SIMULATION OF SINGLE PATCH COLLOIDS

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Declaration

I Najiya K K, Regd.No 22mscphy46 of the Department of Physics declare that this diddertation is based on original ideas and free from plagiarism. Adequate citations and references of original sources have been provided.

I also declare that I have adhered to all principles of academic honesty and integrity and have not misinterpreted or fabricated or falsified any idea/data/fact/source in the dissertation.

I understand that any violation of the above will be the cause of disciplinary action by the Central University of Punjab and can also evoke penal action from sources which have, thus not been properly cited or from whom proper permission has not been taken when needed.

Certificate

This is to certify that the dissertation entitled "SIMULATION OF SINGLE PATCH COLLOIDS" being submitted by Najiya K K, registartion number: 22msc-phy46 to Central University of Punjab, Bathinda for the award of Msc. Degree in the Physics is a Bonafide research work carried out by her under my supervision. The results presented in this dissertation have not been submitted elsewhere for the award of any degree.

In my opinion, the dissertation work has reached the standard of fulfilling of the requirements for the award of master's degree in accordance with the regulations of Central University of Punjab, Bathinda.

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Abstract

Patchy Colloids are colloidal molecules with molecules attached to them as patches. It gives them properties like limited valency and directional bonding. Due to analogous nature of patchy colloids with biomolecular structures like protein, lysosomes viruses etc. they are widely studied to understant the properties of the former molelucles. Patchy colloids also shows similarities to nano molecular structures which are used in construction of new materials. An important property of patchy colloids is that they can self-assemble into different shapes according to the external parameters provided.

In this project we try to vary the parameters packing fraction and patch ratio which is the ratio of the attached patchy molecule to the core molecule and see the effect in the self assembly of the molecule. A model of these patchy colloids in a lattice cell is made and computer simulations are ran varying the above mentioned parameters. Ovito is used for visualisation of the results and to analyse the output.

Contents

List of Tables

List of Figures

Chapter 1

Introduction and Motivation

1.1 Colloidal Molecules

Solutions of 'larger molecules' which exhibit Brownian motion is known as colloids [**dhont1996introduction**]. A mixture of substances in which particles which are substantially larger than the atoms or molecules but not visible to naked eye are dispersed in the other. These insoluble particles known as dispersed phase typically in the range of 1 to 1000 nanometres is distributed within continuous phase. Colloids are relatively more stable. The particles do not settle under gravity due to small size of particles and electrostatic charges on surface which create repulsive forces that prevent aggregation. Another important property of colloids is Tyndall effect. When light passes through the colloid its path is illuminated due the size of the particles.

1.2 Patchy Colloids

Patchy colloids are a class of advanced and versatile class of materials with surfaces engineered to have distinct regions of varying properties. They are hard soft sphere having one or more patches which are attractive arranged at specific sites. The patches are defined as precisely designed specific interaction sites having definite shape. These patches confer the properties like directional and limited valence bonding to the colloidal molecule. They show an-isotropic interactions which refers to the interactions which depend on the orientations between the interacting

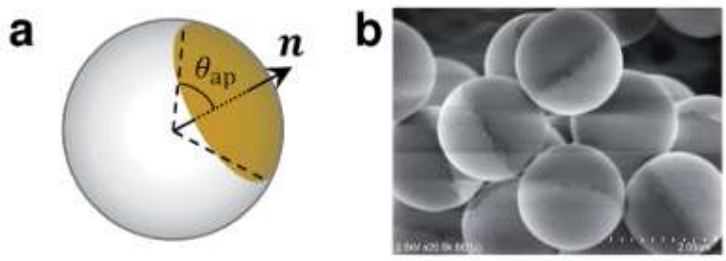

Figure 1.1: Single patch particle (a) Schematic diagram of a single patch colloid with circular patch. Here 'n' is the unit vector directed from centre of patch from centre of particle. (b) SEM image of particle with a hemispherical patch.[**iwashita2014orientational**]

entities. These colloidal molecules can be manipulated physically and chemically due to large control in the inter particle potential between them. Varying the interactions and the local arrangement of particles it is possible to study about the collective behaviour of the particles.[**bianchi2011patchy**, **bianchi2006phase**]

1.3 Janus Particles

These are particles which have patches only on one side of them. These particles have two or more distinct surfaces or regions with different chemical or physical properties. This feature confers the unique properties like dual nature. They can form clusters with controlled size and shape.[**lattuada2011synthesis**]. Due to the bifunctional surface Janus particles have asymmetric properties and directional interactions. Janus particles are made of two distinct compartments that differ in functionality, physical and chemical properties. They can accommodate hydrophilic groups on one half of their surface and hydrophobic on the other half which gives them unique properties.[**lattuada2011synthesis**]

1.4 Process of Self-assembly

Self-assembly of Patchy colloids particularly Janus particles is the process where these anisotropic particles with distinct surface properties form organized structures as a result of the interactions between the particles themselves, often due to weak forces such as van der Waals force or hydrogen bonding.[**oh2019colloidal**, **ou2019synthesis**, **banik2021substrate**, **tan2023development**]. Peculiar fea-

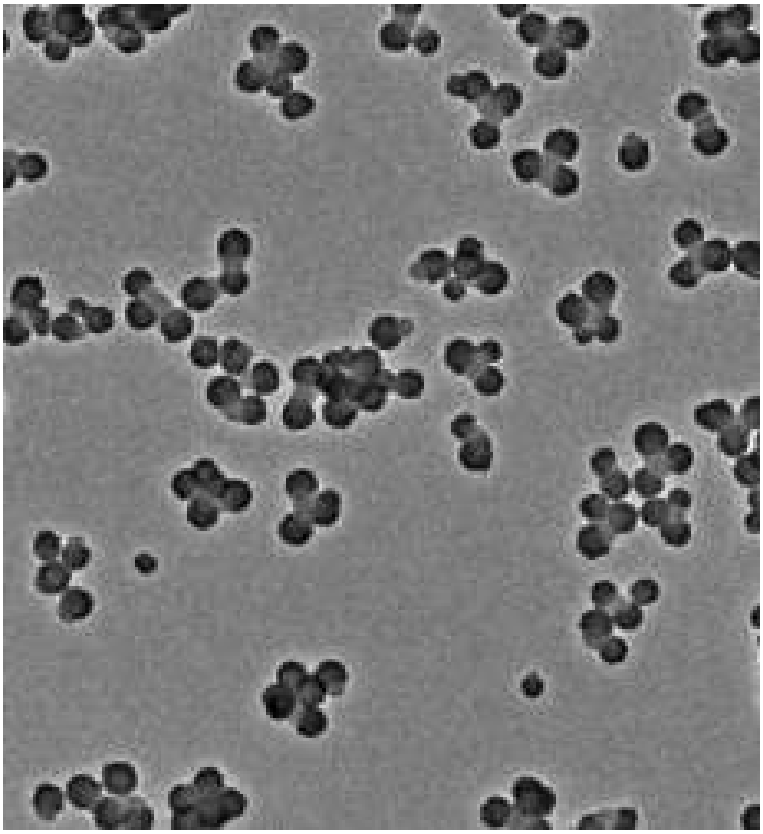

Figure 1.2: Single patch particle Representative TEM images of spatchy colloids of gold decorated on silica lobe[**li2020clustering**]

tures of the patchy colloids and janus particles due to their physical and chemical heterogeneity helps them in the process of self-assembly. The assembly of these particles can be triggered by reducing the solvent quality for the polystyrene chains, leading to the formation of dimers or trimers. [**oh2019colloidal**]. The experimental work on the Kagome lattice self-assembled from triblock patchy particles has led to studies on the phase diagram of the two-patch Kagome lattice, demonstrating the potential for complex crystal structures.[**ou2019synthesis**]. The self-assembly approach is widely used for the competitive surface assimilation of incompatible ligands, such as hydrophobic and hydrophilic ligands, on particle surfaces. This process can occur through radical polymerization, where the effectiveness is influenced by factors like pH, ionic strength, and temperature. The first tri-block copolymers used to form Janus particles were presented by Erhardt and his team in 2001, demonstrating the generation of Janus particles with a southern and a northern hemisphere along with a cross-linked core.[**tan2023development**].

1.5 Computer Simulations in Study of Self-assembly of patchy colloids and Janus particles

For researching the self-assembly of patchy colloids, in particular Janus particles, computer simulations are indispensable. These simulations give a means of investigating and comprehending the assembly processes that take place at the nanoscale level, delivering insightful information on the behaviour and interactions of these intricate systems.[**duguet2016patchy**, **eslami2018self**] Computer simulations allows to explore the effects of different parameters on the self-assembly process such as role of depletion interactions, surface energy and impact of solvent quality of assembly of patchy nanoparticles. [**oh2019colloidal**] [**duguet2016patchy**] Essentially, computer simulations are an effective tool for studying patchy colloids and Janus particles self-assembly because they enable researchers to model and examine the complex processes that lead to the production of complex structures at the nanoscale.

1.6 Motivation

Patchy colloids and Janus particles are currently an intense area of research. Atomic behaviour such as selective bonding and directionality made them important in construction of new nanomaterials as well as for study of proteins, lysosomes, virus etc. Study of self-assembly will help to understand the involvement of factors such as temperature, packing fraction, patch ratio etc.

1.7 Objectives and Organization

1.7.1 Objectives

1 To Study self-assembly of patchy colloids based on a single patch molecule of Polystyrene and TPM (a cross-linked 3-(tri methoxysilyl)

2 To study the factors that help in self-assembly of patchy colloids.

3 To understand the shapes formed by patchy colloids during self-assembly.

1.7.2 Organization of Dissertation

The organization of the dissertation is summarised as follows:

Chapter 1: Introduction

This chapter consist basics of patchy colloids, Janus particles and self-assembly. Definition and importance of patchy colloids are discussed.

Chapter 2: Literature Review

This chapter contain literature review about the past works on the field of Patchy colloids. This chapter is organized with description from respective papers and other literature.

Chapter 3: Molecular Dynamics

In this chapter, the basics of molecular dynamics are included. Model for spherical particles, particle model for simulation of spherical particles, verlet lists, linked cell algorithm etc. are discussed.

Chapter 4: Model and Methods

Model of the particle used in the simulation, potential between the molecules which cause the interactions between them and the simulation set up is are discussed in this chapter

Chapter 5: Simulations

Chapter 2

Review of Literature

2.1 Understanding the Importance of Patchy Colloids

Several interactions in biological world are described as patchy. This includes interactions between several specific proteins such as globular proteins, lysosomes, and supramolecular structures such as viruses. [**lomakin1999aeolotopic**, **hloucha2001patch**, **bianchi2017limiting**]. "Patchy interaction" refers to a type of interaction between particles or molecules where certain regions on the surfaces of these entities exhibit distinct and specific properties. These interactions are a result of limited valence and directionality.

Colloidal particles with chemically or physically patterned surfaces, inducing strong anisotropic, high directional interactions between particles are called as patchy colloids. These patches are limited in number.[**bianchi2011patchy**]. The patches provide colloidal particle directionality and limited valence enabling them to behave like an atom or molecule. DNA oligonucleotides, protein-base biological cross-linkers and biotin-avidin or antibody-antigen binding pairs are used to induce site specific directional bonds between colloids.[**alivisatos1996organization**, **hiddessen2004r**
milam2003dna, **nykypanchuk2008dna**, **park2020dna**].

A unique type of asymmetric colloid particle with two distinct phases, one having patches on its side and the other without any patches is Janus particle. The asymmetric nature of Janus particles confers them the properties of controlled

and directional interactions enabling precise self-assembly. This asymmetry facilitates the design of multifunctional materials, enhances selective binding, and opens avenues for tailoring properties in drug delivery, catalysis, and advanced materials science, making Janus particles pivotal in the development of innovative technologies and applications.[**jie2017janus**] The asymmetry of Janus particles introduces selective interactions between patches, influencing their assembly behaviour. These patchy interactions can be designed to be attractive or repulsive, guiding the particles to arrange themselves in specific orientations.

The selective and directional interactions among the patches induces self-assembly among the particles when they are packed in a confined space. Self-assembly provides an efficient and cost-effective approach to creating complex structures and materials. It leverages the inherent interactions between components to spontaneously organize into ordered arrangements, minimizing the need for intricate and resource-intensive manufacturing processes.

Patchy particles are rich in information about self-assembly. Their coordination number, bond angles, and selectivity, for instance, can all be logically designed by carefully considering the quantity, topological distribution, and chemical makeup of each patch. This however creates a problem of reproducibility of these particles in a controllable and scalable manner. Colloidal solution based on the concept of surface evolution can be presented as a solution for this problem. Colloidal fusion is made on physiochemical algorithm which considers symmetry and composition of the cluster. It is controlled by surface energy minimization.[**gong2017patchy**].

