Assembling anisotropic colloidal building blocks

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Summary

In the *Summary* I will explain to a general public what I've studied in the past four years, how I studied this and why this research is important. Science is something you do together, so with 'I' I also refer to my supervisor, colleaques and the students that contributed to the research presented in this thesis. First, I will shortly introduce the scientific field of colloidal matter followed by a specific explanation of the research I've performed during my PhD. Finally, I'll summarize all my results creatively in a single illustration.

During my PhD-research I studied the behavior of micron-sized particles, so-called colloids. Colloids are not visible by eye since their dimensions are 100-10000 times smaller than the thickness of a hair. To visualize these particles we use instruments such as light and electron microscopes. To measure properties such as the electrical charge of the particles and the visco-elasticity of colloidal suspensions we use analytical methodes such as dynamic light scattering and rheometry.
When scientists study the 'behavior' of materials and particles they investigate the chemical and physical properties of the material. What shape does the particle have? What is the density? Size? Which molecules are present at the surface of the material? And how does the particle respond to its environment? How do particles interact between themselves and can we use this to assemble them into larger structures? All these questions and answers are required to understand why a system 'behaves' in a certain way.

And why do we study colloids? Without many of you realizing it colloids are abundantly present in our daily life. We drink and eat them, we put them on our skin and hair as creams or on the wall in paint. The colloids determine to a great extent the properties of a product. For example, the fatty colloids in milk give milk it's white appearence and the colloids in toothpaste make sure the paste only comes out when you push on the tube. Colloids are therefore crucial components in so-called 'soft materials'.
Insight and understanding of the properties of colloids is required to develop new materials with desired properties such as resistance to extreme force. Scientist are

nowadays very interested in the development of 'smart' materials, materials that respond and adapt to their environment. An example is a temperature sensitive material. A capsule of this material could be programmed to controllably open and close to deliver a medicine locally in the human body. To develop these materials a fundamental understanding of the building blocks is crucial. With my PhD research I've added a small piece to the scientific puzzle of this fundamental knowledge.

The title of my thesis **'Assembling Anisotropic Colloidal Building Blocks'** reveals what my piece of the puzzle is about. As explained, colloids can be used as building blocks for complex materials and structures and **'Colloidal Building Blocks'** refers to this. The building blocks can have different sizes and shapes and everything non-spherical is referred to as **'Anisotropic'**. The colloidal building blocks can be assembled into larger structures, hence the term **'Assembling'**.

In **Chapter 2** I've developed a way to make colloidal building blocks of different shapes and with different surface roughness. In science, the fabrication of molecules or colloids is called *synthesis*. The shape of the colloids was tuned by changing the volume of spheres during synthesis. By first increasing the volume by swelling, followed by decreasing the volume the shell around the spheres collapsed forming one or more dents. The resulting shape is comparable to a collapsed football. The surface roughness on the particles was controlled by adding an additional chemical component, hydroquinone, during the synthesis. Without hydroquinone small nanoparticles were formed that adhered to the larger colloidal spheres introducing surface roughness. By adding hydroquinone the formation of the nanoparticles was surpressed resulting in semi-rough and smooth spheres. Smooth and rough spheres give rise to different properties in suspension. A creme with rough particles is for example less easily spread compared to a creme with smooth particles.

In **Chapter 3** a new method, the *Colloidal Recycling method*, is presented to assemble simple spheres into clusters with complex shapes. The cluster shapes are anisotropic and depend on the number of spheres forming the clusters. The Colloidal Recycling method involves two steps. In the first step spheres are made attractive, sticky, resulting in random clusters of spheres upon collision. In the second step an additional liquid is added with affinity for the colloids. The liquid deposits as small droplets at the contact areas between the spheres in the clusters and acts as lubricating oil between the spheres. The spheres can now slide and/or roll over one another and by merging of the small droplets into one cluster-spanning droplet the clusters reconfigure into compact shapes. Parts of the spheres are protruding from the cluster-spanning droplet and these parts are called patches, areas of a particles that can be made attractive. These clusters are therefore referred to as *patchy particles*. The Colloidal Recycling method is unique since large quantities can be synthesized and the type of colloid and swelling material is highly variable. This offers the opportunity to assemble a diverse range of patchy particles. The assembled patchy particles are interesting as larger, more complex, building blocks to fabricate macro-structures.

In **Chapter 4** I explore the *Colloidal Recycling method* by investigating the effect of the small droplets between the two spheres on the shape of the original spheres and the geometry of the reconfigured cluster. Droplets prefer a spherical shape, since this minimizes the contact area of the liquid droplet with the environment. On the other hand, the spheres try to spread the droplet on their surfaces which would deform the droplet. Our results indicated that a balance is found, where the capillary forces originating from the droplet are strong enough to deform spheres. Soft spheres are so strongly deformed by these forces that the clusters completely merge into one large ball. Rigid spheres deform less resulting in anisotropically shaped patchy particles. We showed that we can use the rigidness of the spheres to control the shape of the final patchy particle.

In **Chapter 5** the knowledge of Chapter 3 and 4 are combined to obtain patchy particles of complex shapes. This was achieved by applying the Colloidal Recycling method to mixtures of spheres with different size and rigidity. By combining soft and rigid spheres unique shapes were obtained where the soft spheres had deformed while the rigid spheres were not. The shape of the reconfigured clusters also depended on the size ratio between the spheres. Spheres of 1 micrometer and 0.23 micrometer, a size ratio of 4.6, formed structures where the larger spheres determined the geometry of the cluster while the small spheres positioned at the contact areas of the larger spheres. The small spheres therefore formed a 'jacket' around the cluster. The 'jacket' introduced surface roughness to the clusters which offers additional opportunities for the self-assembly of these patchy particles into larger structures.

In **Chapter 6** I studied how highly repulsive spheres ordered at an interface between water and oil. Similar to soap molecules, surfactants, colloids attach to water-oil interfaces. At the interface the colloids form ordered patterns, so-called *colloidal crystals*. The spheres were all surrounded by 6 other spheres, which we call hexagonal ordering. We, however, purposely distorted the hexagonal order by introducing elongated impurities, dumbbells, in the hexagonal crystal. The *crystal defects* induced by these distortions depended on the length of the dumbbells. For high particle densities at the interface, the dumbbells could not move anymore, the translational and rotational motion was restricted, and the orientation of the dumbbells in this confined space also depended on the length of the dumbbell. These impurities can be used to change the properties of colloidal crystals such as the mechanical strength. The results provide insight in the formation of defects formed by anisotropic impurities in crystals, which is also observed in biological systems such as virus capsids.

Finally, I've illustrated my PhD research in a creative way, using a cake: