UNIVERSITY OF TURKU

Colloidal self-assembly: Passive vs. Active

Materials Engineering

Bachelor's thesis

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29.4.2025

Turku

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Subject: Materials Engineering
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Title: Colloidal self-assembly: Passive vs. Active
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Number of pages: 32 pages
Date: 29.4.2025

Abstract

Colloidal self-assembly is the spontaneous organization of colloids into an ordered structure. Colloids are nano- to micrometre-sized particles that are suspended in a solvent. In passive colloidal self-assembly colloidal particles interact and organize into an ordered structure that minimizes the system's free energy. In active colloidal self-assembly an external stimulus is directed to the system which enables the colloids to move or interact in desired ways leading to the formation of an ordered structure.

This thesis provides an overview of both passive and active colloidal self-assembly with discussion on the different interactions that drive passive colloidal self-assembly and the different external stimuli that drive active colloidal self-assembly. Several theoretical models that explain colloidal self-assembly are also discussed.

To further investigate passive colloidal self-assembly, molecular dynamics simulations using LAMMPS were run on patchy colloids at varying temperatures. The goal of these simulations was to understand how temperature affects the assembly process.

The simulation results demonstrate that temperature greatly affects colloidal self-assembly. At lower temperatures the assembly proceeds more slowly, but results in stable ordered structures. Higher temperatures disrupt the assembly process leading to disordered and unstable assemblies.

Key words: Colloids, self-assembly, passive colloidal self-assembly, active colloidal self-assembly, DLVO theory, LAMMPS simulations

Kanditutkielma

Oppiaine: Materiaalitekniikka
Tekijä: Lauri Hätinen
Otsikko: Kolloidien itsejärjestäytyminen: Passiivinen vs. Aktiivinen
Ohjaaja: Narayan Gupta
Sivumäärä: 32 sivua
Päivämäärä: 29.4.2025

Tiivistelmä

Kolloidien itsejärjestäytyminen on kolloidien spontaani järjestäytyminen säännölliseksi rakenteeksi. Kolloidit ovat nano- tai mikrometrin kokoisia hiukkasia, jotka ovat suspensiossa liuoksessa. Passiivisessa kolloidien itsejärjestäytymisessä kolloidiset hiukkaset ovat vuorovaikutuksessa ja järjestäytyvät säännölliseksi rakenteeksi, joka minimoi järjestelmän energian. Aktiivisessa kolloidien itsejärjestäytymisessä järjestelmään kohdistetaan ulkoinen ärsyke, joka mahdollistaa kolloidisten hiukkasten liikkeen tai vuorovaikutukset, mikä johtaa säännöllisen rakenteen muodostumiseen.

Tämä kandi tarjoaa katsauksen sekä passiiviseen sekä aktiiviseen kolloidien itsejärjestäytymiseen. Se käsittelee vuorovaikutuksia, jotka ohjaavat passiivista itsejärjestäytymistä, sekä ulkoisia ärsykkeitä, jotka ajavat aktiivista itsejärjestäytymistä. Lisäksi käsitellään useita teoreettisia malleja, jotka selittävät, miksi kolloidien itsejärjestäytyminen tapahtuu.

Passiivista kolloidien itsejärjestäytymistä tutkittiin tarkemmin suorittamalla molekyylidynamiikkasimulaatioita LAMMPS-ohjelmalla laikkukolloideille eri lämpötiloissa. Simulaatioiden tavoitteena oli ymmärtää, miten lämpötila vaikuttaa itsejärjestäytymisprosessiin.

Simulaatiotulokset osoittivat, että lämpötilalla on merkittävä vaikutus kolloidien itsejärjestäytymiseen. Alhaisissa lämpötiloissa järjestäytyminen etenee hitaammin, mutta johtaa stabiileihin säännöllisiin rakenteisiin. Korkeat lämpötilat häiritsevät järjestäytymistä, mikä johtaa epäjärjestyneisiin ja epävakaisiin rakenteisiin.

Avainsanat: Kolloidit, itsejärjestäytyminen, passiivinen kolloidien itsejärjestäytyminen, aktiivinen kolloidien itsejärjestäytyminen, DLVO teoria, LAMMPS simulaatiot

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1 Introduction

1.1 Colloids

Colloids are comprised of colloidal particles and a solution where these particles are suspended [1]. Colloidal particles have uniform size, a specific shape and distinct properties [2]. These particles are nanometre or micrometre in size [2]. Examples of colloids are blood where red blood cells are suspended in water and fog where water droplets are dispersed in air [3].

The colloidal particles are not static in the solvent. The particles are constantly hit with immeasurable collisions from all sides from the solvent molecules. These collisions are random in direction and magnitude. This means that the force acting on the colloidal particle is not zero meaning that the particle is moving in a random direction with a random magnitude. Due to the collisions, the direction and magnitude change constantly. This motion is called Brownian motion. [1]

There are many types of colloids. Depending on the properties of these colloids they interact with each other in different ways. Colloids can interact with each other with interactions such as depletion forces, electrostatic forces or van der Waals forces. These interactions are quick meaning the time it takes for colloids to start interacting is around a microsecond to a nanosecond. [4]

1.2 Self-assembly

Imagine a scenario where all the parts needed for a working car are in a box. After a while the parts spontaneously assemble into a working car. Of course, this is fiction but in real life particles do spontaneously organize themselves into ordered structures [1]. This process is called self-assembly and when the particles are colloids it is called colloidal self-assembly. The ordering arises from weak and non-covalent interactions like depletion or Van Der Waals forces between the colloidal particles or even gravity force [5]. If self-assembly is directed by the properties of the colloids and their interactions it is called passive colloidal self-assembly [4]. If the self-assembly is directed by external stimuli it is called active colloidal self-assembly [4].

1.3 Applications

Colloidal self-assembly has a wide range of applications. Intricate control over the design of the colloids allows scientists to design specific self-assembly processes which enables different

applications. With active colloidal self-assembly even more control can be achieved leading to many applications using active instead of passive colloidal self-assembly. Some of these applications are colour displays, rewritable papers, information decryption, anticounterfeiting, energy storage and actuators.[2]

1.4 Passive self-assembly

In passive self-assembly colloidal particles self-assemble due to the system trying to achieve maximum entropy and minimal free energy in the system [5]. This equilibrium state is achieved because the colloidal particles interact with each other and form an ordered structure [5]. These interactions are determined by the characteristics of the particles used [6]. For example, using particles with cavities, magnetic properties or different shapes allows them to interact in desired ways [6]. This is why colloids are an amazing choice as they can be designed to have specific properties and characteristics.

1.5 Active self-assembly

In active self-assembly colloidal particles self-assemble into ordered structures due to external stimuli like light or a magnetic field. Continuous external energy is directed to the system meaning that, unlike passive colloidal self-assembly, the system remains out-of-equilibrium. This external energy is converted into mechanical motion as well as enhances or overpowers the interactions between colloidal particles. With the movement and interactions enabled by the external energy, colloidal particles organize into an ordered structure. Some of these ordered structures disassemble when the external energy is removed. The colloids' properties also affect how they respond to the external stimuli. This means that the interactions can be tuned more precisely than in passive self-assembly. [4]

1.6 Objectives

The objective of this thesis is to get an understanding of both active and passive colloidal assembly and the differences between them. This is achieved by exploring different interactions between colloids and models that use these interactions to explain why colloids self-assemble. The effect of different external stimuli on colloidal self-assembly is studied to get an understanding of active colloidal self-assembly.

Another objective is to understand the effect of temperature on colloidal self-assembly. This is achieved by running simulations on colloidal self-assembly at various temperatures and analysing the results.