2.2 Research Through Years

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The self-assembly of patchy colloids have studied through years to understand the dynamics of biological molecules and nanomaterials. Despite the accuracy in shape and interaction analogy between colloidal molecules and atoms and additional control in self-assembly, a major drawback for usability of colloidal molecules is that they lack structural flexibility of real molecules. This may affect the as-

sembly and phase behaviour of the colloidal molecules. The generation of flexible colloidal molecules with varying geometrically specified numbers of bound particles is determined by the size ratio of the constituent spheres. Since size ratio also controls the motion range of the colloidal molecules, the flexibility can also be varied. Due to a decreasing amount of available space on the core particles, the assembly rate slowed as the colloidal molecules got closer to the maximum number of bonded particles. Smaller size ratios for a given maximum number of outer particles resulted in slower self-assembly for the same reason.[**chakraborty2022self**]

Changing the flexibility and density of the chains while fixing length can vary the effective interaction induced between the particles. Introducing attractive features may result in potentials having more complex features related bridging phenomena.[**garcia2017effective**]

Conventional patchy colloids are constructed by adding additional attractive patches on an otherwise repulsive surface. A very different type of colloids is now introduced which have repulsive patches on an otherwise attractive surface. They are known as inverse patchy colloids or IPC. Heterogeneously charged patchy surfaces are their most important feature. Complex interactions develop between them due to attractive and repulsive forces acting between the patches lead to separation and orientation between them. IPCs provide the ability to adjust the mesoscopic structures' characteristics before or after the assembly process using external factors like pH and salt content.[**bianchi2017inverse**]

Number of patches and their interactions along with patch decorations determine the dynamics of the self-assembly of colloidal molecules. However, the role of external factors such as pressure and composition of systems cannot be neglected. Though multipatched colloidal molecules tend to be isotropic a range of different shapes including dimers, trimers or rings were observed. Particle configurations are subjected to energy minimizations in an intermediate pressure range.[**doppelbauer2012self**]

In Kern-Frenkel potential model, system will find it convenient to favour the formation of the smallest possible cluster with the same energy when the potential energy per particle remains constant with cluster size. This is because doing so will allow for the maximisation of the total number of clusters and,

consequently, the translational component of the entropy. Percolation qualities are another technique to distinguish between the two phases because the liquid states are constantly percolating while the cluster gas phase is never. We further confirm that the critical point lies inside the percolation zone, indicating that the presence of a percolating network of contacts is a prerequisite for critical occurrences.[**sciortino2010numerical**]

Remya Ann Mathews Kalapurakkal et.al in their study of lobed patchy colloids found that with an increase in polydispersity and the equivalent change in the lobe size, the average number of bonds formed per lobe decreased for smaller lobes and increased for larger lobes, in comparison with the monodispersed cases. This variation led to an increase or a decrease in the spatial order within the self-assembled structures. An increased polydispersity condition also led to the formation of a crystal structure from a disordered phase for the DB particles.[**kalapurakal2023self**]

2.3 Literature Gap

The effect of patch ratio and packing fraction on the self-assembly of single patch colloids is a crucial aspect of understanding the behaviour of these particles. The patch ratio, which is the ratio of the area of the patch to the area of the colloid, plays a significant role in determining the self-assembly behaviour of single patch colloids. [**oh2019colloidal**, **pham2017assembly**]. The packing fraction, which is the ratio of the volume of the colloids to the total volume of the system, also influences the self-assembly behaviour.[**van2018surface**] Understanding these factors is essential for designing and controlling the self-assembly of these particles into specific structures.

While there are several experimental studies on the self-assembly of single patch colloids, there is a need for more detailed investigations into the effects of patch ratio and packing fraction on the assembly behaviour. For example, more experiments could be conducted to study the influence of these factors on the formation of different cluster structures and the overall ordering of the colloids.[**pham2017assembly**]

In this project we study the effect of patch ratio and packing fraction in the self-assembly of single patch colloids. These parameters are varied under fixed potentials among the molecules and the size and shape of clusters is analysed.

2.4 Future Directions and Changes

. Even though there have been great strides made, there are still problems in the field of patchy colloids. These include the evolution of shape control during colloidal quantum-dot growth, solvent-induced nanoparticle assembly, and controlling self-organization through confinement.[**sciortino2010numerical**, **yi2013recent**] Researchers are investigating the creation of useful materials and devices through bottom-up assembly as well as the usage of patchy colloids for tissue engineering applications.[**yi2013recent**, **duguet2016patchy**] The literature analysis concludes by highlighting the increased interest in patchy colloids and their self-assembly, highlighting its potential applications in nanotechnology and materials research. The capacity to create particles with directed interactions has created new opportunities for the investigation of intricate phenomena and the creation of useful materials.[**yi2013recent**, **duguet2016patchy**]

Chapter 3

Molecular Dynamics

Patchy particle interaction occurs by electromagnetic interaction between the patches. We define the potential in a molecular simulation, which could be the WCA potential, the Lennard Jones potential, or another type of potential. The calculation of forces between particles, or the approximate numerical solution of a coupled non-linear differential equation, or the calculation of each particle's trajectory within a system, is the fundamental component of molecular dynamics. Pairwise interactions between the particles and the potential between each pair must be calculated. Molecular dynamics involve three parts:

1 .Summation of the forces and torques.

2 .Integration of the equations of motion.

3 .Data extraction form the computed particle trajectories.

The forces here in consideration are:

1 PS-PS interaction

3 PS-TPM interaction

3 TPM-TPM interaction.

Since our system is periodic, it is unnecessary to describe the boundary condition in the cases where the function is non-periodic. When a particle leaves a periodic system at one side, it is reinserted at the other. Furthermore, considered is the interaction between particles on different sides of the simulation. When

dealing with periodic conditions, the system's size needs to be sufficiently large to prevent artefacts resulting from non-physical correlations between the simulation area's periodically enlarged borders. The interaction forces are independent of the particles' spatial orientation in the significant instance of spherical particles. Since initial conditions are only employed once, no complex algorithms are needed. Long-term conduct frequently occurs without reference to specific initial conditions. Following initialization, the system is numerically integrated until it reaches a steady state as part of the simulation process.

Since initial conditions are only needed once, complex algorithms do not need to be developed to generate them. Many times, a system's long-term behaviour is unaffected by specific beginning conditions.

3.1 Model for Spherical Particles

Colloidal particles are assumed to be hard spheres. Simulations using spherical particles are numerically very efficient since particles colloids. The potentials in play during the simulation are WCA potential between TPM-TPM particles, TPM-PS particles, PS-PS particles.

3.1.1 WCA potential

The Weeks-Chandler-Andersen (WCA) potential is a modification of the Lennard-Jones potential used in molecular dynamics simulations. It is designed to smoothly truncate the standard Lennard-Jones potential at a specific distance, rather than abruptly cutting it off as is typically done. This truncation is useful in simulations where long-range interactions are not significant and computational efficiency is desired. The WCA potential is defined as:

$$V_{WCA} = 4\epsilon[(\frac{\sigma}{r})^{12} - (\frac{\sigma}{r})^{6}] + \epsilon, \tag{3.1}$$

when $r < r_c$ or 0 when $r > r_c$

Here is the distance between two particles, r_c is the cut off distance beyond which potential is truncated to 0. ϵ is the depth of the potential well and σ is

the finite distance at which inter-particle potential is zero. Corresponding force expression is given by

$$F_{WCA} = 24\epsilon[\frac{2\sigma^{12}}{r^{13}} - \frac{\sigma^6}{r^7}] \tag{3.2}$$

The Weeks-Chandler-Anderson potential has significant potential in molecular dynamics simulations, especially for systems where short-range repulsive forces dominate. Its simplicity and computational efficiency make it a valuable tool for studying a wide range of materials, from simple liquids to complex soft matter. However, careful consideration must be given to its applicability and accuracy for specific systems, particularly those where attractive interactions are crucial.

3.1.2 Morse Potential

The Morse potential, also known as the Morse oscillator or the Morse function, is a mathematical model used to describe the potential energy of a diatomic molecule as a function of the distance between its atoms. It is particularly useful in molecular physics, quantum chemistry, and molecular dynamics simulations. The Morse potential is given by the equation:

$$V_M = D(1 - e^{-a(r-r_e)})^2 \tag{3.3}$$

Where D is the dissociation energy representing the depth of the potential well, r is the equilibrium bond length, the distance at which the potential energy is minimized, a is the width parameter controlling the curvature of the potential well.

Corresponding equation of force is given by

$$F_M = 2aDe^{-a(r-r_e)}(1 - e^{-a(r-r_e)})^2 \tag{3.4}$$

The Morse potential is a more realistic model for the potential energy of a diatomic molecule compared to the harmonic oscillator model. It provides a good approximation for the behavior of molecular bonds, particularly in the context of bond dissociation and anharmonicity. Its functional form allows for a better representation of the energy required to stretch and break bonds, making it a

valuable tool in various fields of chemistry and physics.

3.2 Particle Model for Simulation of Particles

Using a particle model that depicts each particle as a point mass at the sphere's core is a popular technique for spherical particle simulations. This simplification enables simple handling of collisions and other interactions as well as effective computing of particle interactions. Here's an overview of the particle model for simulation of spherical particles:

- Particle Representation: A point mass at the sphere's centre represents each spherical particle. The particle's position and velocity in space are represented by the point mass's position and velocity.

- Particle Attributes: Spherical particles can have mass, radius, density, and material qualities (such as elasticity and coefficient of friction) in addition to position and velocity.

- Interaction Calculation: Physical concepts such as Newton's laws of motion and the fundamentals of classical mechanics are used to calculate the interactions between spherical particles. Collisions, electrostatic repulsion, and gravitational attraction are examples of common interactions. The previous section covered the two kinds of particles in the simulation and their interactions.

- Collision Detection and Response: One crucial component of the simulation is identifying collisions between spherical particles. This entails using the locations and radii of two particles to determine if they overlap or encounter one another. For this, collision detection algorithms like geometric intersection tests and bounding sphere collision detection are frequently utilised. A collision response technique is used to ascertain the nature of particle interactions when a collision between spherical particles is detected. This could entail adjusting their velocities to save energy and momentum, addressing interpenetration, and, if required, applying frictional forces. In our simulation, only molecule-to-molecule interactions are considered.

- Integration Algorithm: Using numerical integration procedures as the Verlet algorithm, leapfrog integration, or Runge-Kutta techniques, the positions and velocities of spherical particles are updated throughout time. These methods preserve momentum and energy while guaranteeing a realistic simulation of the system dynamics.

- Boundary Conditions: The borders of the simulation space and the ways in which particles interact with them are specified by boundary conditions. Periodic borders, reflecting boundaries, and absorbing boundaries are examples of common boundary conditions.

3.3 Verlet Lists

Particles frequently interact with one another in molecular dynamics simulations through non-bonded interactions like the Coulombic or Lennard-Jones potential. Nevertheless, it can be computationally costly to calculate every pairwise interaction at every time step, particularly for large systems. This problem is solved by the Verlet list, which keeps track of any particle pairs that are adjacent to one another within a predetermined cutoff distance. To consider changes in particle positions, this list is updated periodically, usually less frequently than the simulation time step. Computational efficiency can be significantly increased by only computing interactions between particles that are included in the Verlet list as opposed to computing every paired interaction at every time step. The steps involved in using a Verlet list typically include:

- Initialization: A Verlet list is created at the start of the simulation by finding particle pairs that are adjacent to one another by a predetermined cutoff distance.

- Updating the Verlet List: The Verlet list is updated periodically to reflect changes in particle locations. A specific condition, like the maximum displacement of particles since the last update, may be used to trigger this update.

- Interaction Calculation: Particle interactions are only calculated for couples

that are present in the Verlet list at each time step of the simulation. This results in a large reduction in the number of pairwise interactions that require computing, improving computational efficiency.

- Periodic Rebuilding: If there are major changes to the system, like particle insertions or deletions, that render the present Verlet list invalid, it can become necessary to rebuild the list from scratch in certain instances.

Overall, the Verlet list approach is a useful optimisation tactic in molecular dynamics simulations, especially for systems with lots of particles or systems where interactions are important only in specific ranges. It permits simulations to run more quickly without compromising accuracy

3.4 Link Cell Algorithm

The Link Cell algorithm is an optimization technique used in computational physics, particularly in simulations involving particle systems like molecular dynamics. It's used to efficiently compute pairwise interactions between particles within a certain cutoff distance by organizing particles into cells and considering interactions only between particles in neighbouring cells. Here's an overview of how the Link Cell algorithm typically works:

- Domain Division: A grid of cells makes up the simulation domain. Every cell is a tiny compartment that is either rectangular or cubic in shape.

- Particle Assignment: Based on its position, each particle in the simulation is given a cell. The usual method for completing this assignment is to identify which cell holds the coordinates of the particle.

- Linking Neighbours: A list of adjacent cells is produced for every cell. Cells that are adjacent to the present cell are those that have the same face, edge, or vertex. By linking, each cell is guaranteed to have effective access to its neighbours' cells for interaction computations.

- Interaction Calculation: Calculate interactions by repeatedly going through each cell and the cells that surround it. Consider solely the interactions

between the particles in each pair of adjacent cells. Comparing this step to computing interactions between every pair of particles in the simulation results in a considerable reduction in the number of pairwise interactions that need to be computed.

- Parallelization: To increase computational performance, especially for simulations involving a large number of particles, the Link Cell algorithm can be parallelized. One way to implement parallelization tactics is to create subdomains inside the simulation domain and allocate a distinct processor or thread to each subdomain.

- Periodic Boundary Conditions: Interactions between particles near the boundaries are considered with extra caution if periodic boundary conditions exist in the simulation region. In these kinds of situations, particles close to one border might interact with those close to the other boundary as though they were in the same periodic image of the simulation cell.

Overall, the Link Cell algorithm is an effective optimization technique for reducing the computational cost of pairwise interaction calculations in particle simulations. It's commonly used in molecular dynamics simulations and other simulations involving large numbers of particles or atoms.

Chapter 4

Model and Methods

The patchy colloid is modelled as a combination of Polystyrene and TPM. These two molecules are fabricated into patchy colloids via a fabrication method which combines the incompatible elements in a cosolvent emulsion droplet and then using phase separation to create patches [**oh2019colloidal**]. Temperature, drag coefficient, spring constant, dissipation constant are fixed for the systems. We fix a lattice cell of constant side length, L and hence constant volume and vary the packing fraction and the diameter of the patches. This results in varied number of colloidal particles in the simulation box. We fixed the packing fraction at different values like 0.02, 0.05, 0.1, 0.15 etc and varied the diameter of the patch as 0.25, 0.5, 1, 1.25 etc. and studied the behaviour of the janus particle.

4.1 Model of the Molecule Used in the Study

. A component of the materials utilised in investigations involving the creation of anisotropic silica/polymer composite particles and the manipulation of colloids for self-assembly is the PS-TPM molecule.[**chang2021controllable**] Along with other compounds like OTS-TPM and PEO-b-PS-TPM, the PS-TPM molecule has been examined in TGA (Thermogravimetric Analysis) graphs, which display weight percentages following heat treatment at various temperatures.[**lavagnini2024simulating**] This molecule contributes to the production of particles with unique characteristics and functions by aiding in the controllable synthesis of patchy particles with customisable geometry and orthogonal chemistry.[**chang2021controllable**]

The PS-TPM molecule, which stands for poly(styrene-co-3-trimethoxysilyl propyl methacrylate), is a crosslinked copolymer that consists of styrene and 3-(trimethoxysilyl)propyl methacrylate (TMSPM) monomers.[**lu2007synthesis**, **vitry2003hybrid**, **jiang2008synthesis**] Since the PS-TPM molecule is essential to creating patchy particles with adjustable geometry and orthogonal chemistry, it has a significant bearing on research on patchy colloids. Styrene and 3-(trimethoxysilyl)propyl methacrylate (TMSPM) monomers make up the PS-TPM molecule, which enables the formation of particles with jagged PS-Br lobes and a smooth p(TPM)/p(TMSPA) patch.[**chang2021controllable**]

4.2 Potentials used in the Simulation

There are two particles in the simulation. Hence there are three interactions: PS-PS interaction, PS-TPM interaction, TPM-TPM interaction. WCA potential is defined for all the interactions. In addition to this PS particles have Morse potential among them.

