THE PENNSYLVANIA STATE UNIVERSITY
SCHREYER HONORS COLLEGE

DEPARTMENT OF CHEMICAL ENGINEERING

SIMULATING REVERSIBLE AGGREGATIONS OF COLLOIDAL PARTICLES

ALAN O. JOHNSON
SPRING 2017

A thesis
submitted in partial fulfillment
of the requirements
for a baccalaureate degree
in Chemical Engineering
with honors in Chemical Engineering

Reviewed and approved* by the following:

Dr. Themis Matsoukas
Professor of Chemical Engineering
Thesis Supervisor

Dr. Themis Matsoukas
Professor of Chemical Engineering
Honors Adviser

Dr. Michael Janik
Professor of Chemical Engineering and Chair of the Brennan Clean Energy Early Career Professorship
Thesis Reader

* Signatures are on file in the Schreyer Honors College.

ABSTRACT

This study used the computational mathematics program, *Mathematica*, to model and simulate reversible aggregations of colloidal particles. Reversible colloidal aggregations can be found in silane-containing colloids at low pH's. The goal of the research was to use the simulation created using *Mathematica* to find the equilibrium size, conformation, and properties, of a reversible cluster at a given temperature, attraction, repulsion, and screening. An initial simulation was conducted which indicated the possibility of an equilibrium structural conformation at dimensionless temperatures of $\Theta = 0.9$ and $\Theta = 1.0$. Another round of simulations was conducted at identical conditions to replicate the apparent minimums present in the first set of data. It was concluded, however, that significant noise in the data cast doubt on whether these apparent minimums indicated an equilibrium conformation of a reversible cluster. Further study will need to be conducted to determine the ideal simulation parameters that will be most ideal for observing an equilibrium conformation. Once these conditions are discovered, a more rigorous sampling method will need to be used to confirm the presence of an equilibrium conformation with confidence if a minimum value in free energy is observed.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

ACKNOWLEDGEMENTS

I want to begin by thanking all the faculty and staff at the College of Engineering at The Pennsylvania State University. The breadth of academic talent that can be found amongst the all professors has been valuable in my development as a chemical engineer. I also want to thank the Schreyer Honors College for giving me the opportunity to enrich my education. Throughout my time as a student in the Schreyer Honors College, I have had the opportunity to take honors level classes that challenged me to think critically about the fundamentals that were taught throughout the course.

Lastly, I want to thank Dr. Themis Matsoukas, who has been my mentor throughout my education at The Pennsylvania State University. Without his passion for the pursuit of knowledge and willingness to instill that same passion in me, the thesis work that follows, and that is to serve as the keystone of my undergraduate education, would have not been as fulfilling for me as a soon-to-be-graduate.

Chapter 1

Introduction

One problem that is often faced in colloidal research is simulating reversible colloidal aggregations of particles to calculate physical properties of colloidal clusters at different conditions.[1] The purpose of this research was to resolve this problem by using a computational mathematics program, known as *Mathematica*, to simulate reversible aggregations in order to gain more knowledge about the equilibrium properties of a cluster at certain temperatures and electrostatic parameters. This simulation, which is based on the prevailing theories derived from the research being done in the field of colloids, can be leveraged to make accurate predictions of reality that can be applied in the field of biotechnology, medical imaging, material science, soft-matter physics, and catalysis.

Colloidal Aggregation

Colloids are substances containing ultramicroscopic particles that are free to move in a medium.[2] Due to van der Waals forces, colloidal particles have a tendency to be attracted to each other and to form clusters. Once a cluster gets too large, the large network of clustered particles will turn a colloid, originally in the liquid phase, into a gel. This tendency for colloidal particles to attract and form large clusters is known as irreversible aggregation. However, irreversible aggregations can be prevented when the colloid experiences steric stabilization forces.[3] These forces allow colloidal particles in a cluster to

---

[1] Bentz, J., and S. Nir. "Aggregation of Colloidal Particles Modeled as a Dynamical Process." Proceedings of the National Academy of Sciences 78.3 (1981): 1634-637. Web.

[2] Law, B. M., J.-M. Petit, and D. Beysens. "Adsorption-induced Reversible Colloidal Aggregation." Physical Review E 57.5 (1998): 5782-794. Web.

[3] Lotfizadeh, Saba, Hassan Aljama, Dan Reilly, and Themis Matsoukas. "Formation of Reversible Clusters with Controlled Degree of Aggregation." Langmuir 32.19 (2016): 4862-867. Web.

break away from the cluster and redistribute in solution. These steric stabilization forces will eventually balance the short-range attractive force and long-range repulsive force in between colloidal particles until the cluster reaches a state of equilibrium. This can be accomplished by lowering the pH of a colloid (**Figure 1-1** and **Figure 1-2**).

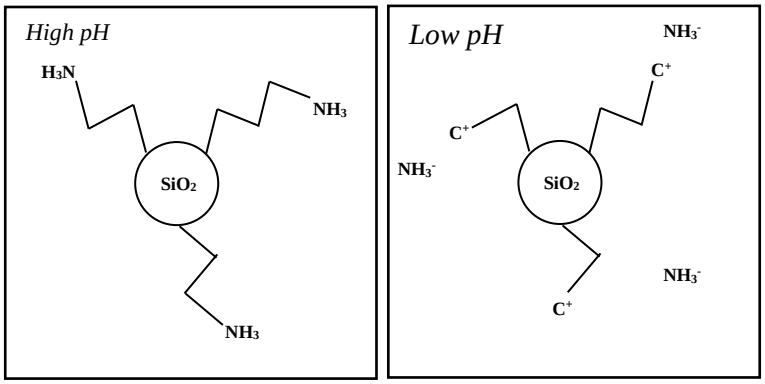

Figure 1-1. At high pH's silanes will exhibit no repulsion. However, when the pH is lowered, the amine groups of the silane will ionize. The result is a silane with positively charged branches with a coating of negatively charged ions resulting in repulsion.