1.7 Summary

Colloids are comprised of nanometre to micrometre sized particles that are dispersed in a solvent while self-assembly is the spontaneous organization of particles into an ordered structure. In passive colloidal self-assembly this ordering arises from the colloids interacting and forming an ordered structure to minimize the free energy in the system. In active colloidal self-assembly an external stimulus is directed to the system to drive and direct the organization. The many applications of colloidal self-assembly include actuators and colour displays. An overview of passive and active colloidal self-assembly can be seen in figure 1.

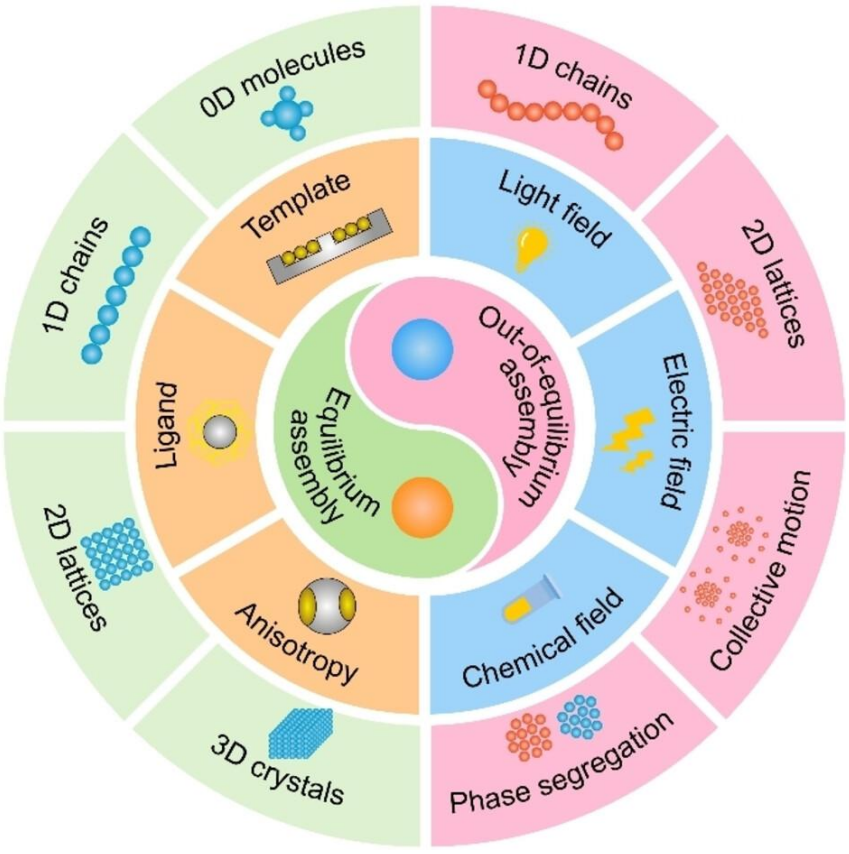


Figure 1: Overview of passive(equilibrium) and active(out-of-equilibrium) colloidal self-assembly. The left side shows different methods used to drive passive colloidal self-assembly and the ordered structures that can be produced. The right side shows different outside stimuli that can be used to drive active colloidal self-assembly. Different ordered structures and exotic properties of active colloidal self-assembly are also shown. Modified from Huang et al. [4]. Copyright 2024 Huang, published by Wiley-VCH GmbH

2 Theory

The main model for explaining colloidal self-assembly is the DLVO theory. It uses the balance between attractive van der Waals forces and repulsive electrostatic forces to explain why colloids self-assemble. However, the DLVO theory is not the only model, and others are explored for passive and active self-assembly. Different structures achieved from colloidal self-assembly are also explored.

2.1 Van Der Waals interactions

Van der Waals (vdW) forces always exist between two atoms, ions or molecules. This force is attractive and arises from three types of dipole-dipole interactions. These three are Keesom, Debye and London interactions. Keesom refers to an interaction between two molecules with permanent dipoles. The negative dipole of one molecule will attract the positive dipole of the other leading to an attractive force between two molecules. Debye refers to an interaction between a permanent dipole and an induced dipole. This induced dipole happens when the electron cloud of a molecule is disrupted by the permanent dipole attracting or repelling the electrons. This interaction leads to an attraction force between the molecules. London refers to an interaction between an induced dipole and another induced dipole. Electrons are constantly moving in the electron cloud. This can lead to an uneven distribution of electron which leads to an induced dipole. This induced dipole interacts with another molecule with the Debye interaction which leads to attractive force between the molecules. This means London interactions can happen between two nonpolar molecules. These three interactions are additive, and they act over relatively short distances. [7]

Van der Waals force between two molecules has a range of a nanometre or less. However, this range is much longer when colloidal particles or other macroscopic particles are considered. This is because the atoms of a particle mutually interact with atoms of the other particles and these interactions are additive leading to a stronger vdW force. The van der Waals interaction energy between two spherical objects is described by the equation

$$W_{vdW}(d) = -\frac{HR}{12d} \tag{1}$$

where R is the radius of the particle, d is the distance between the particles and H is the Hamaker constant. The Hamaker constant describes the magnitude of the vdW attraction between two particles. This equation expresses how big the attraction energy due to vdW forces between two

colloids is and it is one half of the DLVO theory. It also explains how the distance affects the interactions energy meaning the interactions energy decreases as distance between the particles rises. [8]

2.2 Electrostatic interactions

The other half of the DLVO theory is the repulsion force between colloidal particles. This repulsion arises from the colloidal particles' electric double layers interacting with each other. The electric double-layer or EDL consists of surface charges and counterions. When a surface is submerged in a liquid it will acquire a certain electrical charge. The layer of this surface charge is called the stern layer. This charge can appear due to many mechanisms for example, if ions from the solution bind or absorb onto it. However, the system remains neutral because the solution acquires charges with the opposite sign. These charges are usually in the form of counterions, and the amount is equal to the surface charges. The layer of the counterions is called the Gouy-Chapman layer. [9]

When two colloids approach one another their Gouy-Chapman layer overlap leading to an increased counterion concentration between the colloidal particles [9]. This excessive charge leads to a repulsive force between the two colloidal particles. The repulsive interaction energy can be calculated with the Poisson-Boltzmann equation

$$W_{DL}(d) = \frac{2\pi R\sigma^2}{\kappa^2 \varepsilon \varepsilon_0} \cdot e^{-\kappa d} \tag{2}$$

where R is the radius of the particle, σ is the surface charge density, ε is the dielectric constant, ε_0 is the permittivity of the solvent, d is the distance between the particles and κ is the inverse Debye length [8]. Inverse Debye length describes the ionic conditions or ionic strength in the solvent [9]. These conditions heavily affect the interaction distance of electrostatic forces as the ionic strength affects the electric double layer thickness thus affecting range [9]. Equation 2 expresses how big the repulsive energy due to electrostatic forces between two colloidal particles is [9].