4.2.1 WCA Potential

WCA (Weeks -Chandler-Anderson) Potential is given by:

$$V_{WCA} = 4\epsilon[(\frac{\sigma}{r})^{12} - (\frac{\sigma}{r})^{6}] + \epsilon, \tag{4.1}$$

when $r < r_c$ or 0 when $r > r_c$

Here is the distance between two particles, r_c is the cut off distance beyond which potential is truncated to 0. ϵ is the depth of the potential well and σ is the finite distance at which inter-particle potential is zero.

4.2.2 Morse Potential

The potential energy of a diatomic molecule as a function of the distance between its atoms is described mathematically by the Morse potential, sometimes called the Morse oscillator or the Morse function. It is especially helpful in simulations related to molecular dynamics, quantum chemistry, and molecular physics.

The Morse potential is given by the equation:

$$V_M = D(1 - e^{-a(r-r_e)})^2 \tag{4.2}$$

Where D is the dissociation energy representing the depth of the potential well, r is the equilibrium bond length, the distance at which the potential energy is minimized, a is the width parameter controlling the curvature of the potential well.

4.3 Cluster Size Distribution

The cluster size distribution refers to the statistical distribution of the number of particles or entities within a cluster. This distribution is often characterized by a long tail, indicating that there are a few large clusters and many smaller ones. The distribution can be modeled using various mathematical frameworks, including probabilistic models and percolation theory.

Each of the output data is analysed to get cluster size distribution and plotted is used Matlab.

4.4 Simulation setup

A simulation model of a patchy molecule of TPM (a cross-linked 3- (tri methoxysilyl) was made and given appropriate potential between them. It includes interparticle potential and morse potential. We simulated each system of Janus particle, using particle system molecular dynamics and using c++ code. Each system varies from one another in number of particles, since we vary the diameter of the patches and packing fraction. All simulations are performed in cubic lattice cell applying periodic boundary conditions. We fixed the length of side of the lattice cell at 25 units. The number of particles in each system is calculated using equation:

$$N = \frac{\phi L^3}{(\pi/6) + (\pi/6)D^3} \tag{4.3}$$

Where N is the number of particles in the box, L is the side length of the lattice cell, ϕ is the packing fraction of the cell and D is the diameter of the patch. Several sets of simulations are run. In each set, the diameter of the patch is fixed. The number of particles in the simulation box in each value of packing fraction is inserted into the code. In each of the run the simulation get an output result.

In this project, we observe the dynamics of the single patch colloids in low packing fraction, that is less than 0.05. We take the packing fractions, 0.01, 0.02, 0.03, 0.04 and 0.05. The patches of different sizes are considered. Patch ratio less than and greater than the core particle is considered ranging from 0.25 to 1.75 at intervals of 0.25. We get the number of particles for each patch ratio and packing fraction as given in the following table.

1.75	47	94	141	188	235
1.5	68	136	205	273	341
1.25	101	202	303	404	505
1	149	298	448	597	746
0.75	210	470	630	838	1049
0.5	265	531	796	1061	1326
0.25	294	588	300	1175	1469
	0.01	0.02	0.03	0.04	0.05

Table 4.2: Simulation set

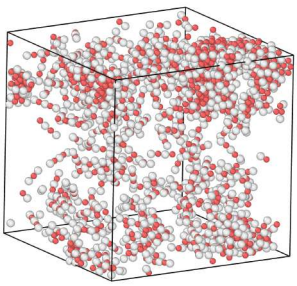


Figure 4.1: Periodic model of simulation of single patch colloids

4.5 Simulation Model

The output file generated is analysed using the Ovito software. Cluster size distribution is studied using the same. The size and distribution of the cluster is tabulated using the software and is used to plot graph using Matlab.

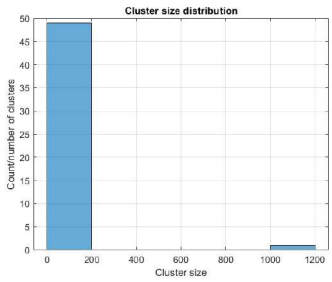


Figure 4.2: Corresponding graph of cluster size distribution of the given periodic model of simulation of single patch colloids

Chapter 5

Simulations

The output data is analysed in ovito. In this project cluster size distribution of the molecules is analysed. Simulation is run on OVITO based on the table 4.2. Cluster size distribution is analysed using OVITO. We set the cut off distance for cluster in each simulation accordingly. The output results and corresponding histograms are given:

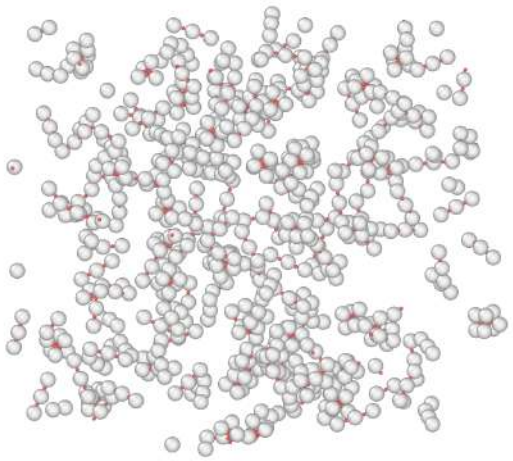
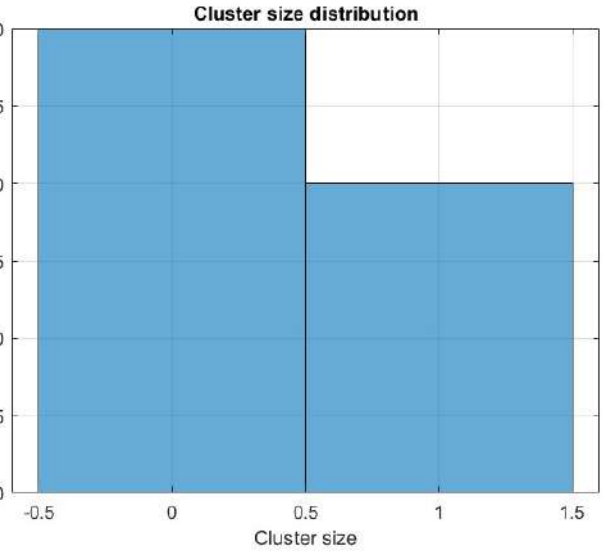


Figure 5.1: Simulation of the patchy colloids with Patch ratio: 0.25, Packing fraction:0.01



e 5.54: Histogram of cluster size distribution of the simulation with cut off
ce for cluster, 1.8

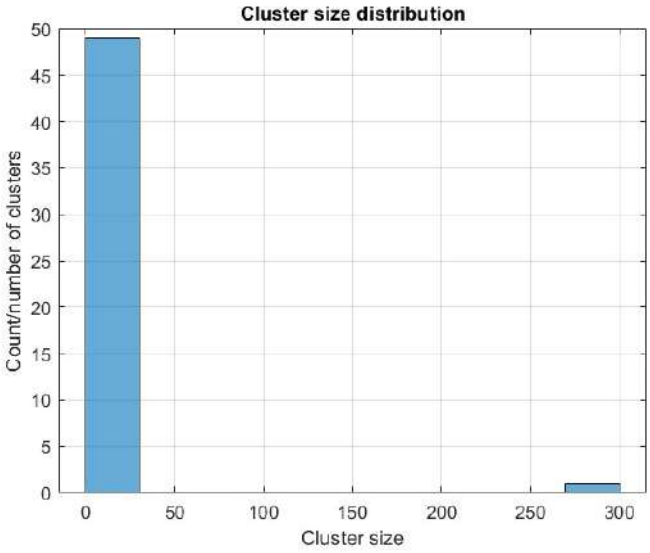


Figure 5.2: Histogram of cluster size distribution of the simulation with cut off distance for cluster, 0.3

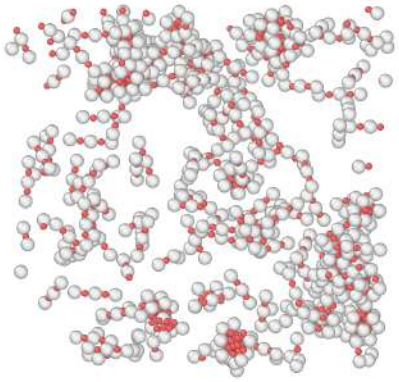


Figure 5.3: Simulation of the patchy colloids with Patch ratio: 0.5, Packing fraction:0.01

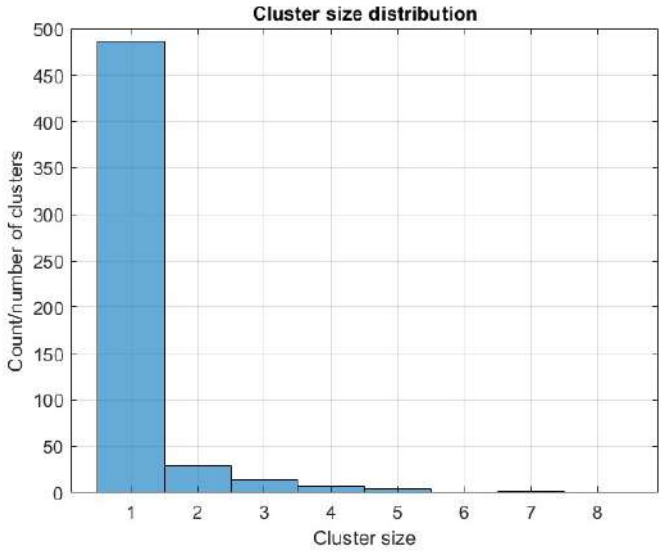


Figure 5.4: Histogram of cluster size distribution of the simulation with cut off distance for cluster, 0.55

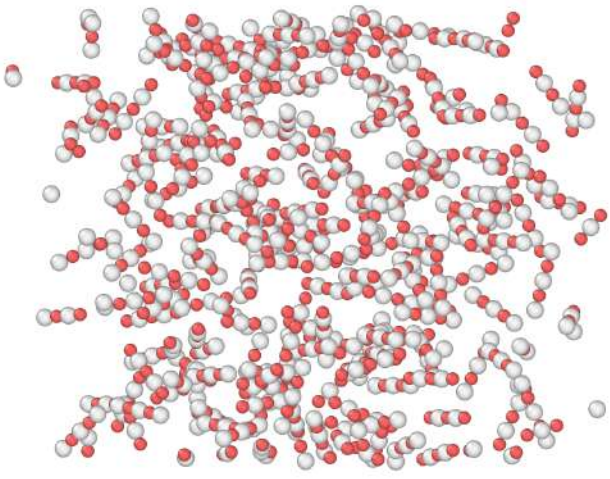


Figure 5.5: Simulation of the patchy colloids with Patch ratio: 0.75, Packing fraction:0.01

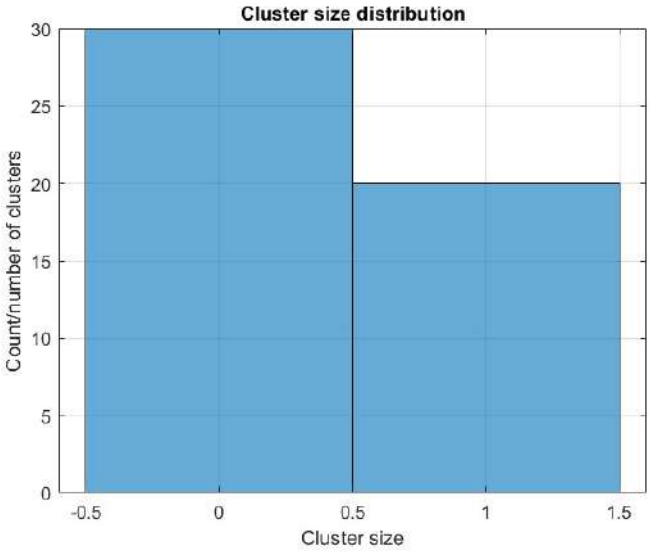


Figure 5.6: Histogram of cluster size distribution of the simulation with cut off distance for cluster, 0.8

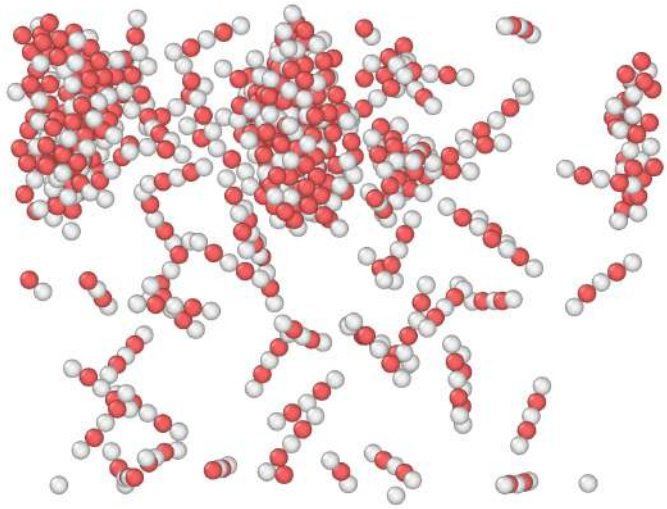


Figure 5.7: Simulation of the patchy colloids with Patch ratio: 1.0, Packing fraction:0.01

