Popular scientific summary

Particles that are a hundred- to ten thousand times smaller than the width of a hair are commonly referred to as colloidal particles. Colloidal particles occur in a variety of products, like foodstuffs (marmelade and dairy products), construction materials (cement) and stained glass. In water, these particles are strongly affected by the Brownian force: an force that was discovered in 1827 by the botanist Robert Brown, when he was using a microscope to look at pollen in water. He discovered that the pollen were vibrating randomly throughout the sample, which turned out to be caused by thermal energy. It became clear that, the smaller the particle, the stronger these vibrations, and we know now that atoms experience this vibration very strongly. Currently, scientists try to understand and describe the behavior of atoms, which is made difficult by the minute size of atoms. Therefore, scientists often study colloids, that exhibit behavior similar to atoms, but are much larger. This larger size allows us to image them with for instance microscopy.

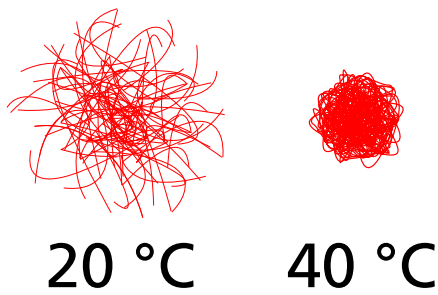

Figure I.1: Schematic drawing of a microgel at different temperatures.

In this thesis we study microgels, a type of colloid that consists of a polymer network. If these networks are placed in water, they swell up into a soft network depicted in Figure I.1. They experience a Brownian force, which is strong enough to overcome gravity. In other words, microgels distribute through the volume and will not deposit to the bottom. Our type of microgels have the remarkable property of being swollen at room temperature, but then collapse above 32 °C. This versatility allows us to use one colloid type for mimicking and studying a wide array of atomic behavior.

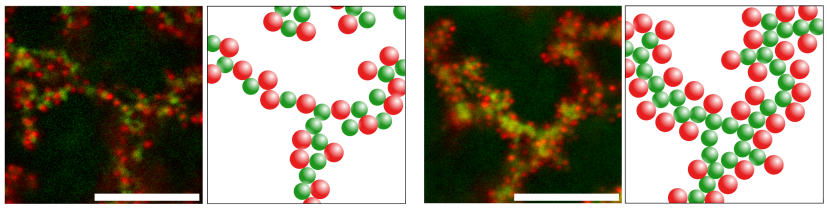

Figure I.2: Microscopy pictures of an identical microgel mixture, heated using two different methods, with schematic representations for clarification. On the left, the mixture is heated rapidly and the red and green microgels bind the first particle they encounter. On the right, a slow temperature increase gives enough time for the green particles to form a green network, after which the red particles deposit on that network. The scale bars represent 10 μm. For comparison, the width of a human hair is approximately 150 μm.

This work studies the collective behavior of microgels. At room temperatures, the microgels behave repulsively, and particles repel each other when at close distances. Collapse causes a particle attraction, and two microgels at high temperatures form a strong bond. At room temperature, the concentration of microgels decides their behavior, and a low concentration allows microgels to freely move through the water. A higher concentration forces microgels to organize into a crystal, to give each particle the largest amount of free space. Heating a microgel system causes them to collapse and form bonds with neighboring particles. Given that the concentration is high enough, the particles form long elastic strands and the system at large will start behaving elastically.

In this work, we study mixtures of two different microgels: one type that collapses at 32 °C and one that collapses at 45 °C. This collapsing behavior yields interesting network behavior: if a mixture is heated to 40 °C, the first particle will form an elastic network, while the second particle still behaves repulsively. Heating the system further to 50 °C makes the second particle to deposit on the already present first particle network, decorating the first strand. Raising the temperature quickly causes the first particle to not have the time to form an network before the second particle collapses, and all particles bind other particles randomly, a process we call homo-gelation. Microscopy pictures of these two types of gels can be found in Figure I.2. The decorated gel networks are stronger than the networks obtained with homo-gelation, allowing us to understand the rigidity of gel networks.

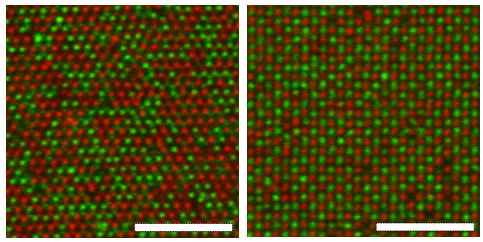

Figure I.3: Microscopy pictures of the same microgel mixture at different salt concentrations. On the left, a lot of salt is present and the green-red attractions are weak, causing the two types of particles to organize randomly. On the right, only a little salt is present and the green-red attractions are strong, and the two particle types organize to put red particles closest to green particles, and vice versa. The scale bars are 10 μm lang.

We also study binary crystals, which are able to transform into another crystal by adding or removing salt. We use positively charged red particles and negatively charged green particles. This causes an attraction between red and green particles, with red-red and green-green combinations repelling. Salt weakens these charge-based forces, and the addition of salt can form a crystal where red and green are distributed randomly, due to there being no preference as to which neighbor a particle has. Removing salt causes the red-green attraction, and particles organize themselves to have as many red-green neighbors as possible.