Assembling anisotropic colloidal building blocks

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CHAPTER 1

INTRODUCTION

1.1 Colloids

Particles with at least one of their dimensions being on the order of a few nm to a few μm are referred to as colloids. Colloids can be different in phase, size, shape and material and are abundantly present in our daily life in soft material products such as drinks, foods, paint, medicine and cosmetics.[1] The particles can be a main ingredient of a product such as fat droplets in milk, but they can also be used to stabilize or encapsulate other components in, for example, shampoo or medicine. Additionally, these particles are frequently used to adapt the visco-elasticity and texture of the product.

When dispersed in a liquid, colloids are influenced by thermal fluctuations of the molecules in the liquid. These fluctuations ensure continuous movement of the particles called Brownian motion. In contrast to atoms and molecules, which are 100 to 100.000 times smaller in size, colloidal particles can be imaged with optical microscopy. This is a powerful tool, since the dynamics and interaction between the particles can be studied in real-time. Colloids are often referred to as big atoms and molecules, since their motion and phase behavior is similar.

Colloidal particles can be used as building blocks for larger structures. By varying the shape, size, material and surface chemistry of the colloids different materials can be formed.[2,3] Similations, theory and models are useful tools to predict into

FIGURE 1.1: Examples of macroscopic products that contain colloidal particles including; milk, paint, ice cream and medicine.

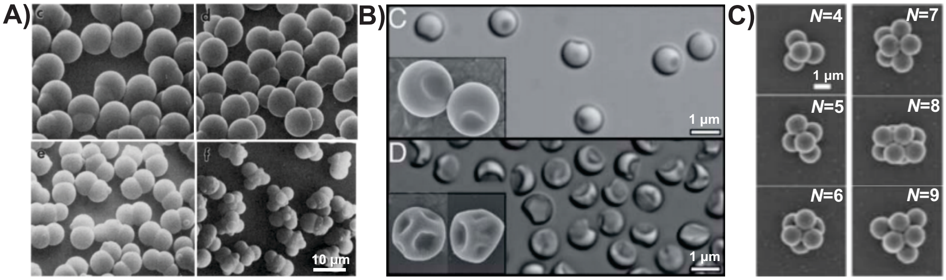

FIGURE 1.2: Polymer colloids with anisotropic shapes. A) Colloids with protrusions formed by swelling crosslinked polymer spheres with additional monomers. B) Dimpled colloids formed by buckling of an elastic shell around deformable polymer spheres. C) Colloidal clusters formed using an emulsion based evaporation method. Reprinted A) from ref. [4] and C) from ref. [5] with permission from John Wiley & Sons, copyright 1990 and 2004. B) was reprinted from ref. [6] with permission from the Royal Society of Chemistry, copyright 2011.

which structures the particles will assemble. Particles with anisotropic shapes or surface chemistry are particularly interesting, since these can assemble into novel structures which could lead to unusual material properties. Complex colloids are also promising building blocks for the assembly of 'smart' materials; materials that respond and adapt their structure to changes in their environment, such as thermo-repsonsive and light-responsive materials.

1.2 Synthesis and fabrication

Synthesis of anisotropic colloids

Colloids can be synthesized out of various materials including metals, polymers and ceramics. In this thesis polymer colloids are mainly considered. Polymer spheres of low polydispersity can be synthesized using various methods such as emulsion or dispersion polymerization.[7,8] The complexity of the particles can be increased by adapting the shape or surface properties of the polymer spheres. For example, by swelling crosslinked polymer spheres with additional monomers one or more protrusions can be formed on the seed particle, resulting in dumbbell, snowman or popcorn-like shapes (see Figure 1.2A).[9,10] The protrusions are formed due to the elastic stress exerted on the crosslinked polymer network upon swelling.[4] The shape of the final particle is determined by the crosslink density and surface properties of the seed particle, the concentration of added monomers and the dispersion medium.

Instead of protrusions, dents can also be formed on the spheres to yield

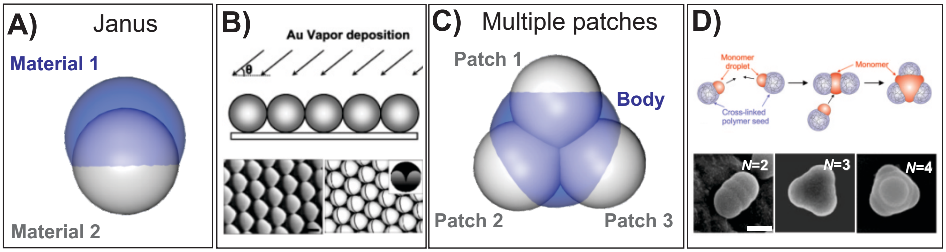

FIGURE 1.3: Patchy particles. A) Illustration of a Janus particle consisting of two different materials. B) Fabrication method for Janus particles based on the deposition of gold on one side of spheres. Scalebar is 2 μm. C) Illustration of a patchy particle with three patches and a 'body' covering the center of the cluster. D) Fabrication method for multi-patched particles based on the assembly of colloids with liquid protrusions. Scalebar is 200 nm. Reprinted B) from ref. [15] and D) from ref. [16] with permission from the American Chemical Society, copyright 2008 and 2009.

anisotropy. Dimpled and crumpled particles can be obtained by buckling an elastic shell around a spherical polymer particle (see Figure 1.2B). Buckling is induced by a pressure difference between the inside and outside of the shell due to a reduction of the volume inside the shell upon polymerization.[6,11,12]

A third example to obtain anisotropically shaped polymer particles is a cluster preparation method, where uniform spheres are assembled into colloidal clusters (see Figure 1.2C). The colloidal clusters can be formed by introducing depletion forces between the spheres[13] or by evaporation of emulsion droplets containing a number of spheres[5,14]. The geometry of the cluster depends on the formation mechanism, the number of spheres in the cluster and the wetting properties of the seed particles.

Fabrication of patchy particles

A separate class of anisotropic colloids are patchy particles. Patchy particles are defined as particles with precisely controlled patches of varying surface and interaction properties.[17–19] These particles are interesting since directional interactions could lead to, for example, reversible binding and open crystal structures.[20,21] We here distinguish between Janus particles, defined as colloid-sized particles with two regions of different surfacechemical composition[22] and particles with multiple patches, see Figure 1.3A and 1.3C, respectively.

The term Janus particles was introduced by P.G. de Gennes during his Nobel Lecture in 1992, referring to the two-faced Roman god Janus. Different methods are known to fabricate Janus particles including glancing angle deposition, where uniform particles are partly sputtercoated with a second material[15] (Figure 1.3B)

and chemical functionalization of part of the particle surface by adding reactive molecules to spheres partly immersed in emulsified molten wax[23]. Patchiness can also be achieved by swelling polymer particles with a different monomer resulting in two different 'faces' due to phase-separation.[24]
On colloids with uniform surface chemistry, patchiness can be introduced by changing the particle shape. For example, dimpled colloids can act as lock-and-key structures using the depletion interaction.[6,11] Depletion was induced by addition of a second colloidal component with the dimensions of the dimples. The overlap volume in the dimple was therefore large resulting in attraction between the dimple and the second colloidal component in the presence of depletant.
The fabrication of particles with multiple patches is often achieved by assembling smaller colloidal spheres into larger structures. For example, colloidal spheres with liquid protrusions can be assembled into patchy particles by merging of the protrusions into a larger droplet, which forms the 'body' of the patchy particle (Figure 1.3C and 1.3D).[16] The part of the spheres protruding from this droplet can act as patches. Anisotropic colloidal clusters can also be adapted to obtain patchy particles by swelling the clusters with an additional monomer, which could form the 'body' of the patchy particle.[25]

Synthesis and fabrication methods have advantages and disadvantages. Preferably, a method yields particles of uniform shape, size and surface chemistry and can be used to obtain a variety of particles with different properties. By preference, a non-toxic medium is used and the synthesis is performed in bulk to obtain a high yield.