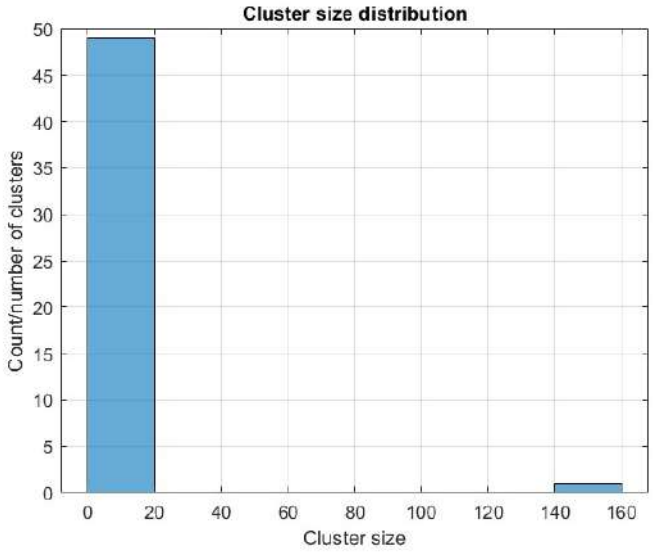


Figure 5.8: Histogram of cluster size distribution of the simulation with cut off distance for cluster, 1.05

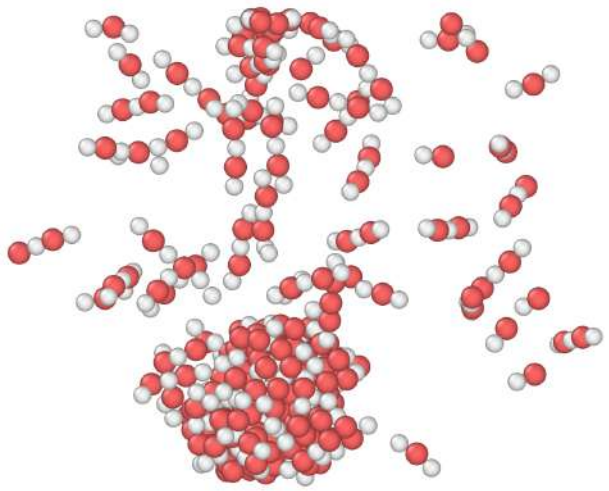


Figure 5.9: Simulation of the patchy colloids with Patch ratio: 1.25, Packing fraction:0.01

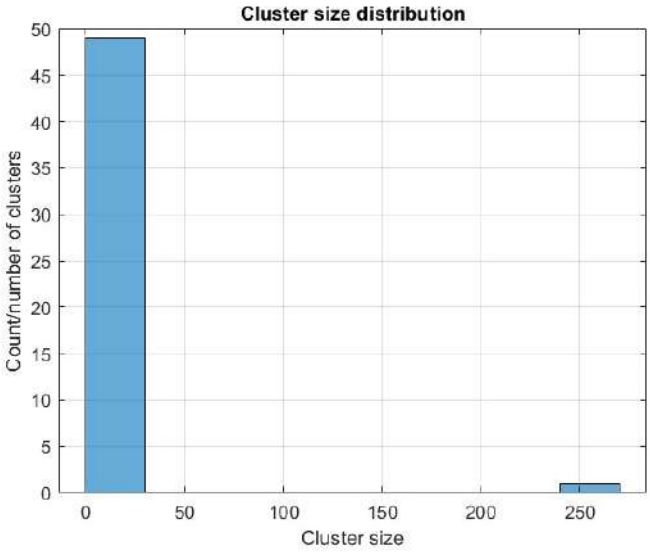


Figure 5.10: Histogram of cluster size distribution of the simulation with cut off distance for cluster, 1.3

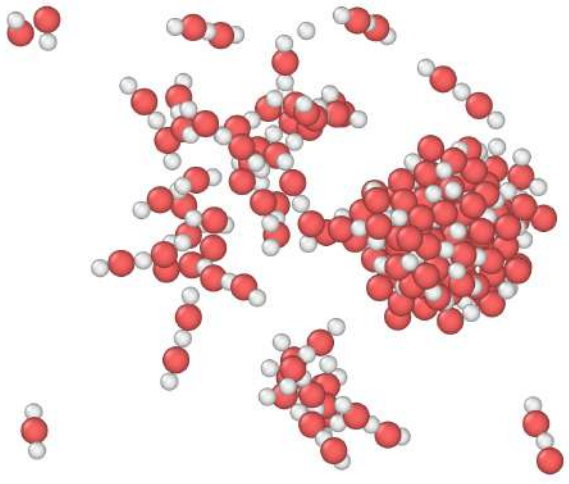


Figure 5.11: Simulation of the patchy colloids with Patch ratio: 1.5, Packing fraction:0.01

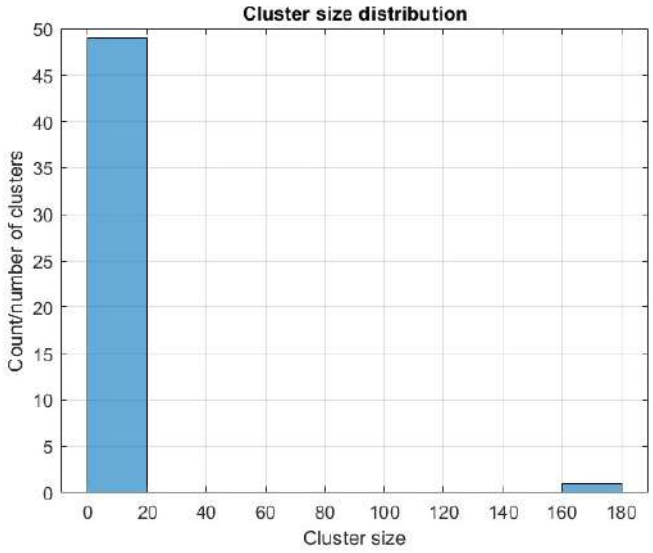


Figure 5.12: Histogram of cluster size distribution of the simulation with cut off distance for cluster, 1.6

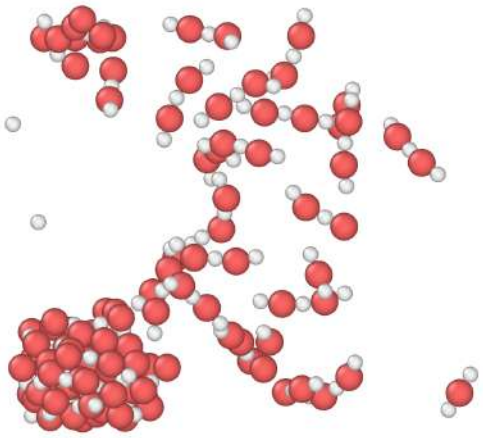


Figure 5.13: Simulation of the patchy colloids with Patch ratio: 1.75, Packing fraction:0.01

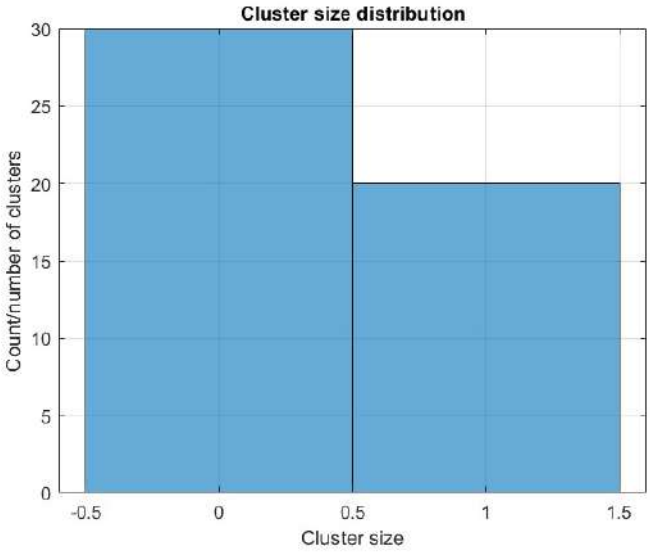


Figure 5.14: Histogram of cluster size distribution of the simulation with cut off distance for cluster, 1.8

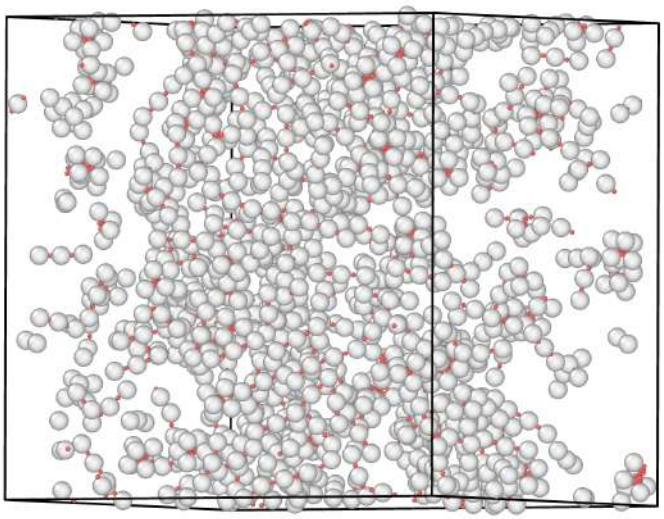


Figure 5.15: Simulation of the patchy colloids with Patch ratio: 0.25, Packing fraction:0.02

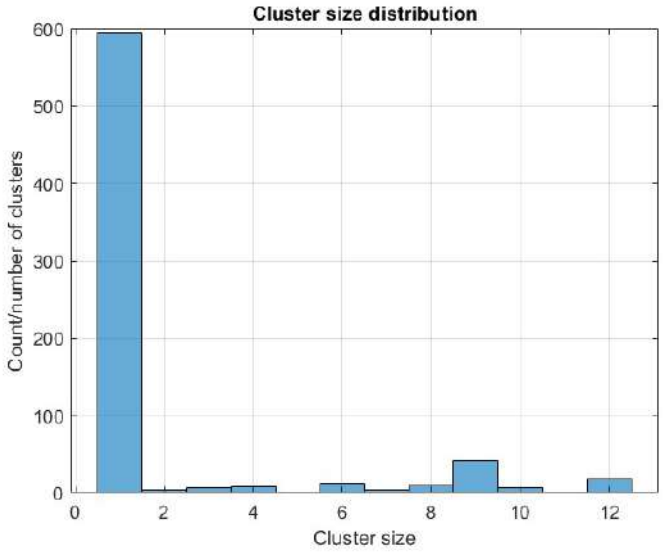


Figure 5.16: Histogram of cluster size distribution of the simulation with cut off distance for cluster, 0.3

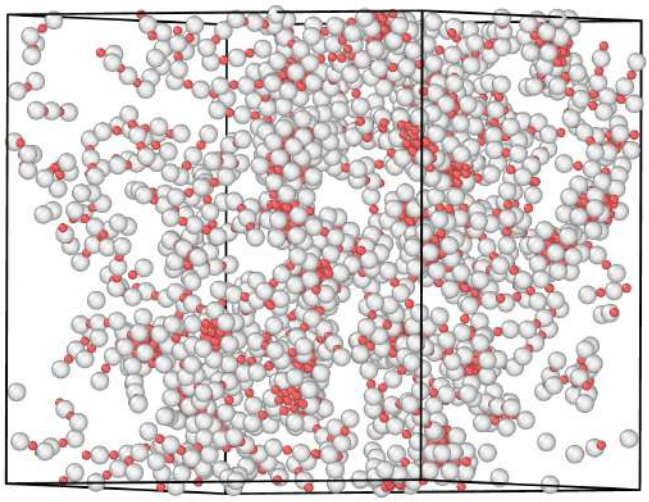


Figure 5.17: Simulation of the patchy colloids with Patch ratio: 0.5, Packing fraction:0.02

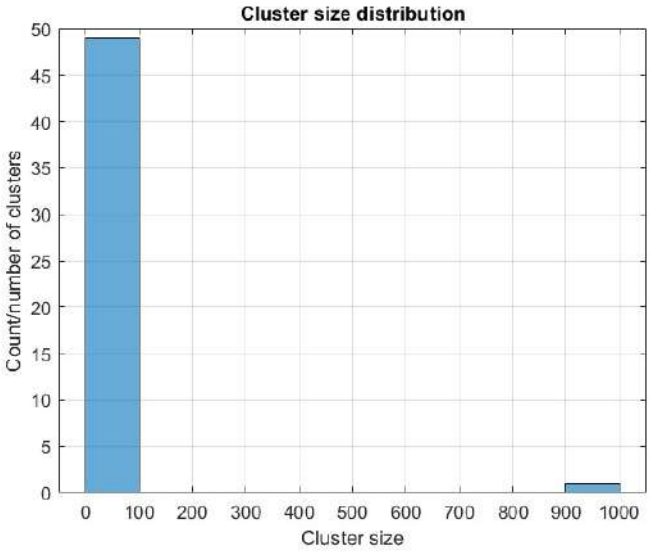


Figure 5.18: Histogram of cluster size distribution of the simulation with cut off distance for cluster, 0.55

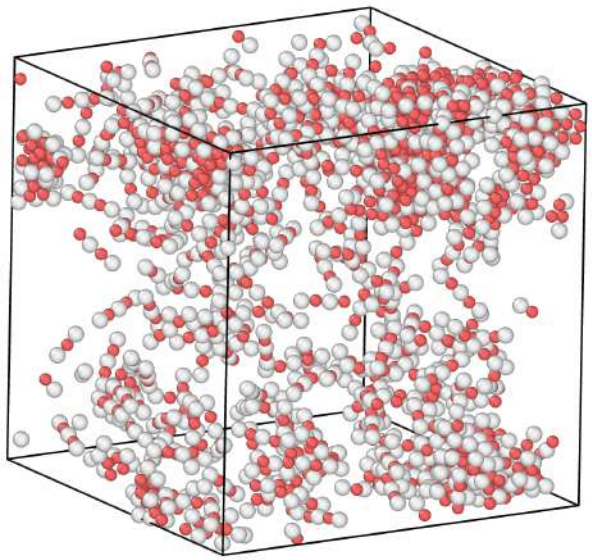


Figure 5.19: Simulation of the patchy colloids with Patch ratio: 0.75, Packing fraction:0.02