2.3 DLVO theory

The DLVO theory is the combination of these two forces. Attractive interactions are provided by Van Der Waals forces and repulsive ones by electrostatic forces. It assumes these are the only interactions between colloidal particles. The theory also considers these forces additive

meaning the total interaction energy can be expressed by combining the interactions energy of both these forces. This is described by equation 3.

$$W_{total}(d) = W_{DL}(d) + W_{vdW}(d) \tag{3}$$

Inserting equations 1 and 2 to equation 3 leads to equation 4.

$$W_{total}(d) = \frac{2\pi R\sigma^2}{\kappa^2 \varepsilon \varepsilon_0} \cdot e^{-\kappa d} - \frac{HR}{12d} \tag{4}$$

This equation describes the total interaction energy between two colloid particles in a solution. When total interaction energy is negative vdW forces prevail and electrostatic forces when it is positive. [8]

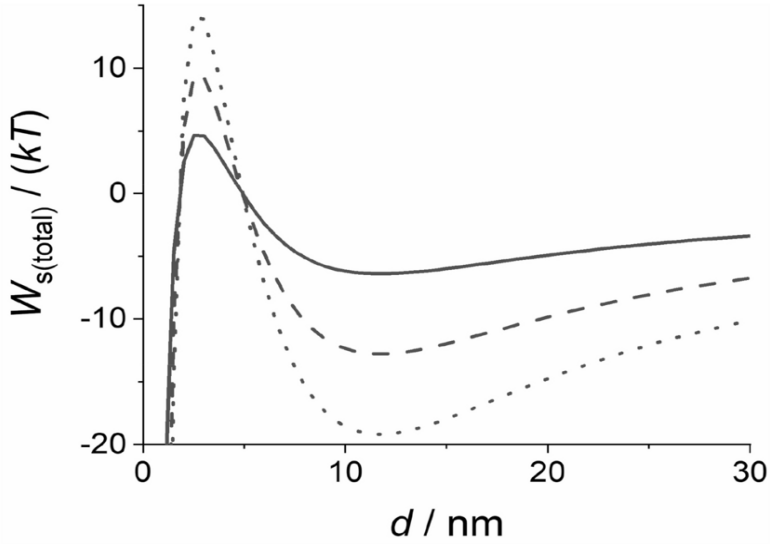


Figure 2: The total interactions energy for particles with different radiuses expressed with equation 4 as a function of the distance between the particles. Dotted line *R*=150nm, dashed line *R*=100nm and Solid line *R*=50nm. Modified from Hernandez [7]. Copyright 2023 Hernandez, published by Springer.

The total interactions energy for colloidal particles with different radiuses expressed with equation 4 as a function of the distance between the particles *d* can be expressed with a graph which can be seen in figure 2 [7]. Three important areas which are the primary minimum, primary maximum and secondary minimum can be seen in the graph [8].

The primary minimum can be seen when distance between particles is very short. In this area van der Waals forces strongly dominate which leads to the particles aggravating irreversibly and not forming ordered structures. To get to the primary minimum particles need to overcome

the primary maximum. This is why it is also called the energy barrier. The energy barrier arises from electrostatic forces dominating at those distances leading to very strong repulsive forces. The height of the energy barrier is influenced by the radius of the particles but also by the colloid's ionic conditions. When particles do not have enough kinetic force to overcome the energy barrier, they can remain dispersed or in certain cases they can become trapped in the secondary minimum. The secondary minimum appears when vdW forces have longer range than the electrostatic forces. Particles trapped in the secondary minimum are considered flocculated which means reversibly aggravated. This means the particles can form weak bonds and sever them to find ordered structures where entropy is maximized, and minimal energy is achieved. [8]

The secondary minimum explains why passive colloidal self-assembly happens. The colloid is designed in a way that the energy barrier is too high to overcome, and the secondary minimum is deep enough so that the colloids do not redisperse. The colloidal particles become trapped in the secondary minimum which leads to the colloidal particles forming an ordered structure.

2.4 Lennard-Jones model

A model for explaining passive colloidal self-assembly is the Lennard-Jones potential. It combines an attractive interaction from vdW forces and a repulsive interaction arising from the particles' electron clouds overlapping [10]. The balance between these two interactions explains why colloids self-assemble into ordered structures.

The Lennard-Jones potential can be expressed with the equation

$$V(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \tag{5}$$

where ϵ is a parameter that determines the depth of the potential well, r is the distance between the particles and σ is the distance where potential energy is zero between the particles [11]. The positive term in the equation denotes the potential of the repulsive force and the negative the potential of the attractive force [11]. Graphically the Lennard-Jones potential can be seen in figure 3 where the potential energy is expressed with equation 5 as a function of the distance between the particles [12].

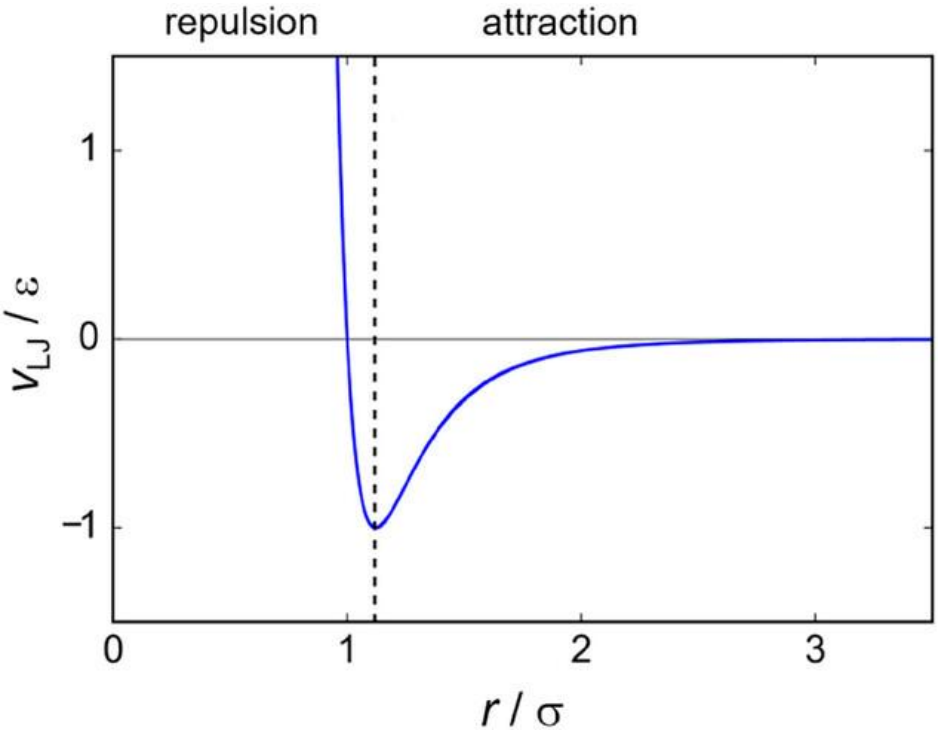


Figure 3: Potential energy as a function of the distance between the particles. Modified from Lenhard et al. [12]. Copyright 2024 Lenhard, published by Wiley-VCH GmbH.

When colloidal particles get closer to each other repulsion forces rise which can be seen as a sharp rise in the potential energy on the graph. The potential energy approaches zero as distance between the particles rises because the particles are too far from each other to interact. When the distance between the particles is $2^{\frac{1}{6}}\sigma$ a potential well can be observed [13]. At this distance the repulsion and attraction forces are balanced meaning the net force between particles is zero and the potential energy reaches its minimal value [13]. This means the colloidal particles have organized into an ordered structure and the system has reached equilibrium [13].

2.5 Hard spheres model

Another model for explaining passive colloidal self-assembly is the hard sphere model. This model extremely simplifies the interactions between colloids. It assumes that there is no attractive force between colloidal particles and the only force is the repulsive force due to the particles' electron clouds overlapping. [14]

The interaction potential for the hard sphere model can be expressed with the equation

$$V(r) = \begin{cases} 0 & (r > 2a) \\ \infty & (r \leq 2a) \end{cases} \quad (6)$$

where r is the distance between the particles and a is the radius of the particles [3]. The interaction potential is zero when the colloidal particles do not touch each other meaning there is no interaction between them [3]. When the particles do touch each other the interaction potential is infinitely positive meaning there is a strong repulsion [3]. The colloidal particles move around until they are locked in place and form ordered structures due to the repulsion forces from surrounding colloidal particles [15].