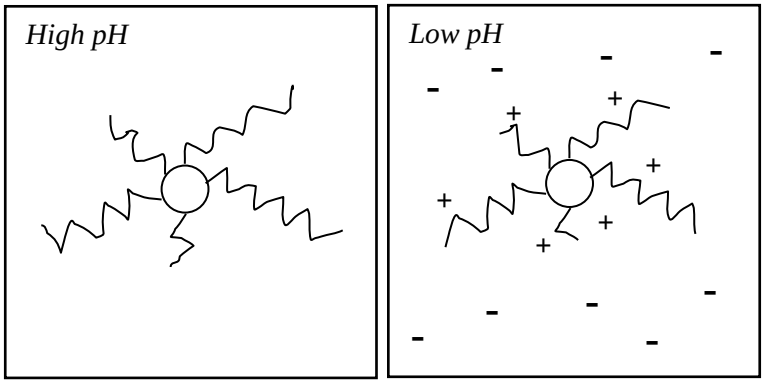

Figure 1-2 General example of example of the phenomenon observed with silanes. The repulsion that results from lowering the pH can be leveraged to prevent irreversible clusters.

These clusters that have the ability to redisperse are referred to as reversible colloidal clusters. As a result of their reversibility, many configurations of a colloidal cluster can exist in the medium at any given time. However, the configuration that is energetically favored is the configuration with the lowest

free energy. This configuration is the most likely to be observed in a mixture, and thus will dominate the macroscopic properties of the colloidal aggregation. The lowest free energy state is referred to as the equilibrium configuration of the colloidal aggregation, and is the configuration that is of most interest in this research. The goal of this research was to determine the distributions of the equilibrium structure of reversible colloidal clusters and to calculate the free energy per particle of these clusters using the *Mathematica* model that was created for the purpose of this research.

Chapter 2

Model

Several assumptions were made in order to simulate the reversible aggregation of colloidal particles using computational software. These assumptions were based on prevailing theory in colloidal research. Specifically, assumptions about the physical structure of reversible colloidal clusters were made in order for the structures to be modeled more easily in *Mathematica*. Additionally, theories from thermodynamics were employed in order to calculate the energy of clusters. The modifications to the physical structure and energy theories were programmed into the computational model of the reversible colloidal aggregations.

Cubic Lattice Model

In reality, colloidal aggregations of particles feature no significant structural patterns. This makes reversible colloidal aggregations very tricky to model computationally as enterprise software that supports this level of flexibility is few and far between. As such, certain simplifications were made in order to model and simulate reversible colloidal aggregations.

Certain assumptions about the structure of reversible clusters were made in order to make the simulation of these clusters feasible. The cubic lattice was chosen because it is the simplest structural pattern to use when modeling the reversible colloidal aggregations (**Figure 2-1**).

Figure 2-1. Using the cubic lattice structure, each particle can have a maximum of six neighbors.

While *Mathematica* can support tetragonal, hexagonal, and many other lattice structures, the cubic lattice assumption models a cluster with a sufficient amount of detail. Utilizing higher order lattice structures can improve the accuracy of the model, but would significantly increase the simulation's runtimes. The cubic lattice provided a useful level of detail while minimizing the simulation's calculation times.

Energy Model

The major goal of the research was to determine the distribution of the equilibrium structures of a reversible colloidal cluster. At equilibrium, a cluster's free energy, which is a function of the cluster's energy, will be minimized. In order to find an equilibrium structure, a cluster's free energy was calculated as a function of the cluster size (**Figure 2-2**). Before this was accomplished, however, a model was developed to calculate the total energy of a cluster of colloidal particles.

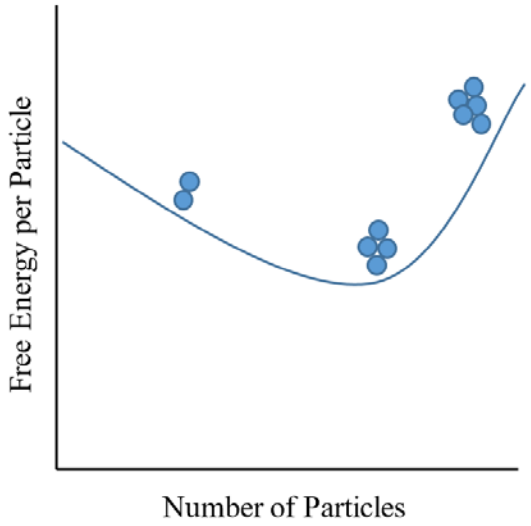

Figure 2-2. The free energy of a cluster will be minimized when the cluster reaches a certain size. In this case, the cluster with 4 particles is the equilibrium cluster.

The simulation leverages a microscopic model (**Figure 2-3**) to calculate the energy of interactions in between individual particles.[4]

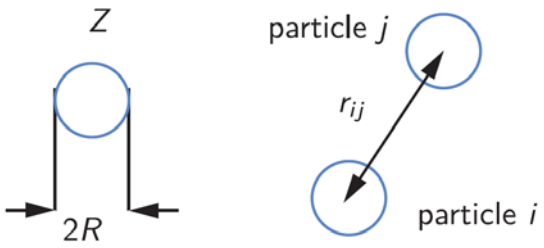

Figure 2-3. Microscopic model for the calculation of the energy of a cluster.

The interaction energy between two particles is calculated as the sum of an attractive interaction that manifests itself on contact and a DLVO repulsion. Attraction is a close-range force that draws two particles closer together and it results from a difference in the charge of two particles.[5] Repulsion is a

[4]Bordi, F., C. Cametti, C. Marianecci, and S. Sennato. "Equilibrium Particle Aggregates in Attractive Colloidal Suspensions." Journal of Physics: Condensed Matter 17.45 (2005): n. pag. Web.