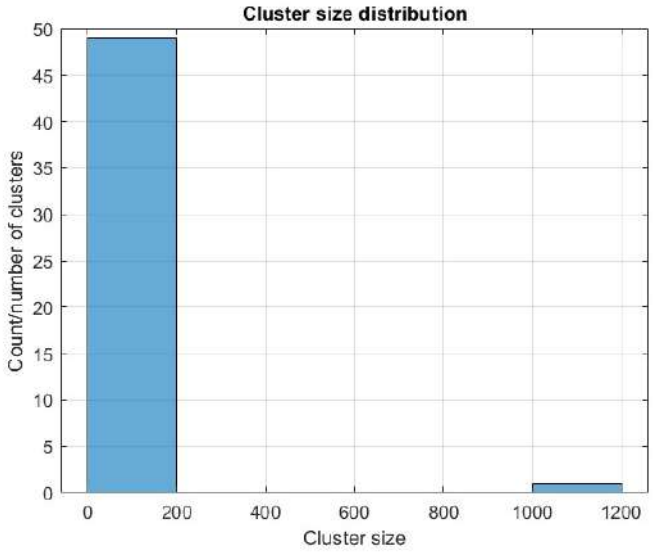


Figure 5.20: Histogram of cluster size distribution of the simulation with cut off distance for cluster, 0.8

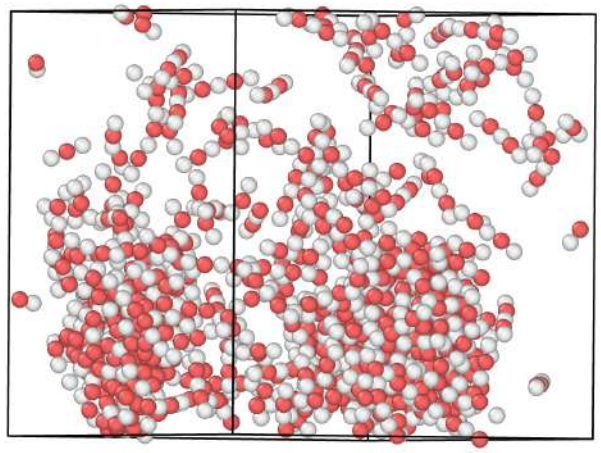


Figure 5.21: Simulation of the patchy colloids with Patch ratio: 1.0, Packing fraction:0.02

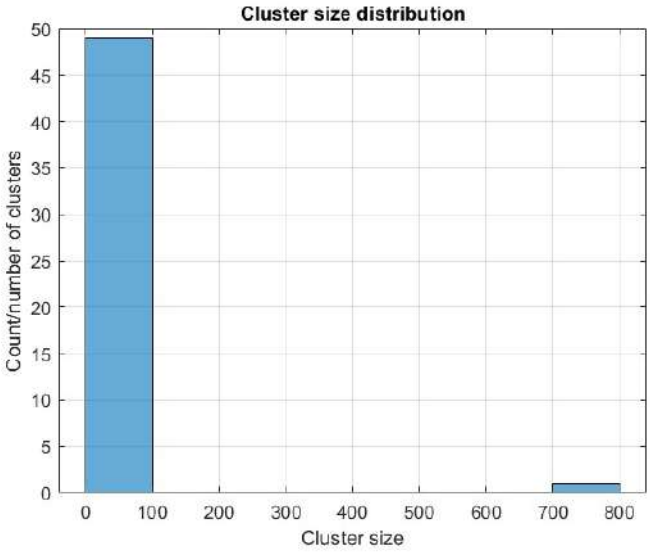


Figure 5.22: Histogram of cluster size distribution of the simulation with cut off distance for cluster, 1.05

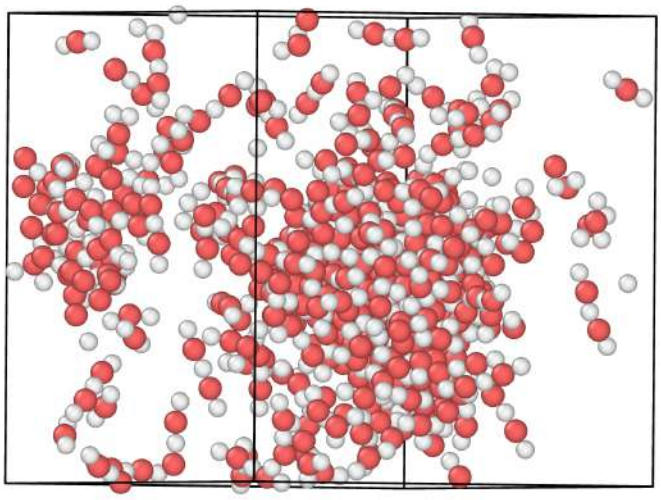


Figure 5.23: Simulation of the patchy colloids with Patch ratio: 1.25, Packing fraction:0.02

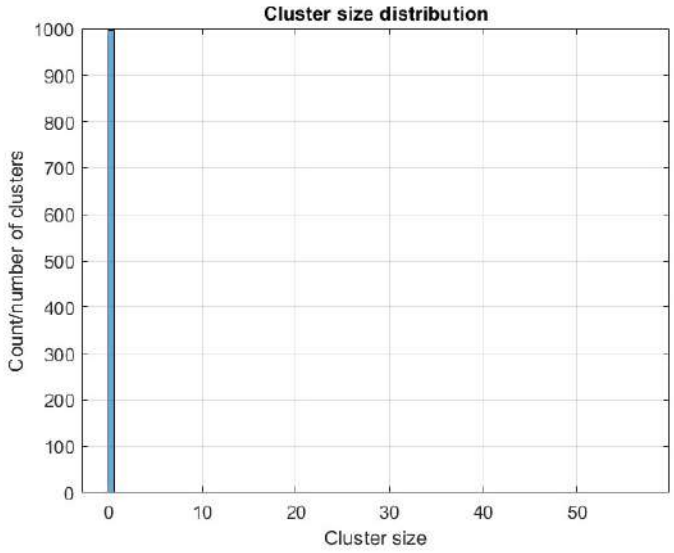


Figure 5.24: Histogram of cluster size distribution of the simulation with cut off distance for cluster, 1.3

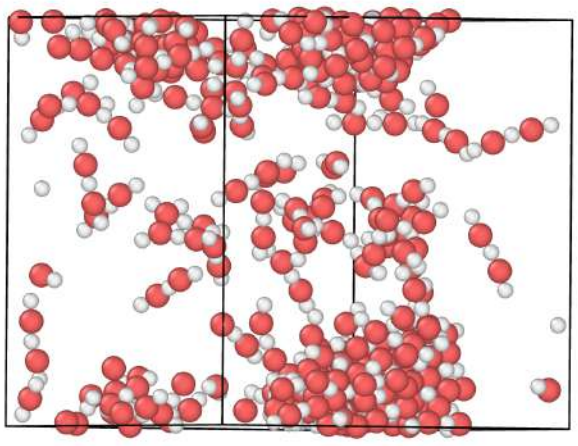


Figure 5.25: Simulation of the patchy colloids with Patch ratio: 1.5, Packing fraction:0.02

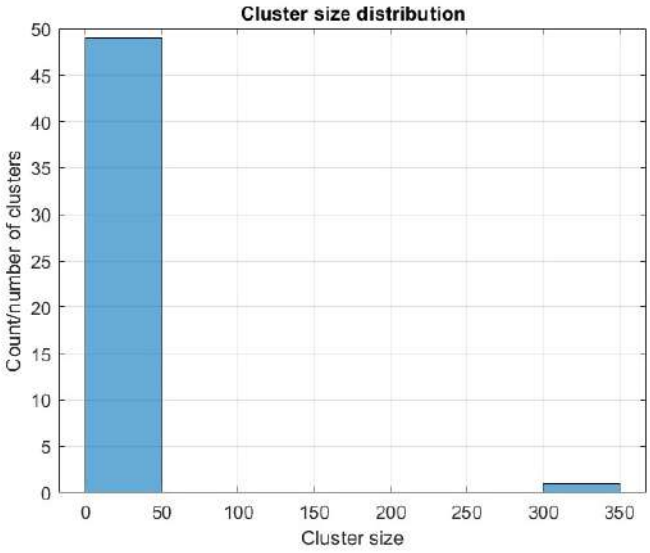


Figure 5.26: Histogram of cluster size distribution of the simulation with cut off distance for cluster, 1.5

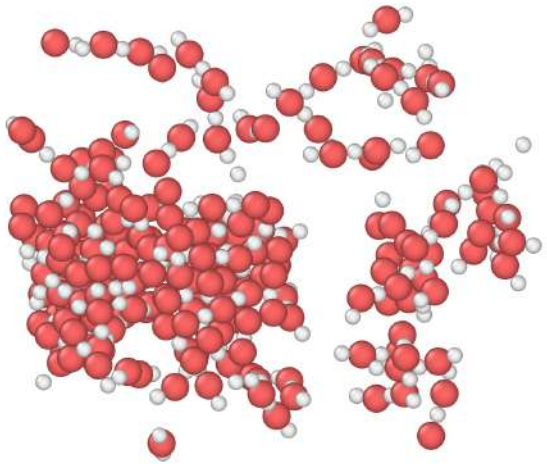


Figure 5.27: Simulation of the patchy colloids with Patch ratio: 1.75, Packing fraction:0.02

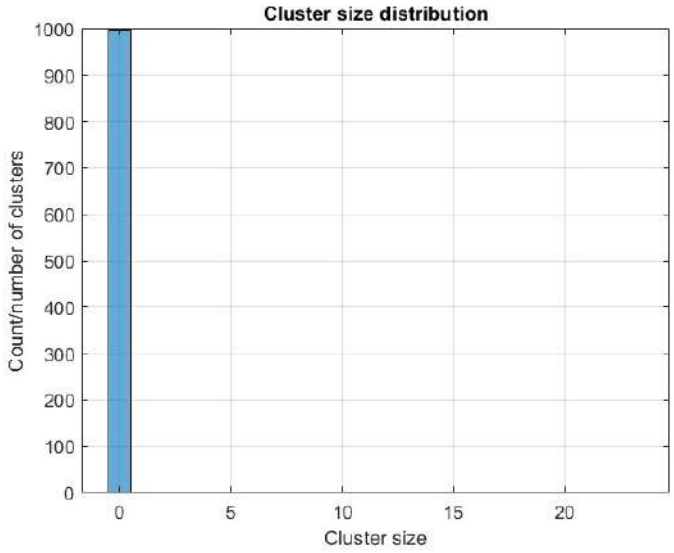


Figure 5.28: Histogram of cluster size distribution of the simulation with cut off distance for cluster, 1.8

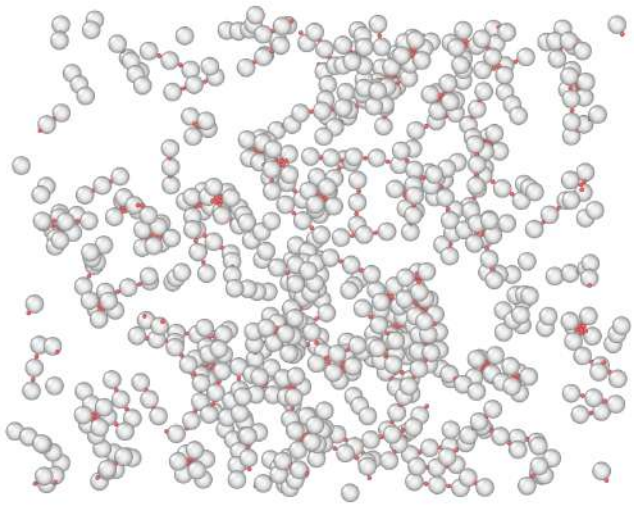


Figure 5.29: Simulation of the patchy colloids with Patch ratio: 0.25, Packing fraction:0.03

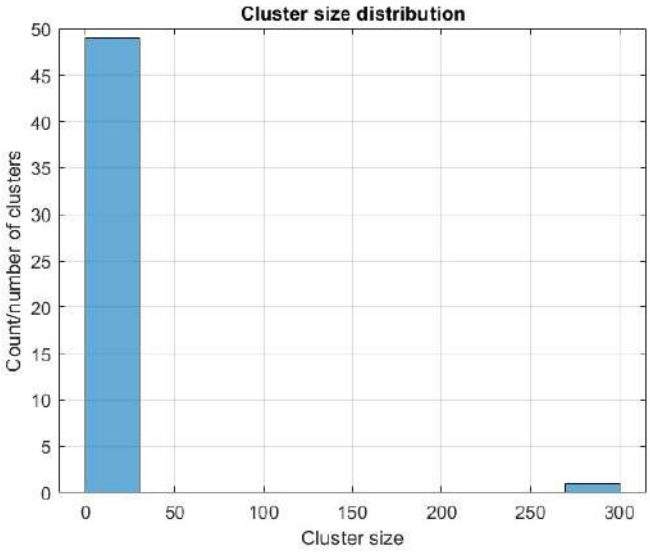


Figure 5.30: Histogram of cluster size distribution of the simulation with cut off distance for cluster, 0.3

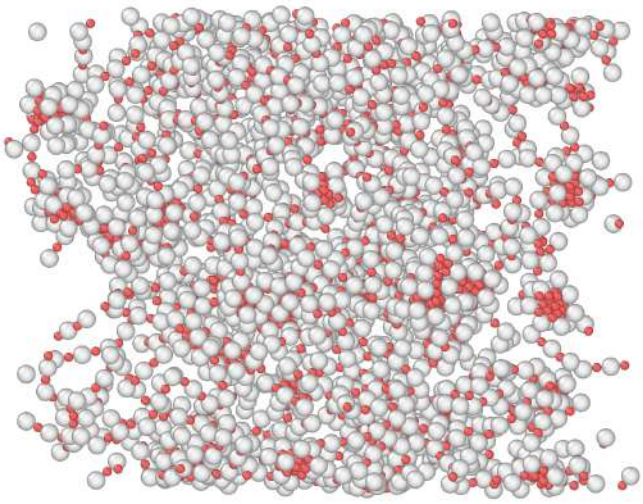


Figure 5.31: Simulation of the patchy colloids with Patch ratio: 0.5, Packing fraction:0.03