2.6 Patchy colloids model

Passive self-assembly can be explained using the patchy colloids model. A patchy colloidal particle consists of a core with discrete regions called patches that have specific interactions properties. The core is considered a hard sphere meaning there is a repulsive force between the particles. The patches provide the attractive interactions between the particles. They interact with other patches which leads to directional bonds. However, the patchy interactions dominate over the core's interactions driving the colloids to self-assemble into ordered structures. [16]

By selecting the number of patches, their placement, size and shape, intricate control over assembly process can be achieved. With this control different ordered structures can easily be produced. For example, colloidal particles organize into different ordered structures depending on the number of patches. Colloidal particles with one patch organized into chain structures. Particles with two patches organized into linear chains while body-centred and face-centred cubic crystals were produced with particles with six patches. [17]

2.7 Janus colloids model

The Janus colloids can be used as a model for explaining active colloidal self-assembly. Colloidal particles that have different properties on opposite sides are called Janus colloidal particles. For example, one side is polar and the other nonpolar or magnetic and paramagnetic. [18]

When an outside stimulus is directed to the Janus colloids, one side of the particle reacts while the other does not. This reaction induces a self-propulsion meaning the colloidal particles start to move. The particles also interact with each other differently depending on the properties of the different sides and these interactions can be enhanced by the outside stimulus. This movement and interactions between colloidal particles allow Janus colloids to form out-of-equilibrium structures. The outside stimulus can be controlled to make the colloidal particles form different kinds of ordered structures. For example, applying different magnitudes of an electric field can make Janus colloids form chains or 2d-crystals. [18]

2.8 Ordered structures

With colloidal self-assembly many ordered structures can be achieved. This ordering is directed by the properties of the colloids. However, outside stimuli can also be used to guide and refine the ordering. This is why many new complex structures can be produced with active colloidal self-assembly. [4]

Colloidal particles can form one-dimensional chains which are one of the simplest structures. These chains are produced when colloids are designed to promote end-to-end attachment. External fields can also be used to further enhance the ordering leading to structures like colloidal wires or filaments. [4]

Two dimensional assemblies can also be produced. One of the most common is a hexagonal close-packet monolayer. Other 2D structures include Kagome, honeycomb and square lattices. Many of these 2D structures are used in photonic applications. [4]

Highly ordered three-dimensional structured can also be achieved. Colloidal particles can organize into crystal structures like face-centred cubic and body-centred cubic lattices. Applications for these structures include advanced coatings and structural materials. In addition to these, colloidal gels and colloidal helices have also been produced. Colloidal gels have an exciting application in self-healing materials. [2]

3 Passive colloidal self-assembly

In the theory portion it was explained how Van der Waals interactions and electrostatic interactions drive colloidal self-assembly. However, depending on the properties of the colloids, there are many more possible interactions. How these interactions drive passive colloidal self-assembly, and the ordered structures achieved are explored in the next parts.

3.1 Interactions between ligands

Ions or molecules that are attached to the surface of colloidal particles are called ligands. Depending on the properties of these ligands they can drive colloidal self-assembly in many ways. For example, neutral ligands that extend to the solvent and provide a physical barrier that prevents colloidal particles from coming close to each other and reactive ligands that form chemical bonds that drive self-assembly. [2]

Hydrogen bonds can be used to drive colloidal self-assembly. This is accomplished by attaching ligands that can form hydrogen bonds to colloidal particles. Hydrogen bond is a force between a hydrogen atom and an electronegative atom. This bond is stronger than the one created by vdW forces but weaker than covalent or ionic bonds. This bond creates an attractive force between particles when they are away from each other and a repulsion force when they are too close together. Using hydrogen bonds to drive self-assembly, colloidal particles that were in the shape of rods were assembled into an end-to-end assembly meaning they formed a linear chain structure. [2]

3.2 Depletion force

Depletion force is an attractive force that arises when there are smaller particles in the colloid's solution. This interaction can be explained with the hard sphere model which states that two particles cannot overlap. When the distance between two colloidal particles is smaller than the diameter of the smaller particles, the area between them is inaccessible to the smaller particles. This causes an osmotic pressure to the colloids which leads to an attractive force between them. This attractive force drives the colloidal self-assembly. The colloidal self-assembly of colloidal cubes driven by depletion forces can be seen in figure 4. [3]

Many different ordered structures have been accomplished with depletion forces. For example, square packing and brick-wall lattices as well as chains comprised of cylindrical plates or

particles. Depletion forces are used to drive self-assembly of fluorescence particles that are used in colorimetric sensing and spectroscopic detection. [2]

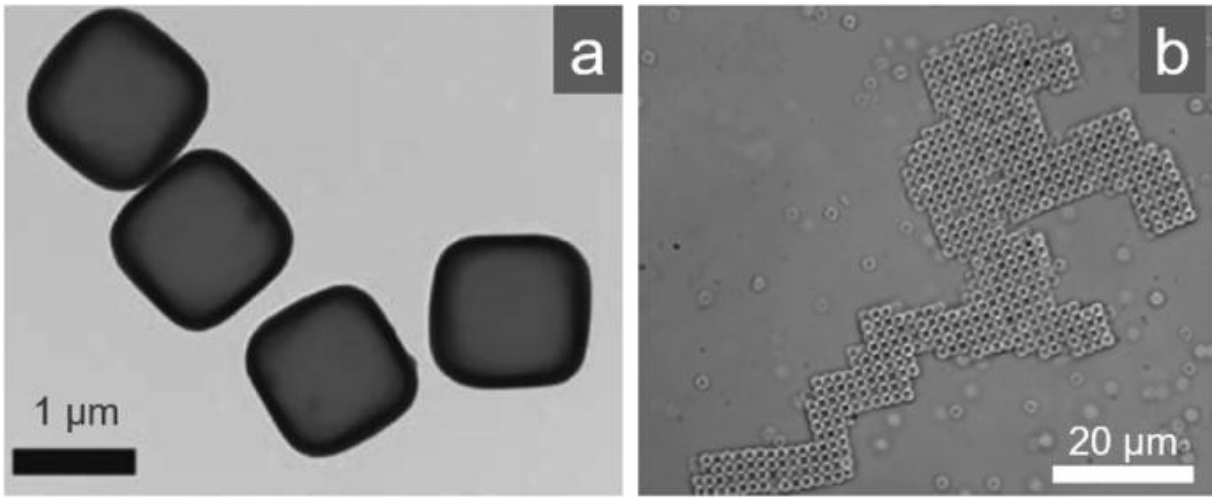


Figure 4: The passive self-assembly of colloidal cubes driven by depletion forces. The colloidal cubes used can be seen in picture a and the ordered structure that was achieved in picture b. Modified from Lekkerkerker et al. [19]. Copyright Lekkerkerker, published by Springer Nature.

3.3 Capillary force

Capillary forces happen at a triple phase boundary of the particles, the liquid these particles are suspended in and a mobile medium like air. The capillary force arises from the liquid surface between two particles deforming due to the surface tension of the liquid coming into contact with the mobile medium. This deformation induces an attractive force between the colloidal particles which drives self-assembly. [7]

Ordered structures such as colloidal crystals like cubic colloidal crystals, colloidal films and zigzag chains have been produced using capillary forces. The colloidal films are especially important as they can be used in functional materials and optical devices which are used in sensing, anticounterfeiting and data storage. [2]

3.4 Template assisted

Template assisted colloidal self-assembly happens locally meaning the colloidal particles are trapped in pre-designed spaces or interfaces. The templates dictate what kind of assemblies are produced but the driving force is still for example vdW or capillary forces. Structures that are otherwise unattainable can be produced with template assisted colloidal self-assembly. The templates can be divided into hard and soft templates based on their deformability. [2]

The hard templates have defined size and shape as well as pre-designed surface cavities. The colloidal particles are trapped in the hard template and self-assemble into the specific size, shape and structure dictated. This is achieved with the pre-designed cavities where the colloidal particles become trapped. Structures like linear or zigzag chains and different colloidal crystals and clusters have been produced with hard templates. [2]

In colloidal self-assembly using soft templated, the volume, shape and interface where self-assembly happens can change during the assembly. The soft templates change its volume and shape during colloidal self-assembly. This means the colloidal particles can change their orientation and position. This means they can move and are not strictly confined into pre-designed cavities. Large colloidal clusters and different 2D colloidal crystals have been produced with soft templates. [2]

4 Active colloidal self-assembly

In the theory it was explained how Janus colloids react to external stimuli to drive colloidal self-assembly. These different types of external stimuli and their applications are explored in the next parts.