[5]Morales, Victor, Juan A. Anta, and Santiago Lago. "Integral Equation Prediction of Reversible Coagulation in Charged Colloidal Suspensions." Langmuir 19.2 (2003): 475-82. Web.

long-range force that pushes two particles farther away from each other and it results from a similarity in the charge of two particles. The interaction energy in between any two particles is defined as $u_{ij,}$ which is a function of the individual energies of the attraction, u_{ij}^{A}, and repulsion, u_{ij}^{R} (**Equation 2-1**).

$$u_{ij} = u_{ij}^{A} + u_{ij}^{R} \quad (Equation\ 2-1)$$

The energy of attraction is a negative value. It is calculated using **Equation 2-2**, where *A* is the strength of interaction per contact point, and b_{ij} is 1 if the particles are touching and zero otherwise.

$$u_{ij}^{A} = -b_{ij}A \quad (Equation\ 2-2)$$

The energy of repulsion is a positive value that is calculated by treating the cluster as a sphere. Note that assuming a spherical cluster deviates from the cubic lattice model. Despite this, because a minimum free energy is relative to all other conformations of a cluster's structure, and all other clusters are simulated using the same assumption, this deviation was not of concern. The energy of repulsion in between two particles is defined using **Equation 2-3**, where *R* is the radius of the particles, *Z* is the charge, *k* is the Boltzmann constant, *T* is the temperature, *e* is the charge of an electron, and κ is the screening length.

$$u_{ij}^{R} = \frac{Z^2 e^2}{4\pi\epsilon_0\epsilon}\left(\frac{e^{-\kappa R}}{1+\kappa R}\right)^2 \frac{e^{-\kappa r_{ij}}}{r_{ij}} \quad (Equation\ 2-3)$$

The energy of interactions in between two particles can now be written as it appears in **Equation 2-4**.

$$u_{ij} = -b_{ij}A + \frac{Z^2 e^2}{4\pi\epsilon_0\epsilon}\left(\frac{e^{-\gamma}}{1+\gamma}\right)^2 \frac{e^{-\kappa r_{ij}}}{r_{ij}} \quad (Equation\ 2-4)$$

Note that the screening parameter (γ) was used when substituting **Equation 2-2** and **Equation 2-3** into **Equation 2-1**. Screening is a phenomenon that weakens repulsive forces that exist in between two particles. The dimensionless value for the screening parameter used in the simulation is given by **Equation 2-5** where κ is the screening length.

$$\gamma = \kappa R \quad (Equation\ 2-5)$$

Decreasing the screening parameter decreases the effective repulsion in between two particles and results in the formation of larger clusters (**Figure 2-4**).

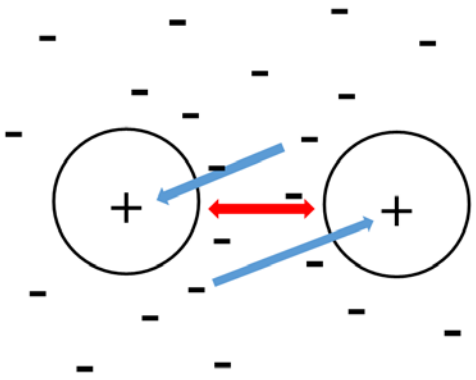

Figure 2-4. The negatively charged ion coating of one particle is attracted to the positive charge of the other particle. This phenomenon reduces the inherent repulsion in between the two positive charged particles.

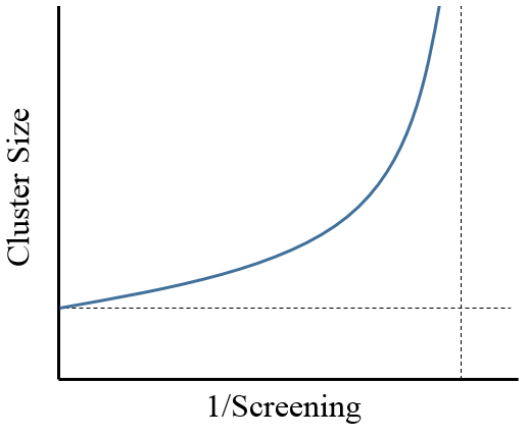

Figure 2-5. As the screening parameter becomes larger, the resulting cluster will become larger.

In order to simplify the calculation of the interaction energy of two particles, **Equation 2-5** is written in dimensionless form. The dimensionless energy, ϕ_{ij}, and dimensionless distance in between two particles, ρ_{ij}, is given by **Equation 2-6** and **Equation 2-7**.

$$\phi_{ij} = \frac{u_{ij}}{kT} \quad (Equation\ 2-6)$$

$$\rho_{ij} = \frac{r_{ij}}{R} \quad (Equation\ 2-7)$$

The dimensionless form of attraction and repulsion used in the simulation are defined in **Equation 2-8** and **Equation 2-9**, where *R* is the radius of the particles, *Z* is the charge, *k* is the Boltzmann constant, *T* is the temperature, and *e* is the charge of an electron.

$$\bar{A} = \frac{A}{kT} \quad (Equation\ 2-8)$$

$$\bar{R} = \frac{Ze^2}{4\pi\epsilon_0\epsilon RkT} \quad (Equation\ 2-9)$$

Using these dimensionless values, the interaction energy of any two particles is thus defined by **Equation 2-10**.

$$\phi_{ij} = -\bar{A}b_{ij} + \bar{R}\left(\frac{e^{-y}}{1+y}\right)^2 \frac{e^{-\gamma\rho_{ij}}}{\rho_{ij}} \quad (Equation\ 2-10)$$

The total energy of a cluster is calculated as the sum of the interaction energies of every pair of particles in a cluster, and is given by **Equation 2-11**. Note that the coefficient before the summation is necessary to ensure that pairs of particles are not double-counted.

$$\frac{E}{kT} = \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}\phi_{ij} \quad (Equation\ 2-11)$$

Finally, the total energy of the cluster can be written as it appears in **Equation 2-12**.