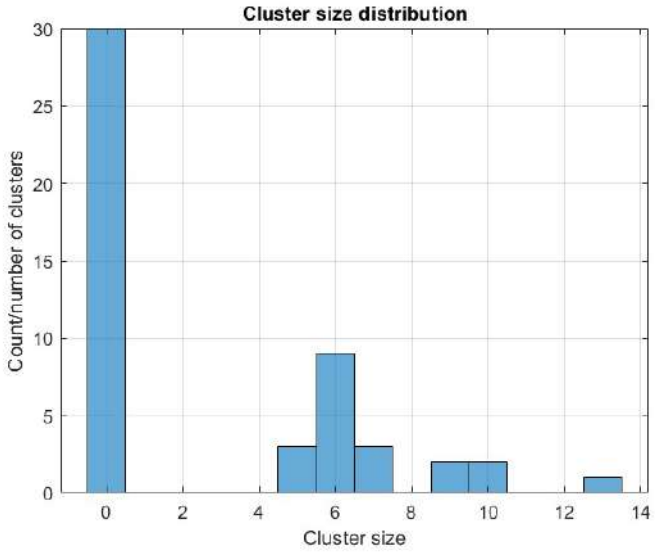


Figure 5.32: Histogram of cluster size distribution of the simulation with cut off distance for cluster, 0.55

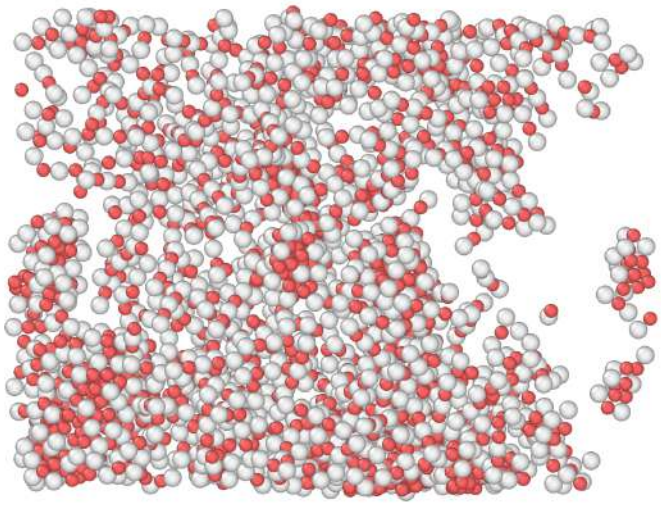


Figure 5.33: Simulation of the patchy colloids with Patch ratio: 0.75, Packing fraction:0.03

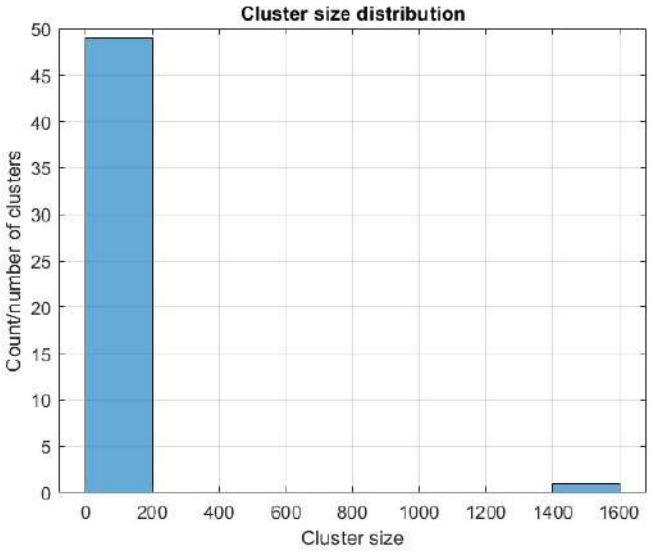


Figure 5.34: Histogram of cluster size distribution of the simulation with cut off distance for cluster, 0.8

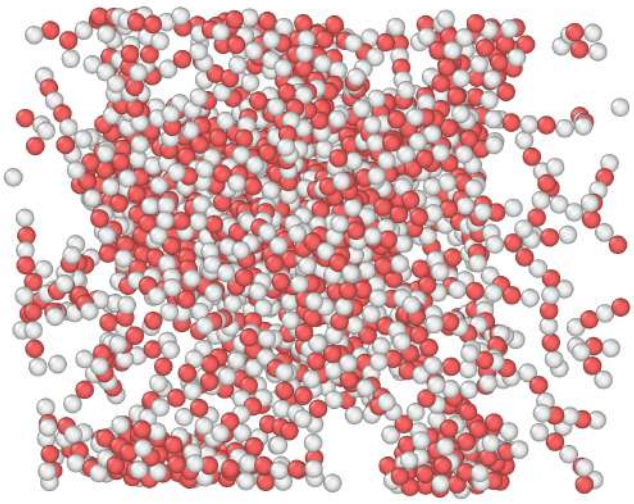


Figure 5.35: Simulation of the patchy colloids with Patch ratio: 1.0, Packing fraction:0.03

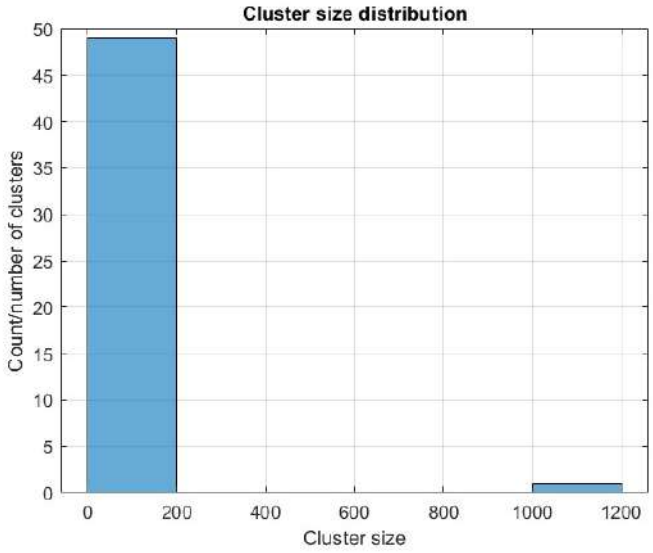


Figure 5.36: Histogram of cluster size distribution of the simulation with cut off distance for cluster, 1.05

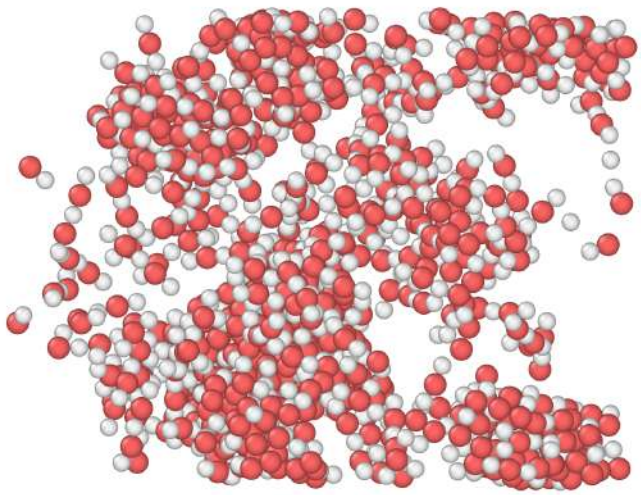


Figure 5.37: Simulation of the patchy colloids with Patch ratio: 1.25, Packing fraction:0.03

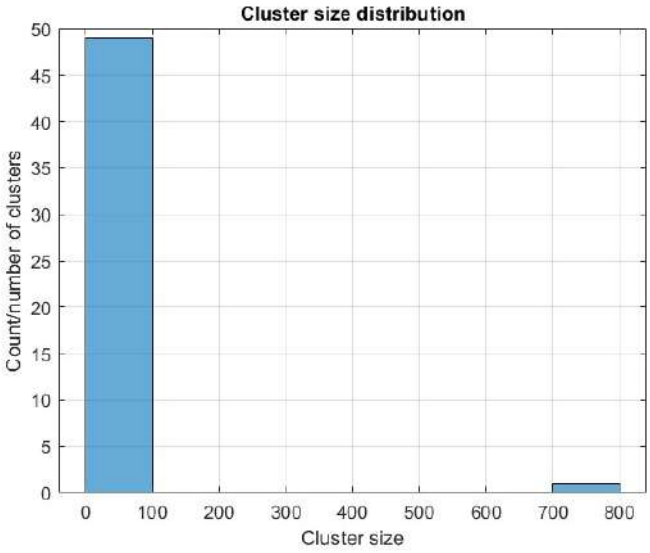


Figure 5.38: Histogram of cluster size distribution of the simulation with cut off distance for cluster, 1.3

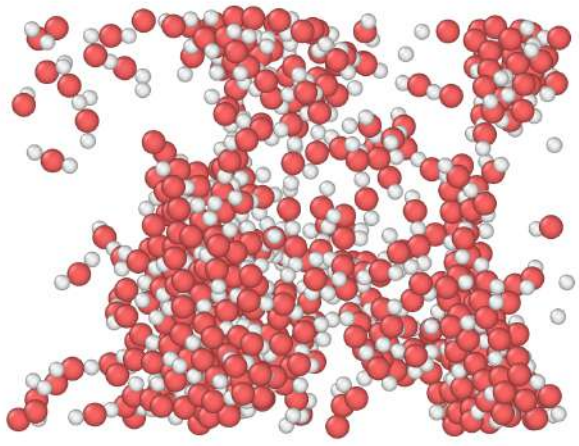


Figure 5.39: Simulation of the patchy colloids with Patch ratio: 1.5, Packing fraction:0.03

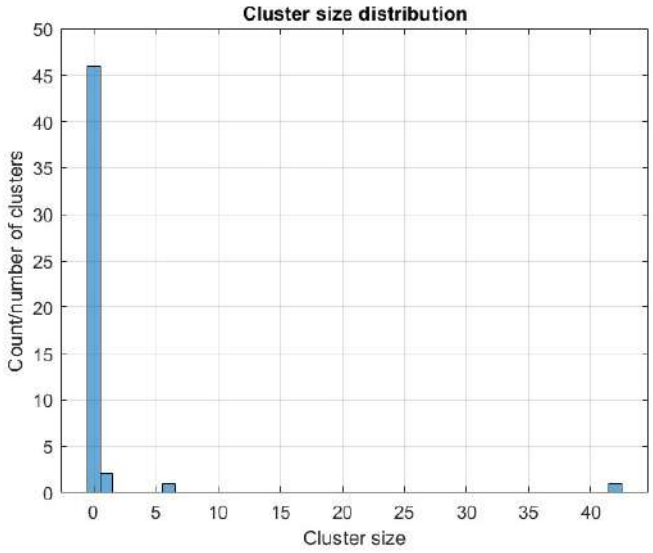


Figure 5.40: Histogram of cluster size distribution of the simulation with cut off distance for cluster, 1.6

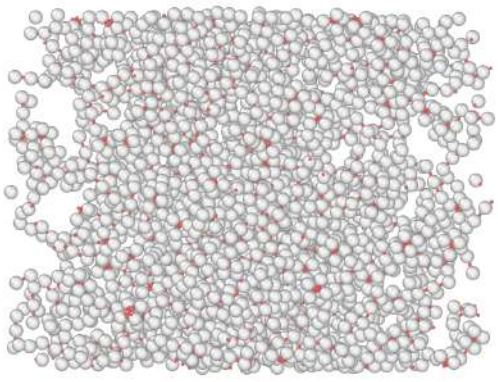


Figure 5.41: Simulation of the patchy colloids with Patch ratio: 1.75, Packing fraction:0.03

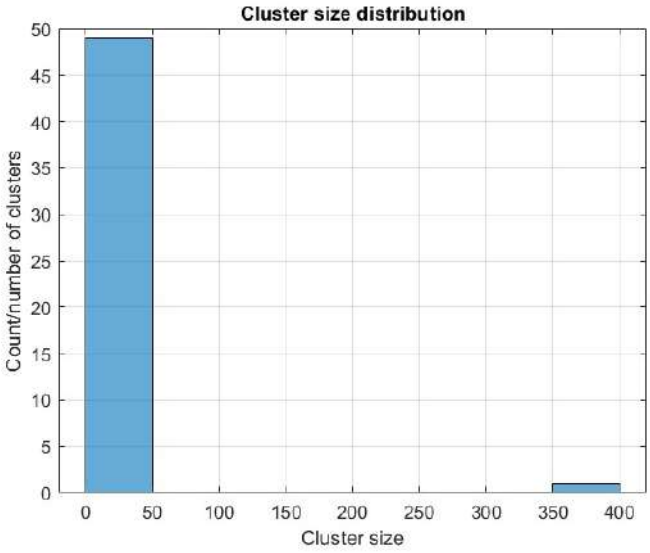


Figure 5.42: Histogram of cluster size distribution of the simulation with cut off distance for cluster, 1.8

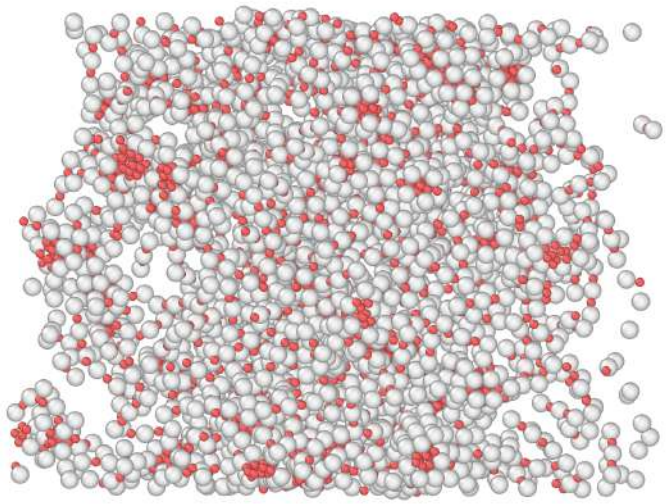


Figure 5.43: Simulation of the patchy colloids with Patch ratio: 0.5, Packing fraction:0.04