4.1 Magnetic field driven

A magnetic field can be used to drive active colloidal self-assembly. This field powers the propulsion of colloidal particles. It also enables or amplifies interactions between the colloidal particles. A high control over the assembly process can be achieved by tuning the strength, angle and spatial distribution of the magnetic field. Electromagnet or permanent magnets are used to easily create a magnetic field. [20]

Magnetic field driven colloidal self-assembly has many applications. In colour displays and filters the magnetic field can be used to drive self-assembly so that the ordered structures exhibit designated patterns and different colours. Another application is a magnetic actuator where the self-assembly of colloidal particles embedded in an actuator can be driven by an external magnetic field which induces magnetic actuation. [2]

4.2 Electrical field driven

Active colloidal self-assembly can be driven by an electric field. The electric field powers the propulsion of the colloidal particles and affects the assemblies. In addition to propulsion, the electric field affects the interactions between colloidal particles. These drive the colloidal particles to form ordered structures. The field can be AC or DC and many parameters like field strength, direction of the field and frequency can be changed. This enables high control over the structures produced and the self-assembly process. [4]

Colour displays and filters are one of the applications of electric field driven colloidal self-assembly. The external field drives self-assembly which invokes colour changes. Sensors are another application for electric field driven self-assembly. Here the colloids sense an external electric field and self-assemble into ordered structure to exhibit for example a specific colour. [2]

4.3 Light driven

Light driven colloidal self-assembly refers to active colloidal self-assembly where colloidal particles absorb the optical energy and convert it into a localized field for self-propulsion. This motion and the interactions between colloidal particles can drive colloidal particles to organize into ordered structures. Light offers a high degree of control because it can be focused on specific spots and many of its parameters like intensity, polarization and wavelength can easily be modified. In figure 5 colloids can be seen assembling into ordered structures as the light intensity directed to them increases. [4]

Light-driven actuators are one of the applications of light driven colloidal self-assembly. They convert the energy from the light to movement or mechanical deformations. Light driven self-assembly can also be used for energy conversion where the colloids' ordered structures convert light into heat or electricity. Anticounterfeiting and information encryption is another application where light driven self-assembly can be utilized. Light with specific parameters can be used to produce specific ordered structures to reveal hidden information. [2]

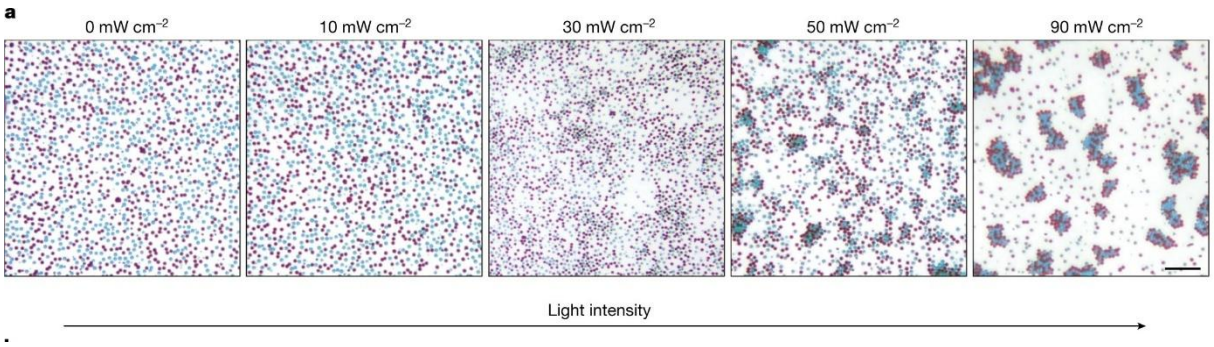


Figure 5: Ordered structures forming under different light intensities. Modified from Zheng et al. [21]. Copyright 2023 Zheng.

4.4 Chemical field driven

Chemical field driven active self-assembly is driven by chemical reaction happening on the surface of the colloidal particles or in their surroundings. These reactions can be created by the colloidal particles themselves or by external sources. These reactions induce a chemical gradient to which the colloidal particles respond. This response leads to the particles organizing into ordered structures. A high level of control over the assembly process can be achieved by controlling the chemical environment and by designing the colloidal particles to have specific catalytic properties. [4]

There are many important applications that use chemical field driven colloidal self-assembly. One of these is chemical sensors that are used to detect various molecular binding events. It can also be used for colorimetric meaning the ordered structure exhibits a different colour depending on the external chemical stimuli. Another application is chemically responsive actuators where the chemical stimuli drives colloidal self-assembly which powers actuation. [2]

5 Simulations

The simulations for this thesis are intended as simplified and illustrative models to understand the fundamental physical processes underlying colloidal self-assembly. This means that the interactions potentials and parameters are chosen for qualitative insight rather than quantitative comparison with specific experimental systems.

5.1 Simulation setup

Colloidal self-assembly can be simulated with LAMMPS. It is a molecular dynamics program, and the name stands for Large-scale Atomic/Molecular Massively Parallel simulator. [22] The placement of colloidal particles in the system can be visualized with OVITO. It is a 3D visualization software, and the name stands for The Open Visualization Tool. [23]

To simulate colloidal self-assembly setup is needed meaning the particles, their dynamics and interactions potentials must be determined. In the simulations patchy particles are used. There are two types of cores and eight types of patches. This means that one type of core has four different patches, and the other type of core has the other four. These patchy particles can be seen in figure 6. The movement of these particles is simulated by using Brownian dynamics. Brownian motion is explained in the introduction and the simulation mimics this motion.

The interactions between colloidal particles that drive self-assembly are simulated using the Lennard-jones and cosine-squared potentials. A Lennard-Jones potential is determined between the cores which leads to an attractive interaction between the cores at long distances and a repulsive interaction at close range. A cosine-squared potential is determined between the patches at close range which has a higher interaction potential than the Lennard-Jones potential. This leads to the patches attracting each other and forming directional bonds.

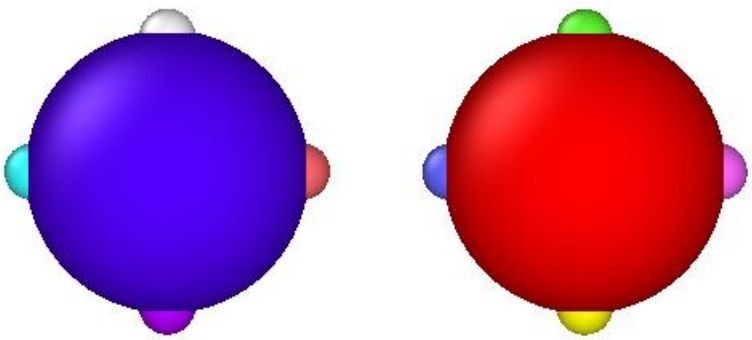


Figure 6: The patchy colloidal particles used in the simulations. [21]

Lennard-Jones units are used in the simulations. These units are dimensionless and used to simplify the results. The units consist of three fundamental quantities for energy, mass and distance which are all set to 1. Other quantities, such as temperature, are multiples of the fundamental quantities.

5.2 System setup

The system is set up as a 2-dimensional square with 100x100 LJ units. 400 patchy colloidal particles are placed in the square and the placement can be seen in figure 7. The time step is set to 0.001 and the simulation is set to run for 10000000 steps. The system's temperature is set to 1. The friction or the dampening effect of the system is set to 0.1. One simulation is run with these setting. Five more simulations are run where the temperature is lowered or raised.