1.3 Particle interactions

In a colloidal dispersion, both attractive and repulsive forces act on the colloids. The net interaction energy between colloids is defined as,

$$U(r)_{net} = U(r)_{att} + U(r)_{rep}, \tag{1.1}$$

where $U(r)_{att}$ is the attractive interaction energy and $U(r)_{rep}$ is the repulsive interaction energy. A stable colloidal dispersion is obtained when the net interaction energy is positive and a negative net interaction energy leads to aggregation of the particles. One source of attraction between all colloidal particles stems from the van der Waals forces. The van der Waals interaction energy between two spheres at separation distance r of equal radius R, with R»r, is defined as,

$$U(r)_{vdW} = -\frac{AR}{12r}, \tag{1.2}$$

where A is the Hamaker constant.[26] Equation 1.2 indicates that van der Waals forces are long-ranged, but typically only at short r strong enough to compete

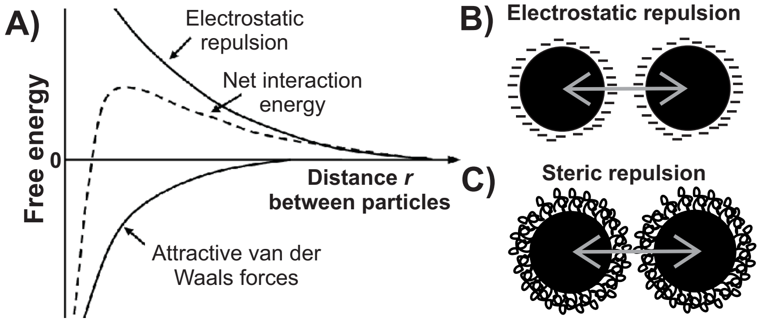

FIGURE 1.4: Colloidal stability. A) The free energy profile of two colloids at different separation distance *r*. At short distances particles attract due to van der Waals forces. Aggregation can be prevented by prohibiting close contact between the particles by; B) Charging the surface of the colloids resulting in electrostatic repulsion or by C) The introduction of a molecular layer of polymers at the surface of colloids.

with other forces. Aggregation can therefore be prevented by prohibiting close contact of the particles (Figure 1.4A). This can be achieved by introducing a repulsive Coulomb force by charging the colloid surface. A repulsive electric double layer will be formed around the charged particles with bound and diffusive ions from the medium accumulated at the surface. The electrostatic double layer interaction energy for two spheres with radius R at a separation distance r is defined as,

$$U(r)_{elec} = \frac{ZRe^{-\kappa r}}{2}, \tag{1.3}$$

where Z is the interaction constant, which is analogous to the Hamaker constant A, and depends only on the surface properties of the particles.[26] κ^{-1} is the Debye length which describes the characteristic length or 'thickness' of the diffuse electric double layer near the charged surfaces and is defined as,

$$\kappa^{-1} = \left(\frac{\epsilon_0 \epsilon_r k_B T}{e^2 \rho_i z_i^2} \right)^{0.5}, \tag{1.4}$$

where ϵ_0 is the vaccuum permittivity, ϵ_r the relative static permittivity, e the dielectric constant of the medium and ρ_i the ionic concentration of ions i with valency z_i in the bulk. When κ^{-1} is large enough, $U(r)_{elec} > U(r)_{vdW}$ resulting in a positive net interaction energy and thus a stable colloidal dispersion.
Colloids can also be stabilized sterically, by introducing a molecular, often polymer, layer at the surface of the colloids as illustrated in Figure 1.4C. The molecular layer prohibits close contact and thus attraction by van der Waals forces.