$$\bar{E} = -\bar{A}b_{ij} + \frac{\bar{R}}{2}\left(\frac{e^{-y}}{1+y}\right)^2 \sum_{i=1}^{N}\sum_{j=1}^{N}\frac{e^{-\gamma\rho_{ij}}}{\rho_{ij}} \quad (Equation\ 2-12)$$

Free Energy

The free energy of a cluster is the dimensionless form of the Gibb's free energy of a cluster. Having said that, the same information that can be derived about a cluster from the Gibb's free energy can also be derived from the free energy. The free energy, $\bar{F}$, of a cluster, which is given by **Equation 2-13**, is a function of dimensionless energy, $\bar{E}$; dimensionless entropy, $\bar{S}$; and dimensionless temperature, Θ.

$$\bar{F} = \bar{E} - \Theta\bar{S} \quad (Equation\ 2-13)$$

To calculate the free energy of a cluster, first the energy of the cluster has to be calculated for every cluster size at dimensionless temperatures from $\Theta = 1.0$ to $\Theta = 0.0$ using the simulation. Dimensionless temperature is defined as a ratio of the cluster's temperature to a characteristic temperature, which can be assumed to be room temperature (**Equation 2-14**).

$$\Theta = \frac{T_{cluster}}{T_{characteristic}} \quad (Equation\ 2-14)$$

Using this dimensionless temperature and energy, the entropy of the clusters were also evaluated from Θ=1.0 to Θ=0.0 using the relationship given in **Equation 2-15**, which assumes constant volume.

$$\bar{S} = \int_0^{\Theta} \frac{1}{\Theta} \frac{d\bar{E}}{d\Theta} d\Theta \quad (Equation\ 2-15)$$

After calculating all entropy values, there is enough information to calculate the free energy for all the clusters at all experimental temperatures. Plots of free energy and free energy per particle as functions of cluster size are created to determine the equilibrium cluster size. Determining the distribution of equilibrium properties at this cluster size is the goal of this research.

Chapter 3

Method of Simulation

The energy model used in this research requires that hundreds of thousands of calculations be performed to determine the equilibrium structure and properties of a colloidal cluster. Computational software was employed to simulate various cluster conformations and accurately calculate each conformation's corresponding free energy in a relatively short amount of time. *Wolfram Mathematica* was the chosen software package for the simulations conducted for this research.

Wolfram Mathematica

Wolfram Mathematica is a highly developed computational software that synthesizes a broad range of programming paradigms with powerful mathematical functions. These unique characteristics of the program make it an excellent simulation tool in the fields of actuarial science, statistics, and high-level mathematics. Because of this software's versatility, it often sees use outside these fields. One function utilized in this research to model reversible colloidal aggregations is called graph theory. Graph theory is a functionality built into *Mathematica* that allows for the modeling, analysis, synthesis, and visualization of graphs and networks. Graph theory utilizes vertices and edges to represent a network; each vertex can be used to represent a colloidal particle and each edge can be used to represent the interaction energy of two particles. This unique feature made *Mathematica* the ideal platform to simulate reversible aggregations using the cubic lattice structural model (**Figure 3-1**).

```
Graph[{1 ↔ 2, 1 ↔ 3, 1 ↔ 4, 1 ↔ 5, 1 ↔ 6, 1 ↔ 7,  2 ↔ 8, 2 ↔ 9, 2 ↔ 10, 2 ↔ 11, 2 ↔ 12, 3 ↔ 13, 3 ↔ 14, 3 ↔ 15, 3 ↔ 16, 3 ↔ 17, 4 ↔ 18, 4 ↔ 19,
  4 ↔ 20, 4 ↔ 21, 4 ↔ 22, 5 ↔ 23, 5 ↔ 24, 5 ↔ 25, 5 ↔ 26, 5 ↔ 27, 6 ↔ 28, 6 ↔ 29, 6 ↔ 30, 6 ↔ 31, 6 ↔ 32, 7 ↔ 33, 7 ↔ 34, 7 ↔ 35, 7 ↔ 36, 7 ↔ 37},
 VertexCoordinates → {1 → {0, 0, 0}, 2 → {1, 0, 0}, 3 → {0, 1, 0}, 4 → {0, 0, 1}, 5 → {-1, 0, 0}, 6 → {0, -1, 0}, 7 → {0, 0, -1}, 8 → {1.25, 0, 0},
  9 → {1, 0.25, 0}, 10 → {1, 0, 0.25}, 11 → {1, -0.25, 0}, 12 → {1, 0, -0.25}, 13 → {0.25, 1, 0}, 14 → {0, 1.25, 0}, 15 → {0, 1, 0.25},
  16 → {-0.25, 1, 0}, 17 → {0, 1, -0.25}, 18 → {0.25, 0, 1}, 19 → {0, 0.25, 1}, 20 → {-0.25, 0, 1}, 21 → {0, -0.25, 1}, 22 → {0, 0, 1.25},
  23 → {-1.25, 0, 0}, 24 → {-1, 0.25, 0}, 25 → {-1, 0, 0.25}, 26 → {-1, -0.25, 0}, 27 → {-1, 0, -0.25}, 28 → {0.25, -1, 0}, 29 → {0, -1, 0.25},
  30 → {-0.25, -1, 0}, 31 → {0, -1, -0.25}, 32 → {0, -1.25, 0}, 33 → {0, 0, -1.25}, 34 → {0.25, 0, -1}, 35 → {0, 0.25, -1}, 36 → {-0.25, 0, -1},
  37 → {0, -0.25, -1}}, VertexStyle → {1 → Red, 2 → Red, 3 → Red, 4 → Red, 5 → Red, 6 → Red, 7 → Red}, EdgeStyle → Thick, ImageSize → Large]
```