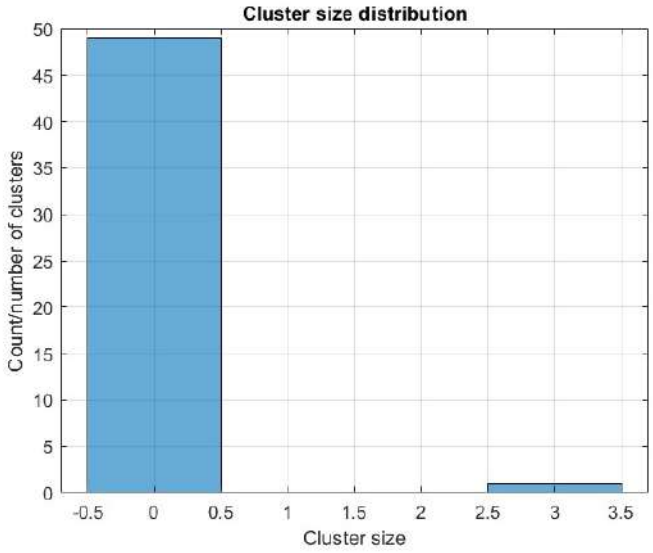


Figure 5.44: Histogram of cluster size distribution of the simulation with cut off distance for cluster, 0.55

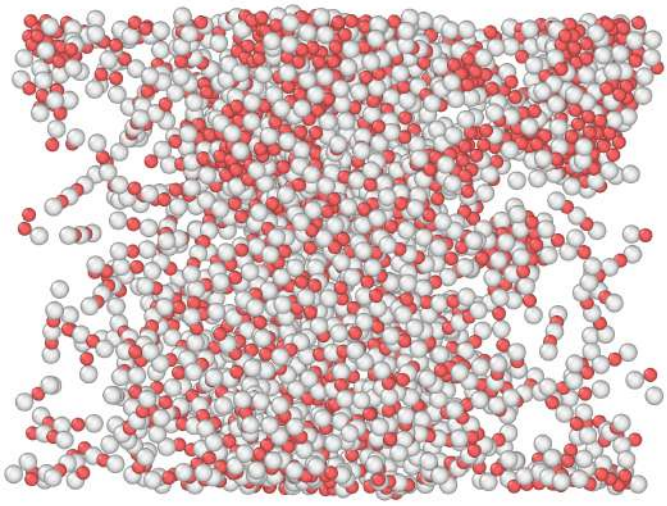


Figure 5.45: Simulation of the patchy colloids with Patch ratio: 0.75, Packing fraction:0.04

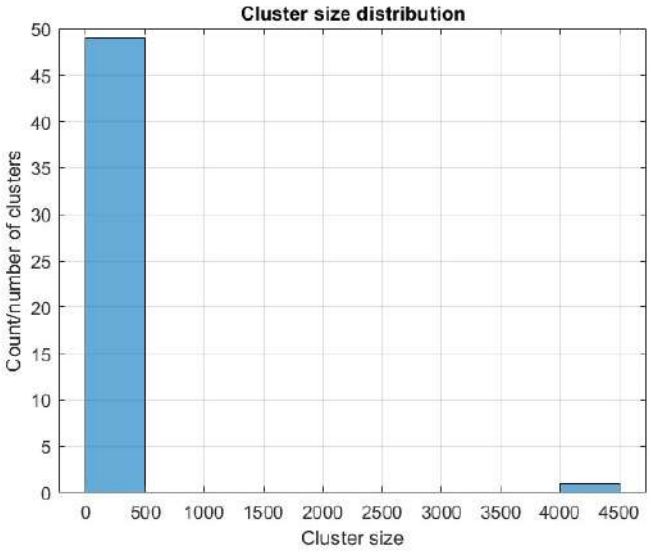


Figure 5.46: Histogram of cluster size distribution of the simulation with cut off distance for cluster, 0.8

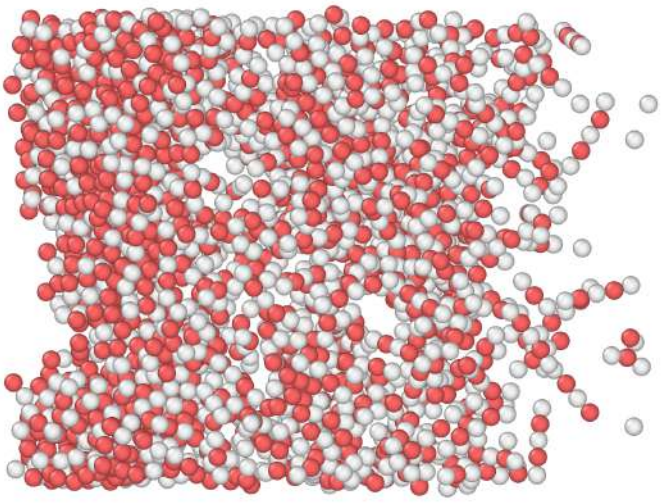


Figure 5.47: Simulation of the patchy colloids with Patch ratio: 1.0, Packing fraction:0.04

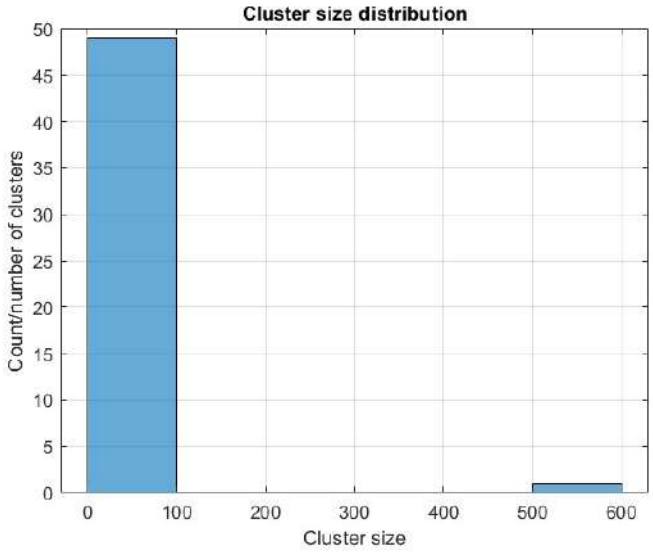


Figure 5.48: Histogram of cluster size distribution of the simulation with cut off distance for cluster, 1.05

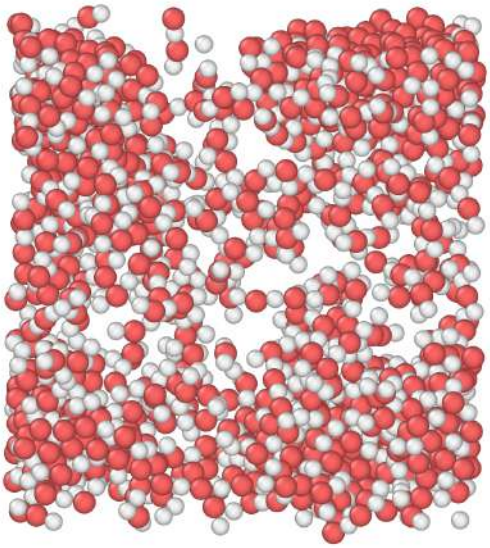


Figure 5.49: Simulation of the patchy colloids with Patch ratio: 1.25, Packing fraction:0.04

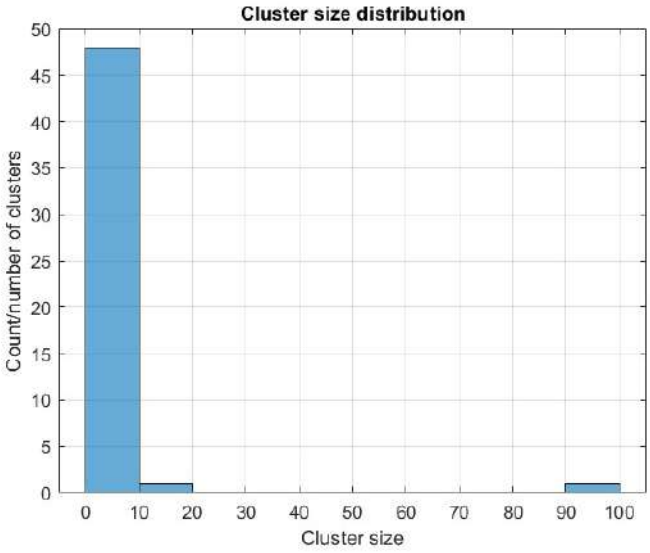


Figure 5.50: Histogram of cluster size distribution of the simulation with cut off distance for cluster, 1.3

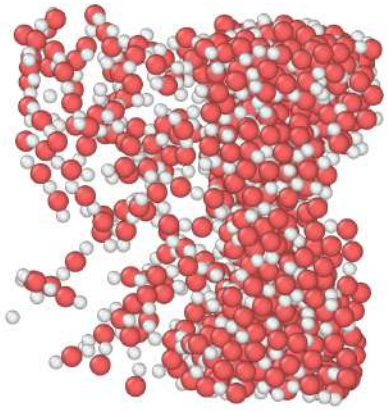


Figure 5.51: Simulation of the patchy colloids with Patch ratio: 1.5, Packing fraction:0.04

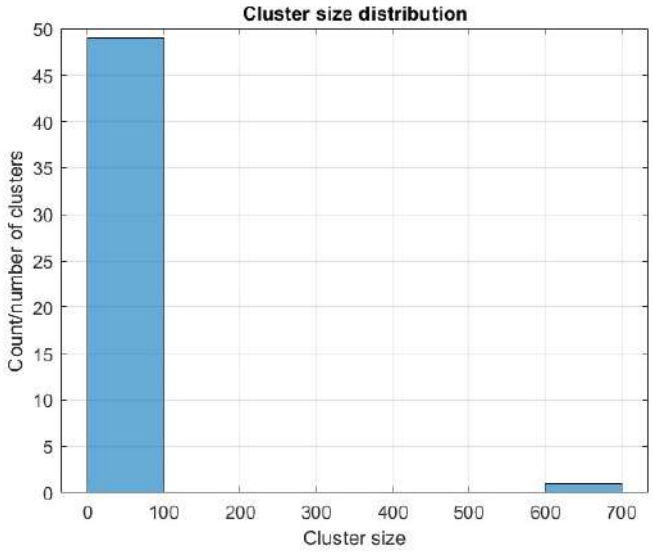


Figure 5.52: Histogram of cluster size distribution of the simulation with cut off distance for cluster, 1.6

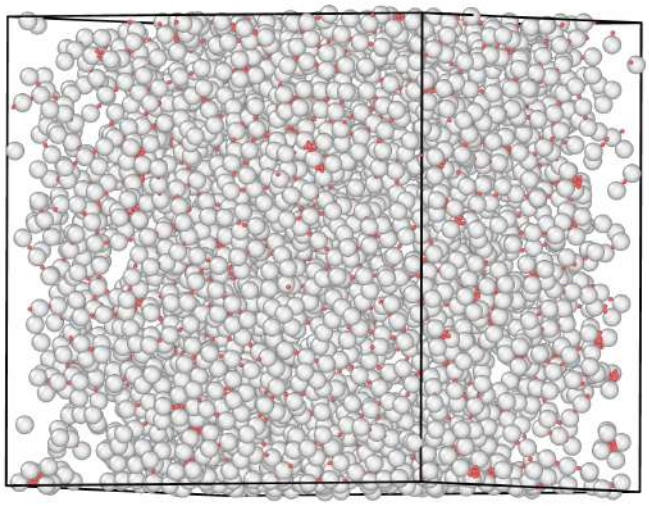


Figure 5.55: Simulation of the patchy colloids with Patch ratio: 0.25, Packing fraction:0.05

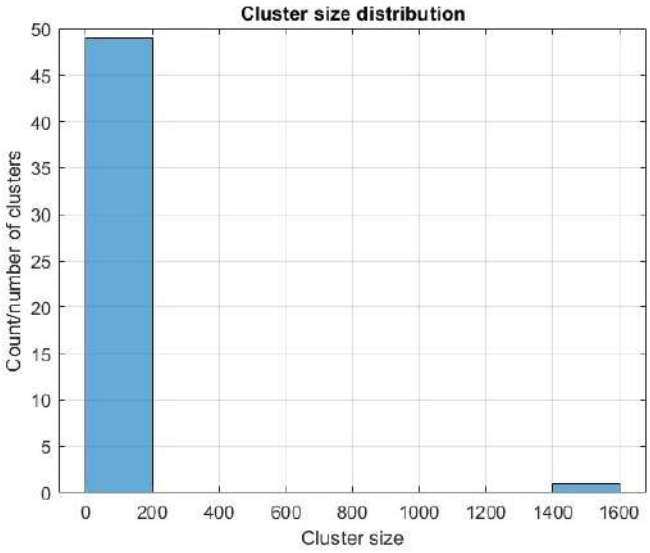


Figure 5.56: Histogram of cluster size distribution of the simulation with cut off distance for cluster, 0.3

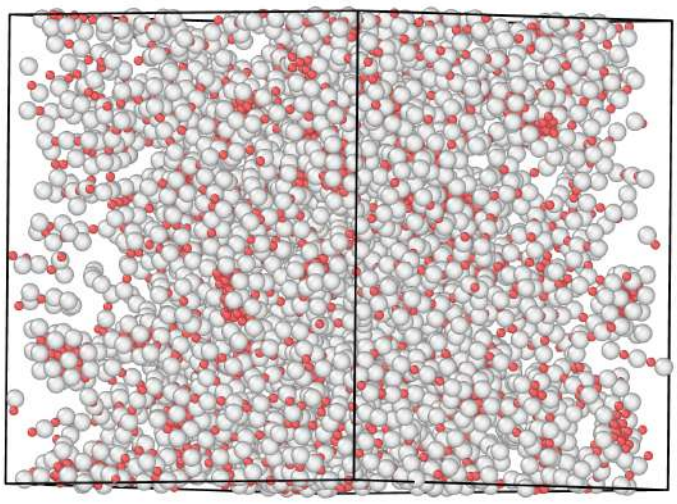


Figure 5.57: Simulation of the patchy colloids with Patch ratio: 0.5, Packing fraction:0.05