The simulation is set up to track the temperature, pressure and total energy of the system as well as pairwise interaction energy between particles in the system. LAMMPS calculates the total energy of the system by summing all the pairwise potential energies between the particles and the kinetic energy of the particles. These pairwise interactions are the attractive and repulsive forces modelled using the Lennard-Jones and cosine-squared potentials. The values are exported every 100000 steps. In addition, the location of the particles in the system is also exported every 100000 steps.

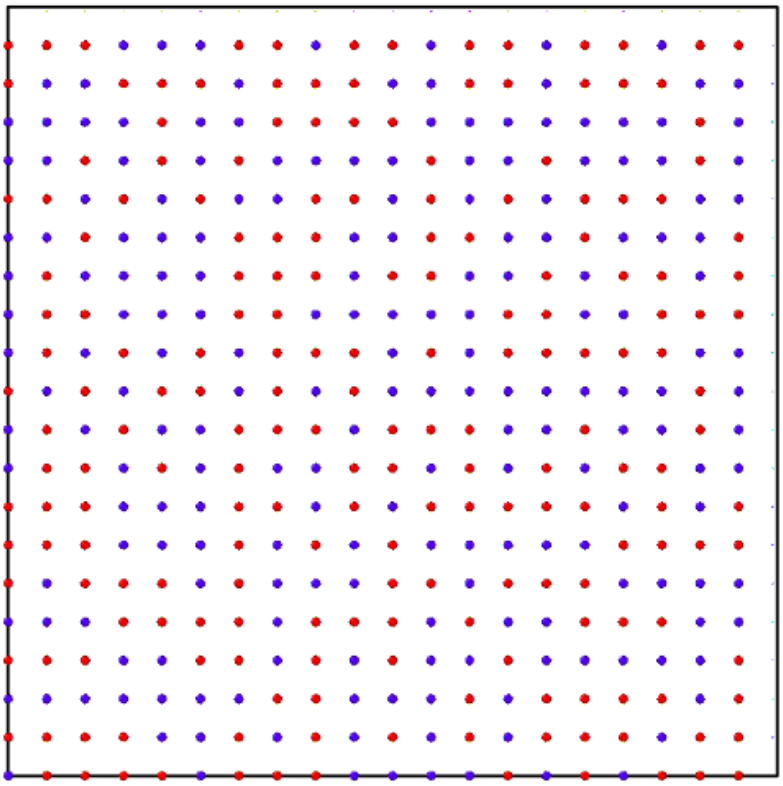


Figure 7: The placement of the particles at the start of the simulations. [21]

6 Results and observations

6.1 Temperature dependency of colloidal self-assembly

Six simulations with varying temperature were run to explore the effect of temperature on passive colloidal self-assembly. In simulation 1, 2, 3, 4, 5 and 6 the temperatures were 0.4, 0.6, 0.8, 1, 1.2 and 1.4 respectively.

6.1.1 Total energy of the system

In table 1 the total energy of the system every 2000000 steps is expressed for all the simulations. The total energy of the system was recorded every 100000 steps for all simulations. This led to a hundred data points of the step the simulation was on and the total energy of the system. Using these data points graphs were made where the total energy of the system is plotted against the simulation step. These graphs are shown in figure 8.

Table 1: The total energy of the system for all simulations every two million steps.

Step/Temperature	**Sim 1 (T=0.4)**	**Sim 2 (T=0.6)**	**Sim 3 (T=0.8)**	**Sim 4 (T=1)**	**Sim 5 (T=1.2)**	**Sim 6 (T=1.4)**
2×10^6	-0.7653	-0.9739	-1.017	-0.9602	-0.8384	-0.4781
4×10^6	-1.143	-1.350	-1.361	-1.395	-1.176	-0.8224
6×10^6	-1.409	-1.483	-1.472	-1.523	-1.326	-0.9425
8×10^6	-1.565	-1.588	-1.639	-1.718	-1.502	-1.151
10×10^6	-1.664	-1.700	-1.725	-1.787	-1.573	-1.131

Using table 1 and figure 8 several observations can be made. In all the simulations the total energy of the system decreases as the simulation progresses and the lowest value is achieved at the end of the simulation. Simulation 4 had the lowest total energy while simulation 2 and 3 had similar but slightly higher values. In Simulation 1 the total energy was even higher. However, in simulations 5 and 6 the values were considerably higher than in all other simulations with simulation 6 having the highest total energy. Another thing that figure 4 shows is that in simulations 1, 2, and 3 the total energy decreases smoothly while in simulation 4 it fluctuated a little bit and in simulations 5 and 6 it fluctuated noticeably.

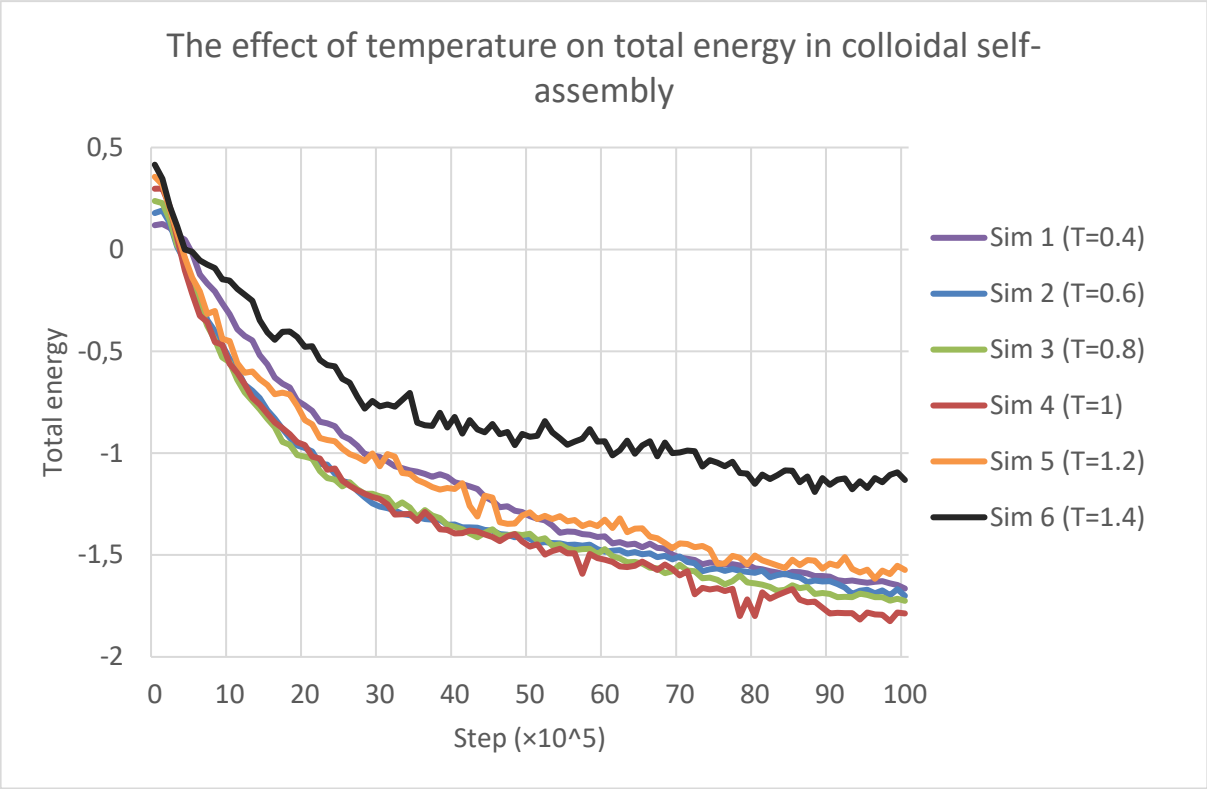
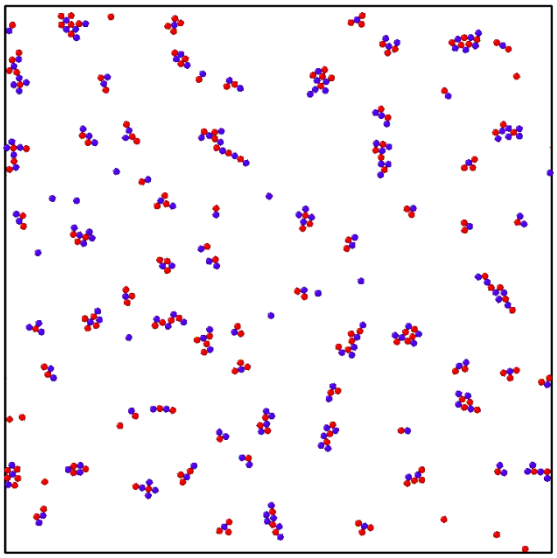


Figure 8: The total energy of the system plotted against the simulations step for all simulations.