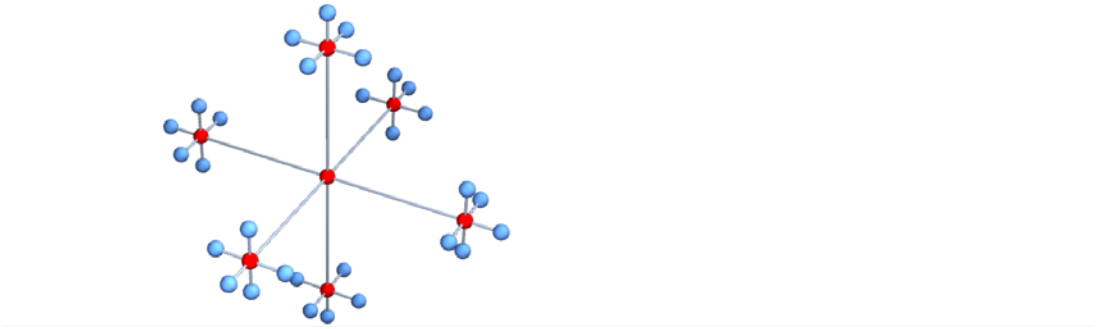

Figure 3-1. Screen capture of Mathematica demonstrating graph theory. The red vertices indicate the core cubic lattice structure of the cluster's particles, while the blue vertices indicate all the potential bonding sites for neighboring particles.

Simulation

In order to simulate reversible aggregations with a reasonable degree of accuracy, the mechanism with which these colloidal clusters restructure had to be replicated within the computer model. This was accomplished by structuring the simulation to make use of the Monte-Carlo Method. At the beginning of the simulation, a cluster containing *N* colloidal particles with a defined strength of attraction, repulsion, and screening, is initialized (**Figure 3-2**), and the initial conformation of the cluster is constructed (**Figure 3-3**).

```
BASE CASE (Use these as the default case)
    repulsion=10.0;
    attraction=-2.0;
    screening=1.0;
    temperature=1.0;
    saveDataParticleEnergy=False;

repulsion = 10.0;
attraction = -2.0;
screening = 1.0;
temperature = 1.;
saveDataParticleEnergy = False;

numberOfParticles = 27;
init[numberOfParticles, attraction, repulsion, screening]
Initialization complete.
```

Figure 3-2. Screen capture of Mathematica demonstrating the initialization of the cluster. Note that the number of particles, repulsion, attraction, and screening are all user inputs.

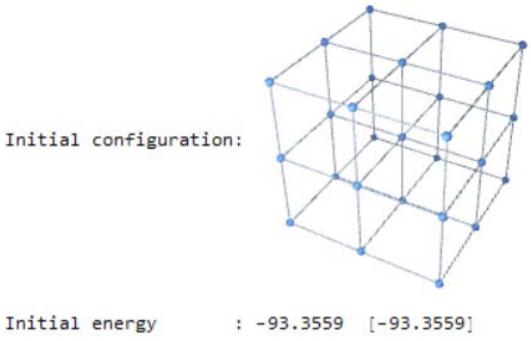

Figure 3-3. Screen capture of Mathematica demonstrating the initial conformation of a colloidal cluster containing 27 particles.

A particle is then selected at random and moved to a random position on the cluster (**Figure 3-4**).

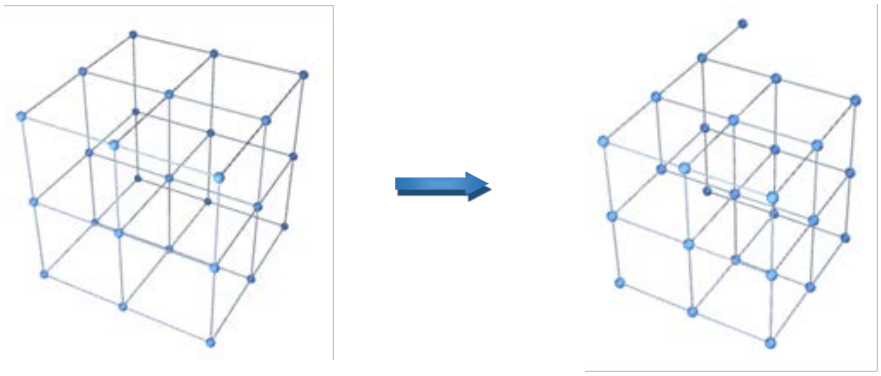

Figure 3-4. Screen capture of Mathematica demonstrating the random selection, and repositioning of a particle.

The probability that the new conformation is accepted is proportional to the equilibrium constant for the cluster. Whether the new conformation is accepted or rejected is decided using the Metropolis Algorithm. The simulation draws a random number between 0 and 1, and accepts or rejects the new cluster according to the following postulate: if RND < $e^{-\Delta E}$, then accept the new conformation; else, reject the new conformation.

This process is repeated for a set number of iterations until the properties of the cluster approach constant values. As the simulation progresses, *Mathematica* collects and stores physical data, including radius of gyration, energy, and number of bonds, for every conformation that is accepted using the Metropolis Algorithm. This data is then plotted as functions of the simulation iteration, and the distributions of values of this data are shown next to these plots (**Figure 3-5**).