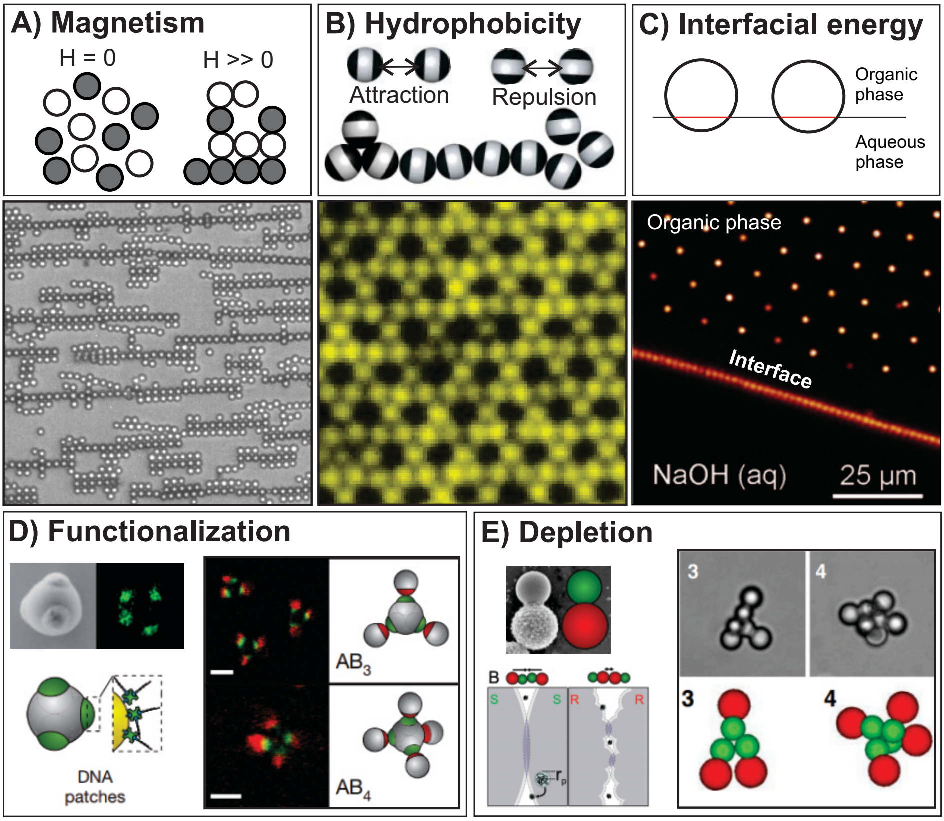

FIGURE 1.5: Microscopy images of self-assembled micron-sized polymer colloids using different assembly mechanisms. A) Dia- and superparamagnetic polymer spheres self-assembled in networks of alternating strings by aligning oppositely to an external magnetic field H. From ref. [27]. B) Triblock Janus particles arranged on a Kagome lattice due to the hydrophobic attraction between isolated patches on the spheres. C) Colloids adsorbed to a spherical organic-aqueous interface to decrease the interfacial energy. D) Particles with patches functionalized with complementary single DNA-strands assembled into colloidal molecules due to DNA binding. E) Dumbbell colloids with a rough and a smooth surface lobe, self-assembled by depletion forces. Reprinted B) from ref. [21] and D) from ref. [25] with permission from Springer Nature, copyright 2011 and 2012. C) and E) were reprinted from ref. [28] and ref. [29], respectively, with permission from the National Academy of Sciences U.S.A., copyright 2007 and 2012.

1.4 Colloidal self-assembly

Self-assembly mechanisms

Due to the Brownian motion of colloids and their tunable interaction profile colloids can self-assemble into larger structures. To obtain colloidal crystals with rich phase behavior or optical or mechanical properties anisotropic colloids or mixtures of different particles are often used. Self-assembly can be achieved via different assembly mechanisms. For example, two-dimensional networks of alternating strings of dia- and superparamagnetic polymer spheres were realized using an external magnetic field.[27]. The dia- and superparamagnetic particles aligned oppositely to the external magnetic field yielding a square packed network (see Figure 1.5A). In Figure 1.5B the hydrophobic attraction between parts of triblock Janus particles was used to form two-dimensional Kagome lattices of low packing density.[21] Colloids can also assemble at an interface between liquid and gas[30] or two immiscible liquids, as shown in Figure 1.5C for polymer spheres at an aqueous-organic interface[28]. Binding a particle to an interface decreases the interfacial area A and thus the interfacial energy, which is defined as, $E = \gamma A$, where γ is the surface tension (Figure 1.5C). Particle stabilized emulsions are referred to as Pickering emulsions, which are used in a variety of application fields including foods, cosmetics and medicine.[31]
Three-dimensional self-assembled structures were, for example, formed by particles functionalized with single DNA-strands. Mixing patchy particles with complementary DNA-strands resulted in the formation of colloidal molecules due to DNA binding (Figure 1.5D).[25] The depletion interaction was also be used to form three-dimensional structures. By introducing depletant to dumbbell shaped particles with a rough and a smooth lobe attraction between the smooth lobes was induced (see Figure 1.5E).[12,29,32] The shape of the structures depended on the number of particles in the cluster and the size ratio between the two lobes.