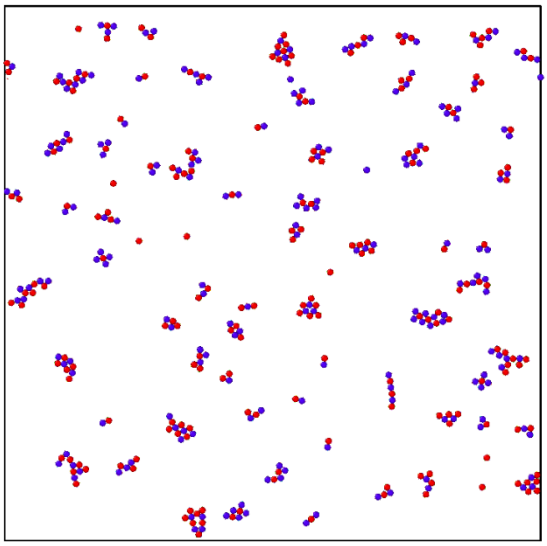
6.1.2 Clusters

In figure 9 the positions of the colloids and the clusters formed at the end of the simulations are shown. In figure 10 a bar graph of the different sized clusters formed in the simulations is shown. Various observations can be made with these figures.

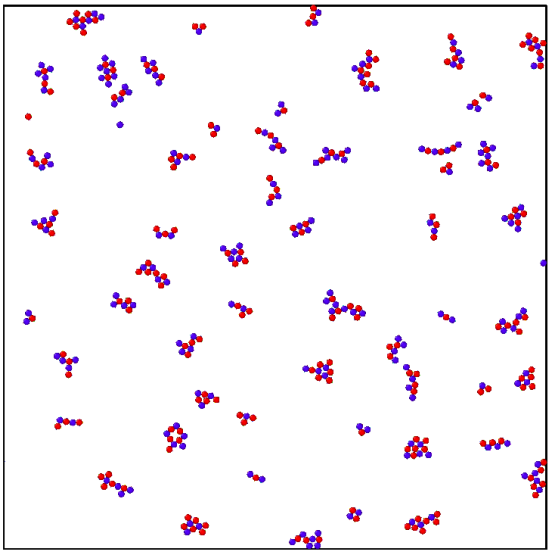
All the simulations had clusters with only one colloid. Simulation 3 had the least of them with simulation 2 having a couple more. Simulations 1 and 4 had the same amount but a few more than simulations 3 and 2. Simulations 5 and 6 had significantly more than others with simulation 6 clearly having the most of them. The largest cluster of 27 colloids formed in simulation 5. In simulations 4 and 6 the biggest cluster was 20 colloids formed. In simulation 3 a cluster of 16 colloids formed while in simulations 1 and 2 only a cluster of 14 colloids formed. In simulations 1 and 2 the clusters were relatively small with a few medium-sized clusters while in simulation 3 the clusters were bigger with more medium-sized clusters forming. In simulation 4 more larger clusters formed with most clusters being at least medium-sized. In simulations 5 and 6 large clusters formed but many small clusters also formed with them being even more frequent in simulation 6.



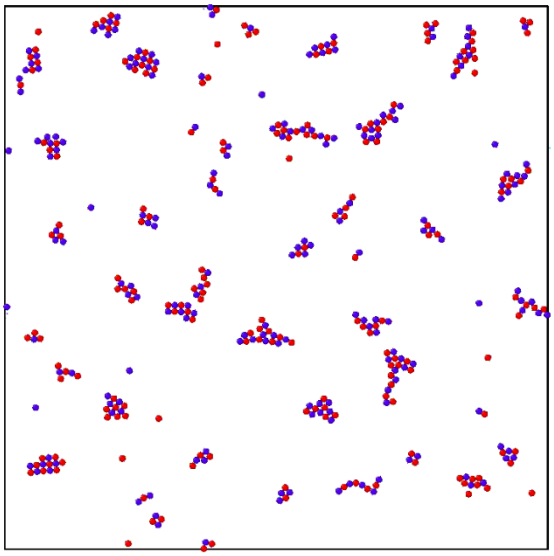
Sim 1 (T=0.4)



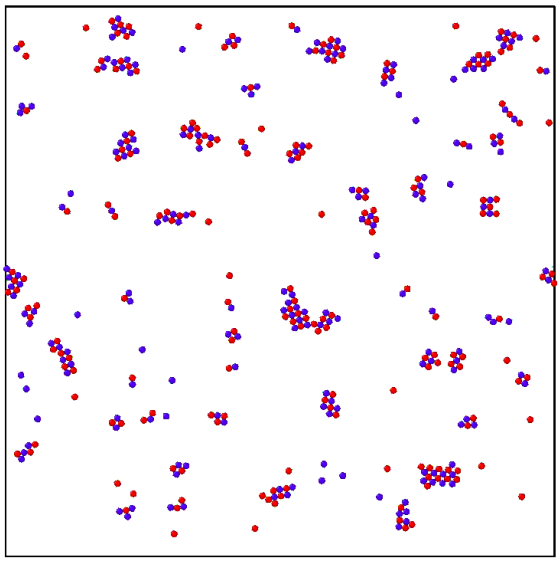
Sim 2 (T=0.6)



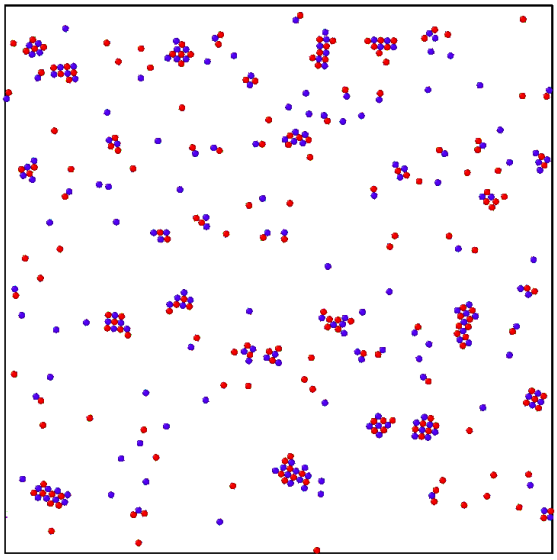
Sim 3 (T=0.8)



Sim 4 (T=1)



Sim 5 (T=1.2)



Sim 6 (T=1.4)

Figure 9: The placement of the colloidal particles and the clusters formed at the end of the simulations. [21]