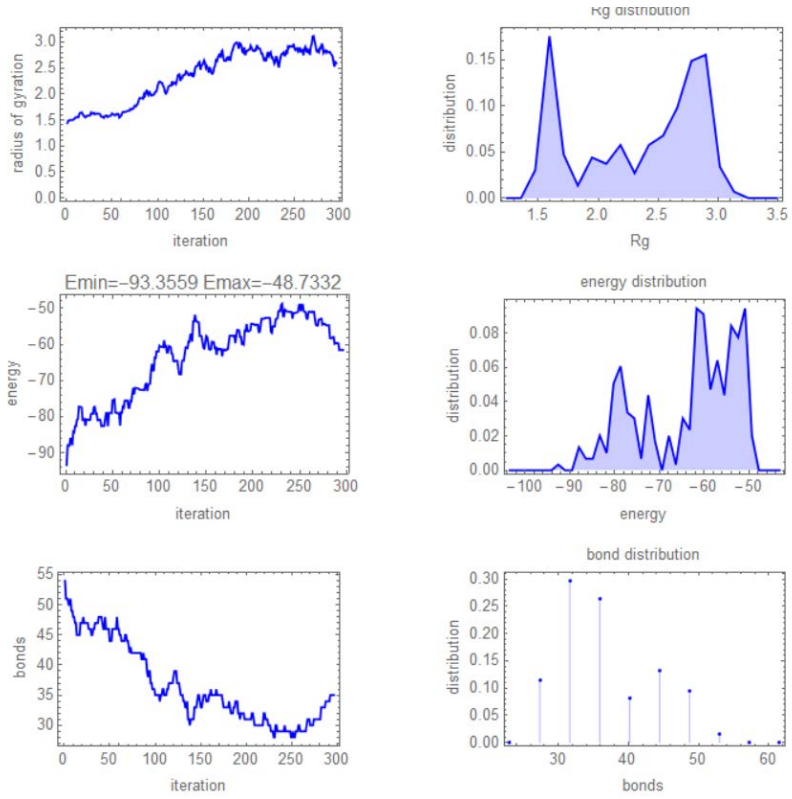

Figure 3-5. Screen capture from Mathematica demonstrating the data gathering capabilities of the simulation.

Data Processing

The data that was collected in the simulation then needs to be manually processed according to the established energy model to obtain a free energy for every conformation that was accepted using the Metropolis Algorithm. The energy data that is obtained from the simulation can be plotted as a function of temperature. According to prevailing thermodynamic theory, the energy of the cluster should decrease as the temperature is decreased, until it reaches its minimum as the temperature approaches absolute zero (**Figure 3-6**).

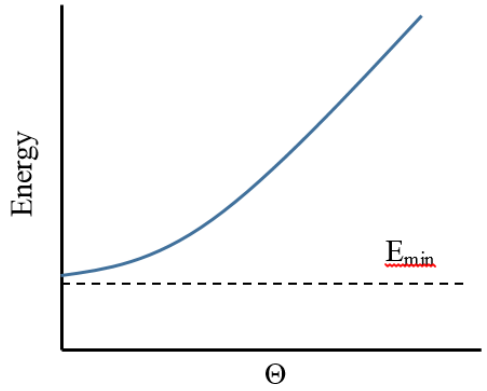

Figure 3-6. The energy of the cluster decreases with temperature until it reaches its minimum energy as Θ→0.

According to **Equation 2-15**, integrating this plot with respect to temperature will yield the entropy of the cluster at a defined temperature. After calculating the entropy of a variety of cluster sizes at temperatures ranging from $\theta = 0.0$ to $\theta = 1.0$, the simulation must is run several more times to obtain plots of energy as a function of the number of particles in a cluster at the same temperatures that were used when calculating the entropies. The simulation is run for several trials at each cluster size and temperature to eliminate any outliers from the data. The corresponding list of energies can now be used along with the entropies calculated at all the temperatures to determine the free energy of the clusters using **Equation 2-13**. These free energies are then plotted as a function of cluster size (**Figure 3-7**).

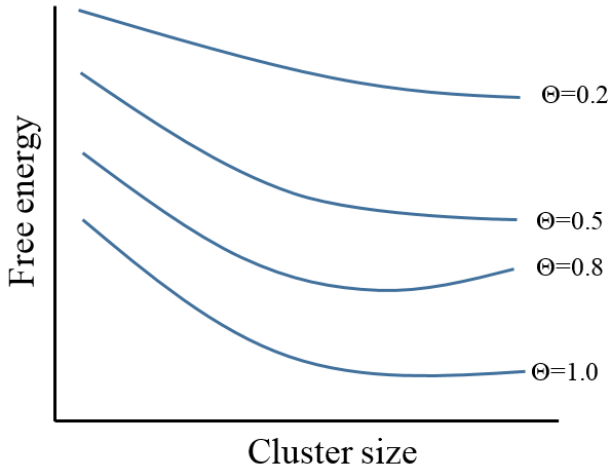

Figure 3-7. The above plot is an example of how the free energy is plotted as a function of cluster size at various temperatures. The plots do not represent any data obtained from research.

Any minimums present in this plot indicates the equilibrium cluster size at a given temperature. If a minimum structure is obtained, the properties of the data can be extracted and examined in *Mathematica*.

Chapter 4

Results

The initial simulations yielded the plot observed in **Figure 4-1**, which was conducted for a cluster with 27 particles. As the temperature decreases, the average energy of all the iterations approaches a minimum value of -93.3559, which corresponds to the energy of the initial cubic structure. This corresponds to expectation because as the temperature decreases, only lower energy configurations will be accepted which would drive the average energy of all the iterations to the value of its minimum energy configuration, which is more times than not, the initial cubic configuration.

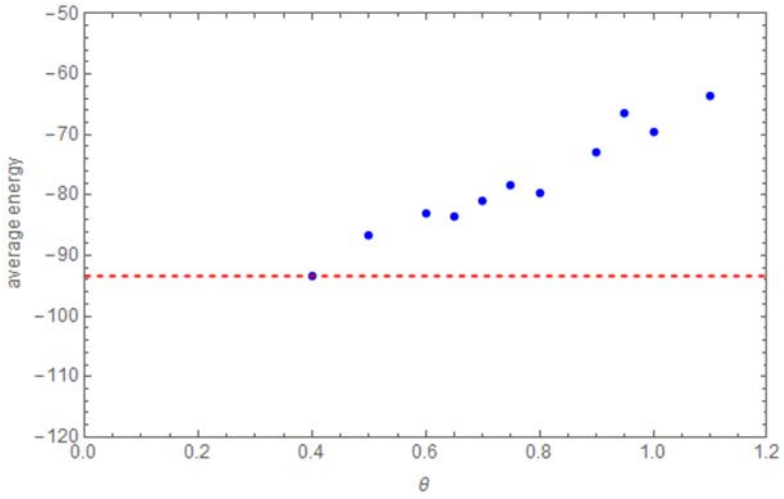

Figure 4-1. Plot of average energy versus dimensionless temperature for a cluster with 27 particles.