These examples emphasize the self-assembly possibilities of colloids. By tuning and controlling the physical properties of the colloidal building blocks and the assembly pathway, a variety of colloidal structures can be formed. This could lead to materials with advanced properties such as high material strength or 'smart' materials that change their structure under the influence of light, temperature, pH or other environmental parameters.

Colloidal crystals and defects

Colloidal crystals are ordered arrays of monodisperse colloids, where the crystal order can be described by repeating subunits.[35] Spheres often order on a hexagonal lattice where, on a planar surface, all spheres are surrounded by six neighboring spheres. Defects in hexagonal crystals appear for spheres not surrounded by

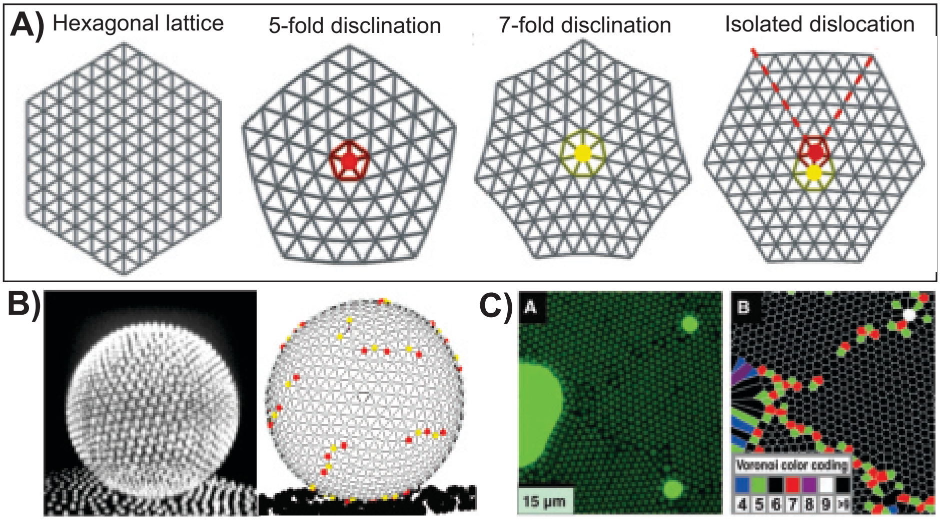

FIGURE 1.6: Colloidal crystals and crystal defects. A) Illustration of a hexagonal lattice, 5-fold and 7-fold disclinations and an isolated dislocation. B) Confocal microscopy image and Delauney triangulation of a spherical oil droplet stabilized in an aqueous phase by interfacially bound pMMA spheres. The diameter of the droplet $\sim 60\ \mu$m. A) and B) were reprinted from ref. [33] with permission from Springer Nature, copyright 2012. C) Confocal microscopy image and Voronoi diagram of an planar hexagonal crystal of spheres distorted by large impurities. The impurities are connected by grain boundaries. Reprinted from ref. [34] with permission from The American Association for the Advancement of Science, copyright 2005.

six spheres, which results in disclinations and dislocations, see Figure 1.6A.[33,36] A collection of dislocations can result in the formation of a grain boundary.