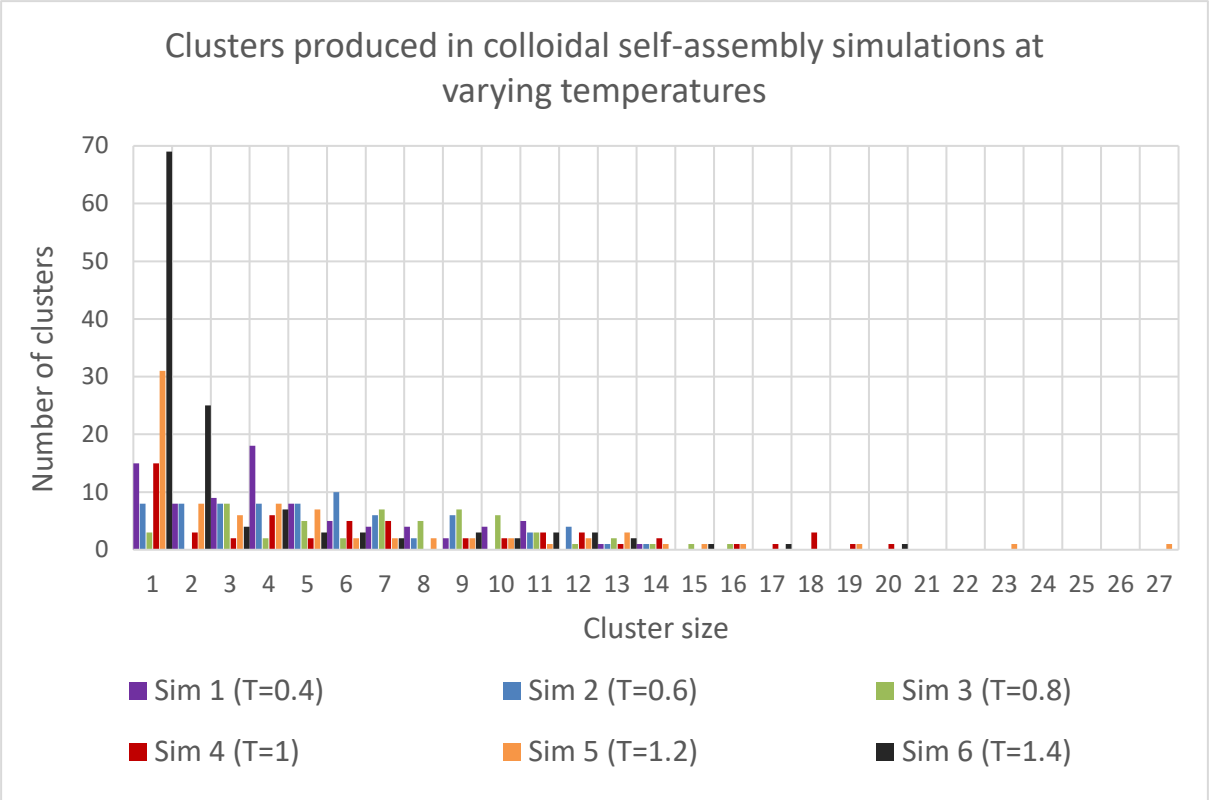


Figure 10: A bar graph of the different sized clusters formed in the simulations

6.2 Discussions

6.2.1 Total energy analysis

The results show the effect of temperature on colloidal self-assembly. The constant decrease of the total energy indicates that in all the simulations the system progresses towards equilibrium and a stable configuration. However, at different temperatures the rate of energy decrease and the final total energy varies considerably.

At a temperature of 1 and lower the rate of energy decrease was steady meaning the colloidal particles steadily assembled into ordered structures. As temperatures got lower the total energy got higher. This can be explained by the lower thermal energy leading to a lower thermal motion. This means that the colloidal particles could not interact as much which means they did not have as many chances to form ordered structures.

At a temperature of 1 the balance between the thermal energy and the attractive forces between colloidal particles was optimal leading to the particles having enough mobility but still being able to form ordered structures. At temperature 0.4 the colloidal particles moved so slow they had very few chances to interact leading to the least stable ordered structure out of the lower temperatures.

At temperature higher than 1, the total energy did not decrease steadily instead fluctuating. The total energy also rose as temperatures got higher with it being considerably higher at temperature 1.4. These higher values and fluctuation can be explained by the increase in thermal energy. This increase leads to excessive thermal motion which disrupted the self-assembly process. The thermal motion was so strong it prevented colloidal particles from forming an ordered structure leading to a less stable configuration and a higher total energy.

6.2.2 Cluster analysis

The results of the clusters formed show the effect of temperature on colloidal self-assembly. Depending on the temperature the size of the clusters as well as the number of clusters formed varied drastically.

At a temperature of 1 the thermal energy was quite high which led to the formation of large clusters but also some single-colloid clusters meaning dispersed colloidal particles. The thermal motion was high enough that the colloidal particles could move around and interact with each other and low enough that it did not significantly disrupt the formation of clusters. This led to a stable configuration.

At temperature lower than 1 the thermal energy was lower. The reduced thermal motion meant colloidal particles could not move around as much which led to less interactions between the particles. However, when particles did interact with each other, they were more likely to stick together and not break off from the cluster. This process is called nucleation, where once a colloidal particles form clusters, it is energetically favourable for them to remain together rather than separate. This is why only small clusters formed but it also explains the reduced number of single-colloid clusters. Despite the smaller clusters, lower temperatures led to stable configurations.

The low thermal energy also explains the increase in dispersed particles at the lowest temperature. The colloidal particles had such low motion that the simulation was too short for them to form more clusters. Given more time it can be assumed that these dispersed clusters would have formed or joined clusters.

At temperatures higher than 1 the thermal energy was higher which led to increased thermal motion. This meant that the colloidal particles had excessive motion which disrupted the assembly process. Many colloidal particles remained dispersed as they broke off from clusters or could not interact with each other to form or join clusters. However, the higher mobility also led to the sporadic formation of large clusters where the particles could not separate from the cluster. Even with these large clusters, the achieved configurations were not stable.

6.2.3 Conclusions

At a temperature of 1 a stable ordered structure is achieved. At lower temperatures the self-assembly process slows down, but the achieved ordered structures are stable and given more simulation time they could be even more stable than what is achieved at a temperature of 1. At higher temperatures the increased thermal motion disrupts the assembly process leading to a disordered and unstable structure. Therefore, lower temperatures could be useful for certain colloidal self-assembly processes while higher temperatures should generally be avoided.

7 Conclusion and outlook

An overview of passive and active colloidal self-assembly was provided highlighting the equilibrium state achieved in passive in contrast to the out-of-equilibrium behaviour seen in active self-assembly. The theoretical section detailed important theoretical models that explain why colloidal self-assembly happens. These models were the DLVO theory as well as Lennard-Jones, hard sphere, patchy colloids and Janus colloids models.

The different interactions between colloidal particles that drive passive colloidal self-assembly were explored. These interactions included depletion and capillary forces as well as ligand-mediated binding and some of the ordered structures achieved with them were shown. Active colloidal self-assembly was analysed by discussing the different external stimuli that drive it. Magnetic, electric, light and chemical stimuli were investigated and some of the applications using these were shown.

To complement the theoretical understanding, the passive colloidal self-assembly of patchy colloids was simulated with LAMMPS at various temperatures to study the effect of temperature on the assembly process. The simulation results demonstrate that temperature greatly affects colloidal self-assembly. At lower temperatures the assembly proceeds more slowly, but results in stable ordered structures. Higher temperatures disrupt the assembly process leading to disordered and unstable assemblies.

Looking ahead, the simulations could be expanded to study colloidal self-assembly more. The same simulations could be repeated with different starting positions for the particles. Additionally, external stimuli could be used to explore the effect of temperature on active colloidal self-assembly. These would provide more information on both active and passive self-assembly but also allow comparison between them.

Overall, this thesis examined passive and active colloidal self-assembly through both theoretical and computational perspectives. With this combination a clear understanding of colloidal self-assembly and the effect of temperature on it was achieved.

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