Table 4-1. Simulation parameters for Figure 4-1

Number of Particles	27
Temperature (θ)	0.0-1.0
Attraction	-2.0
Repulsion	10.0
Screening	1.0

This simulation was repeated many times for a variety of different cluster sizes, and the results of which can be seen in **Figure 4-2**. The same trend that was observed in the initial simulation perpetuates throughout all the other simulations.

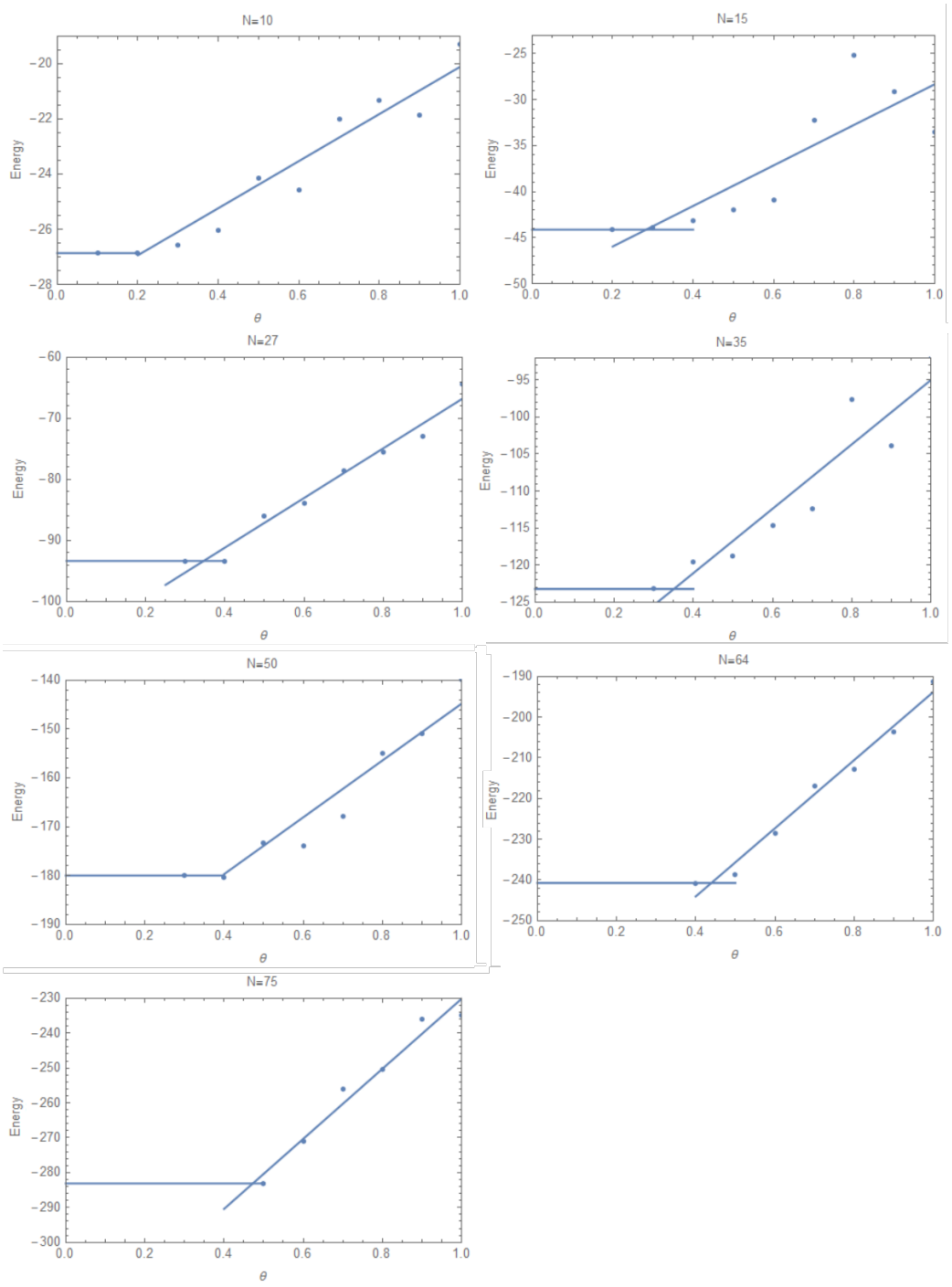

Figure 4-2. Results of simulations for cluster sizes ranging from 10-75 particles.

Table 4-2. Simulation parameters for Figure 4-2

Number of Particles	10-75
Temperature (θ)	0.0-1.0
Attraction	-2.0
Repulsion	10.0
Screening	1.0

After obtaining the fits for the positive, linear portion of these plots, the energies, entropies, and free energies per particle were plotted as a function of cluster size at all the experimental temperatures, which can be seen in **Figure 4-3**, **Figure 4-4**, and **Figure 4-5**.