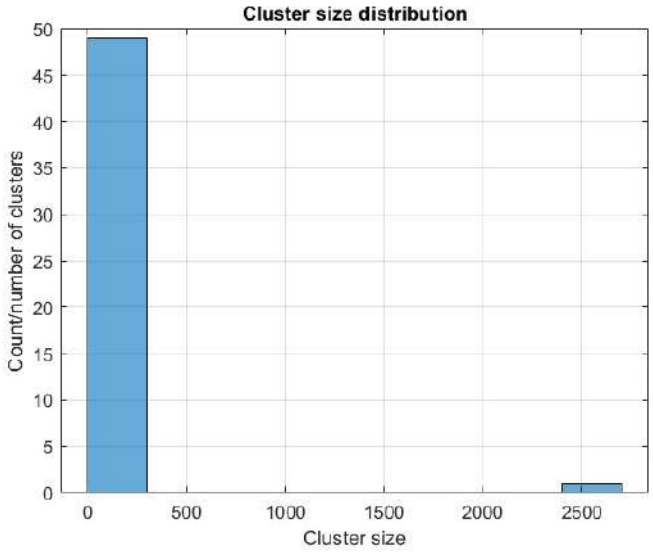


Figure 5.58: Histogram of cluster size distribution of the simulation with cut off distance for cluster, 0.55

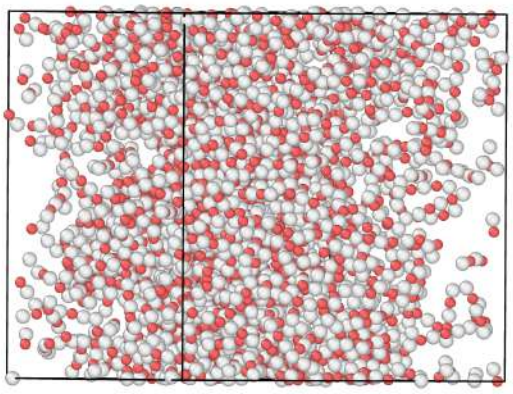


Figure 5.59: Simulation of the patchy colloids with Patch ratio: 0.75, Packing fraction:0.05

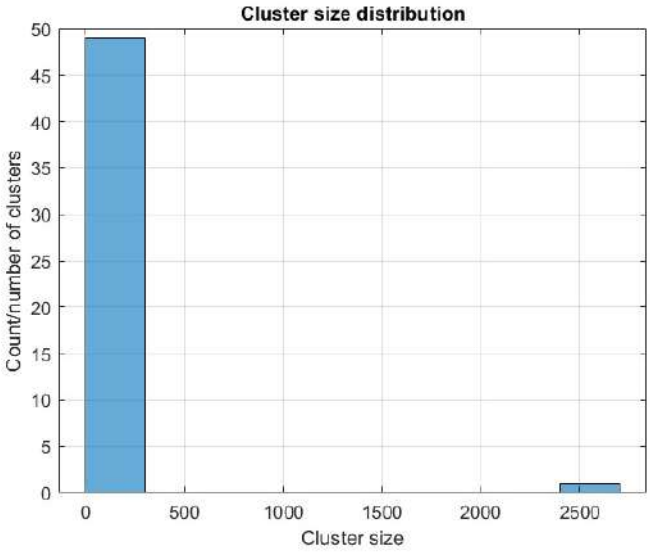


Figure 5.60: Histogram of cluster size distribution of the simulation with cut off distance for cluster, 0.8

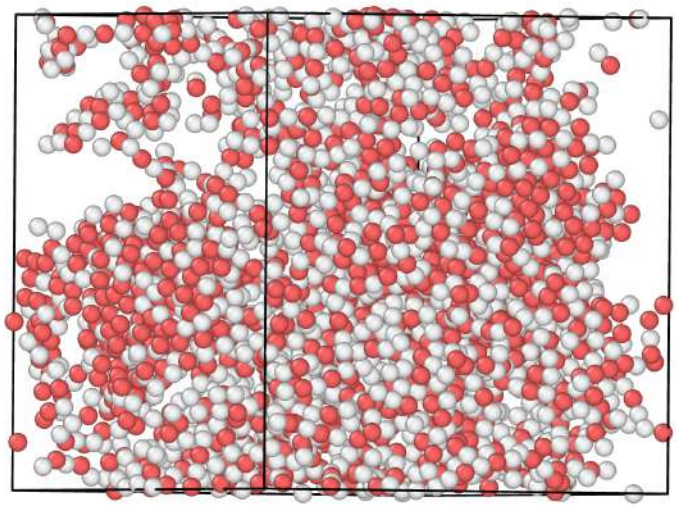


Figure 5.61: Simulation of the patchy colloids with Patch ratio: 1.0, Packing fraction:0.05

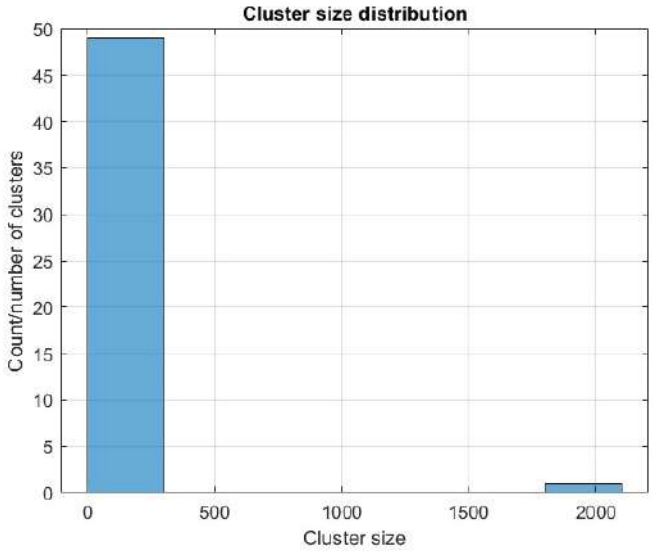


Figure 5.62: Histogram of cluster size distribution of the simulation with cut off distance for cluster, 1.05

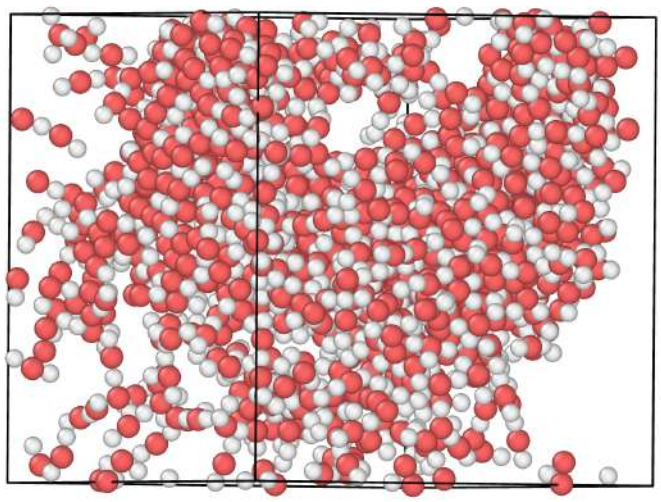


Figure 5.63: Simulation of the patchy colloids with Patch ratio: 1.25, Packing fraction:0.05

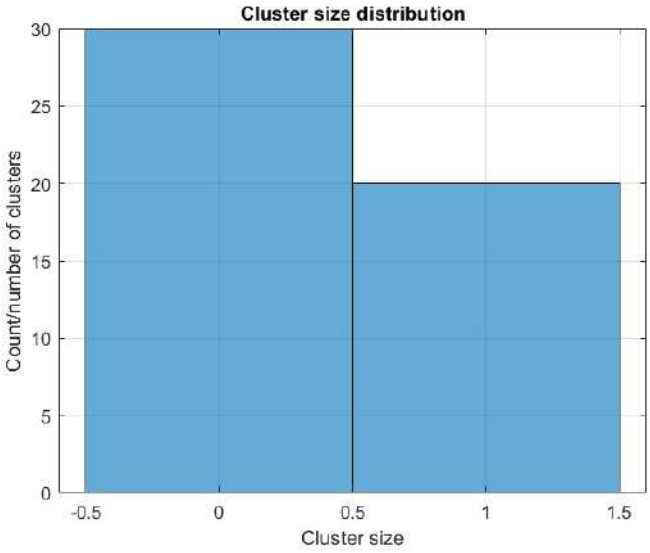


Figure 5.64: Histogram of cluster size distribution of the simulation with cut off distance for cluster, 1.3

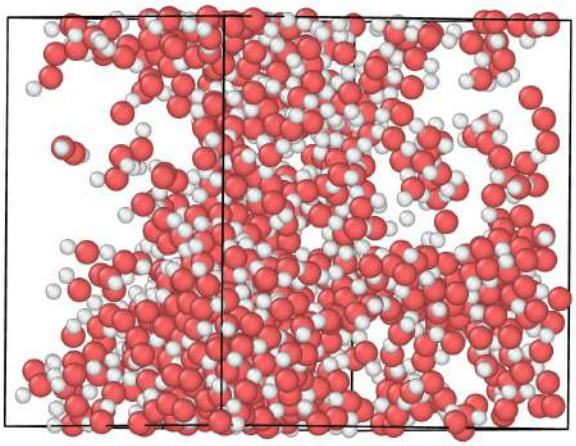


Figure 5.65: Simulation of the patchy colloids with Patch ratio: 1.5, Packing fraction:0.05

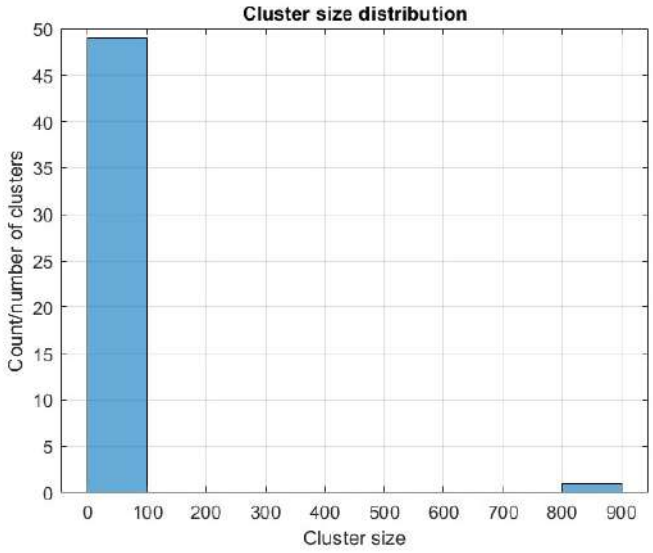


Figure 5.66: Histogram of cluster size distribution of the simulation with cut off distance for cluster, 1.6

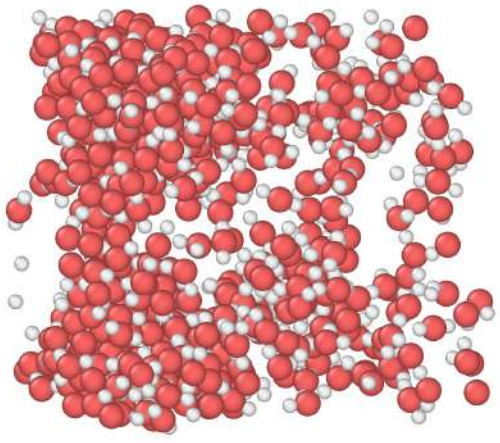


Figure 5.67: Simulation of the patchy colloids with Patch ratio: 1.75, Packing fraction:0.05

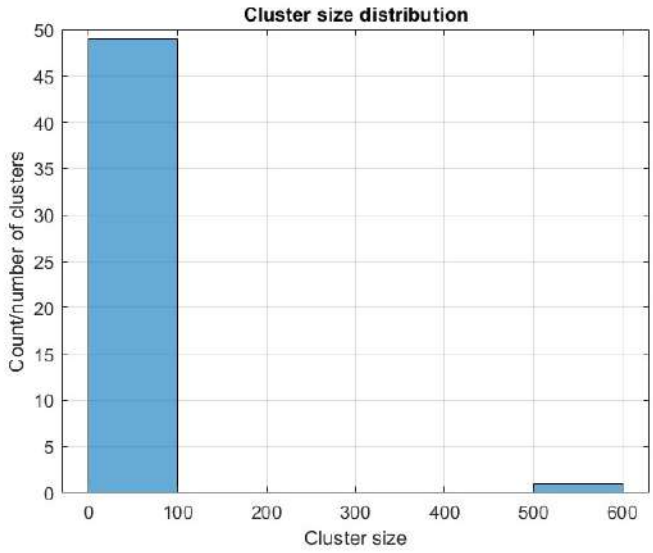


Figure 5.68: Histogram of cluster size distribution of the simulation with cut off distance for cluster, 1.8

Chapter 6

Results and Discussions

Analysing the ovito file we can see that for low patch ratio, i.e less than one or when the patch is less than the size of the core molecule, micelle formation is observed at larger scale. When patch size is greater than one or when the patch is greater than the size of the core molecule, micelle formation is not observed. Small linear molecules or dimers are observed.

In both the cases, clusters of larger size are observed. However the number of the larger cluster is very limited. Now, considering different packing fraction,for fixed patch ratio, as packing fraction increases, number of patchy colloids also increases. But if we examine the histograms along with this data, we can see that there is no significant increase in the number of smaller clusters, either micelles or smaller polymers such as dimers or trimers except in few cases. In these exceptional cases, where the number of small clusters increase drastically, there is no larger clusters formed. Hence we can conclude that there is no significant effect of packing fraction in self-assembly of single patch colloids.

Chapter 7

Conclusion

Patchy colloids are area of intensive research due to their unique property of directional bonding and colloidal valence. They can be used in construction of new nano materials as well as for study of biological structures. Patchy colloids can self-assemble into different structures according the provided parameters. In this project we consider two parameters, patch ratio and packing fraction and examine their role in self assembly and structure formed during the process. From the examination of the output data from the simulation using Ovito and Matlab, it is observed that for packing fraction less than 1, or when size of the patch is less than the size of the core molecule, there is a tendency to form micelles, whereas in high packing fraction or when the size of the patch is higher than the core molecule, micellar molecules are not formed but small linear polynomials such as dimers and tetramers are formed. A common structure observed in both cases is that there larger clusters formed. reference