge University Press, 1999).
- [241] L. Tong, R. R. Gattass, J. B. Ashcom, S. He, J. Lou, M. Shen, I. Maxwell, and E. Mazur. Subwavelength-diameter silica wires for low-loss optical wave guiding. *Nature* **426**, 816 (2003).

List of Publications

To date the following publications based upon work in this thesis have been published or submitted:

C. Fernández-Rico, T. Yanagishima, A. Curran, D.G.A.L. Aarts and R.P.A. Dullens, *Synthesis of Colloidal SU-8 Polymer Rods using Sonication*, **Advanced Materials**, 31, 1807514 (2019). (Chapter 3).

C. Fernández-Rico, M. Chiappini, T. Yanagishima, H. de Sousa, D.G.A.L. Aarts, M. Dijkstra and R.P.A. Dullens, *Shaping colloidal bananas to reveal biaxial, splay-bend nematic and smectic phases*, **Science**, 369, 950–955 (2020). (Chapters 4 & 5).

C. Fernández-Rico, J. S. Urbach and R.P.A. Dullens, *Synthesis of Rough Colloidal SU-8 Rods and Bananas via Nanoprecipitation*, **Langmuir**, 37, 9, 2900–2906 (2021). (Chapter 7).

C. Fernández-Rico and R.P.A. Dullens, *Hierarchical self-assembly of colloidal bananas into vortex phases*, Accepted in **PNAS**, (2021). (Chapter 6).

Other publications from the author include:

S. Ouhamji, B. van Ravensteijn, C. Fernández-Rico, K. S. Lacina, A. P. Philipse and A. Petukhov, *Chiral colloids from isotropic spheres*, **ACS Nano**, 12, 12089 (2018).

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