In a monodisperse colloidal system crystal defects can be induced by vacancies or interstituals, substrate curvature or impurities. The number and type of defects originating from substrate curvature depends on the sign and degree of the curvature.[33,37] A confocal microscopy image of a colloidal crystal of polymer spheres adsorbed to a spherical organic-aqueous interface is shown in Figure 1.6B.[37] The fluorescent colloids arranged in a regular pattern and stabilize the organic droplet in the aqueous phase. The curvature of the interface induced the formation of topological defects; while most spheres are surrounded by six neighboring spheres, some spheres have only five or seven neighbors, resulting in disclinations, dislocations and short grain boundaries.

Large spherical impurities in a crystal of spheres induced the formation of large grain boundaries, as shown in Figure 1.6C.[34] The distortion of the hexagonal order by the impurities also frustrated the crystal growth. The presence of dumbbells in a hexagonal crystal of spheres also strongly affected the crystal properties. The dumbbells formed dislocation cages that restricted the dislocation motion and introduced glassy dynamics.[38,39]

The presence of defects influences the crystal properties, such as the orientation, mechanical strength and crystal melting and formation processes. By controllably introducing defects by substrate curvature or doping with impurities, the properties of crystals and thus materials can be tuned.

1.5 This thesis

In this thesis colloidal polymer spheres are used as a starting point to form anisotropic and patchy particles and to assemble and distort colloidal crystals of spheres.

In **Chapter 2** a synthetic method is presented that can be used to tune the shape and surface roughness of polystyrene particles. Linear polystyrene spheres were swollen with styrene and 3-(Trimethoxysilyl)propyl methacrylate(TPM) at different styrene:TPM ratio's. At TPM concentrations $\geq 50\%$ dented colloids were formed. We hypothesize that the TPM molecules formed a shell on the surface of the particles since the silane groups in TPM prefer to be in contact with the water. At a sufficient shell thickness the TPM shell buckles when the core volume decreases, which occurs during polymerization. The surface roughness of the particles was controlled by an additional chemical component, hydroquinone, which inhibits the formation of small secundary nuclei during polymerization. Smooth surfaces were formed in the presence of hydroquinone and rough surfaces when hydroquinone was absent.

In **Chapter 3** we present a method, the "colloidal recyling" method, to reconfigure aggregates of polymer spheres into patchy particles. Colloidal aggregates were formed by the de-stabilization of charge-stabilized colloids due to the addition of salt. Reconfiguration of the aggregates was achieved by introducing organic liquid with affinity for the aggregates to the colloidal dispersion. We hypothesize that the organic liquid deposited as droplets at the contact areas between the spheres, which drastically lowers the van der Waals attraction. The spheres in the clusters could therefore rearrange their position, which lead to compact patchy shapes once the small droplets merged into one larger droplet. With this method bulk quantities of patchy particles can be assembled of various consistencies since the colloid and swelling material can be varied.

In **Chapter 4** we investigated how polystyrene spheres with different crosslink density were deformed by the capillary forces exerted by the organic droplets on the particles during reconfiguration. Clusters of seeds with low crosslink density completely merged into larger spheres, whereas the shape of the original spheres was increasingly preserved at increasing crosslink density.

In **Chapter 5** the knowledge of Chapter 3 and 4 was used to form complex particles with different patch types by combining mixtures of spheres with different sizes and crosslink density. Unique shapes were obtained by combining soft and rigid spheres and a combination of spheres with size ratio 4.6 resulted in particles with both chemical and physical patchiness.

In **Chapter 6** we assembled colloidal crystals of highly repulsive spheres at a planar water-oil interface. We introduced anisotropic impurities, dumbbells, of different lengths to the crystal and studied the dynamics and position of the dumbbell and crystal defects induced by these impurities. The crystal distortion was determined by the length of the dumbbell, where the number of neighboring spheres increased with the length of the dumbbell. We also studied the effect of the confinement of the crystal on the rotational and translational motion of the dumbbells. The motion of confined dumbbells was largely restricted and a preferred dumbbell orientation with respect to the crystal orientation was measured which was determined by the interaction energy profile between the dumbbell and the surrounding spheres.