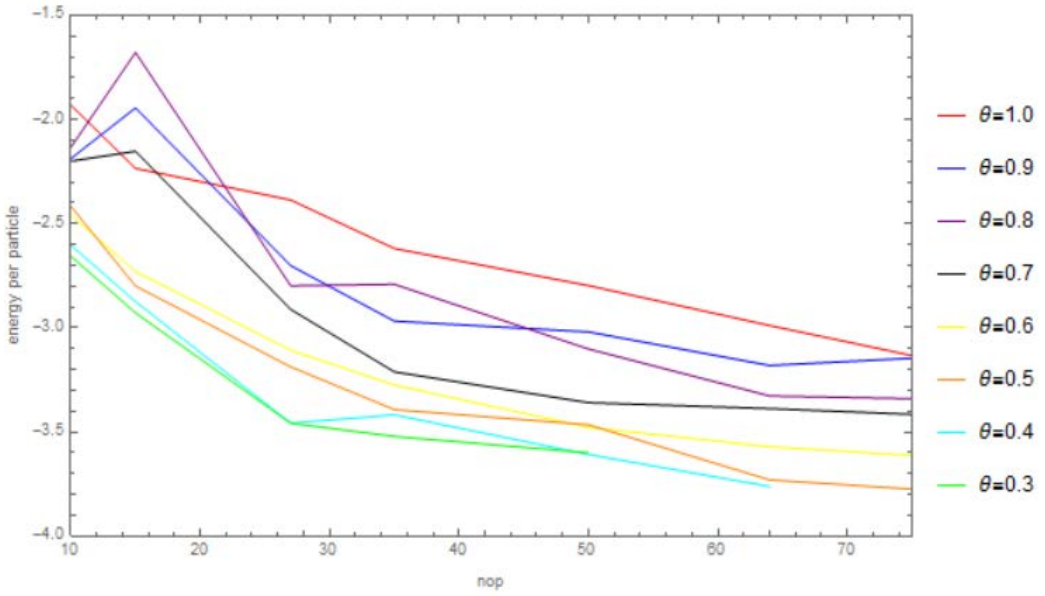

Figure 4-3. A plot of energy per particle as a function of cluster size at all experimental temperatures.

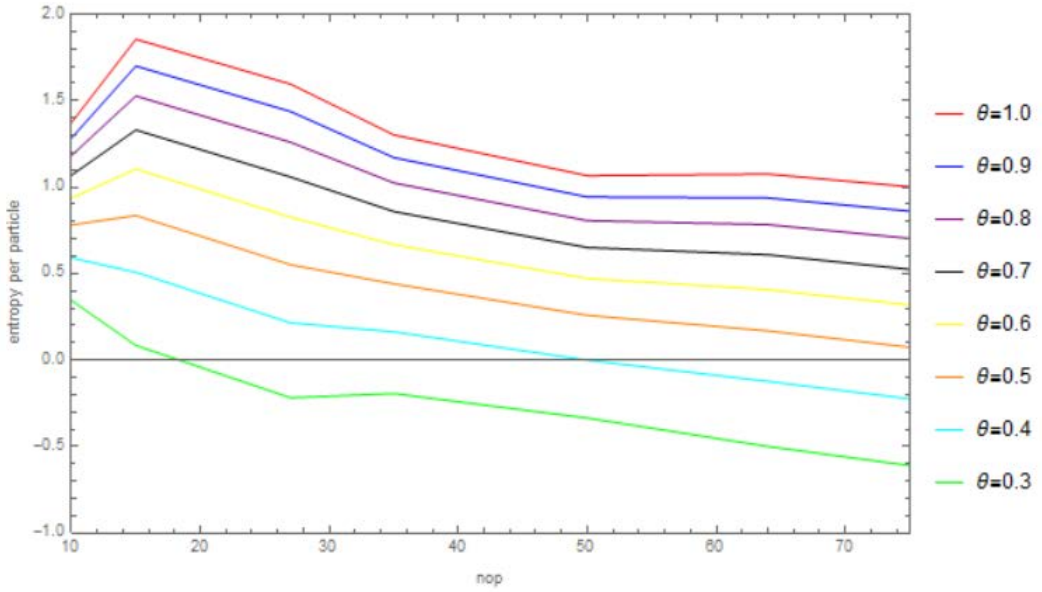

Figure 4-4. A plot of entropy per particle as a function of cluster size at all experimental temperatures.

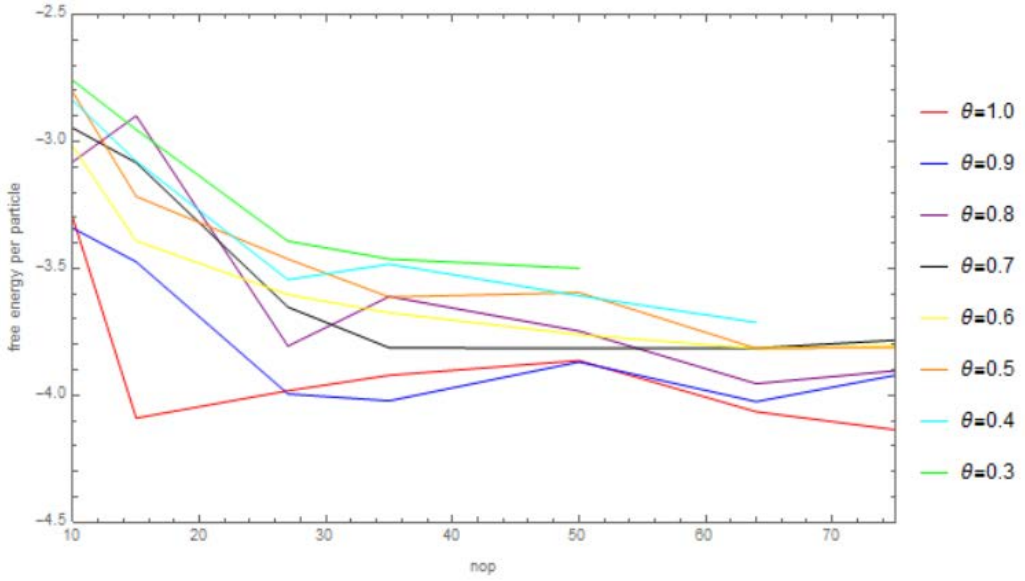

Figure 4-5. A plot of free energy per particle as a function of cluster size at all experimental temperatures.

Table 4-3. Simulation parameters for Figure 4-3, Figure 4-4, Figure 4-5

Number of Particles	10-75
Temperature (θ)	0.0-1.0
Attraction	-2.0
Repulsion	10.0
Screening	1.0

After looking at this data, it is obvious that there are a few potential minimums in the free energy per particle at a variety of the temperatures. This would indicate an equilibrium cluster size, the properties of which would be of greatest interest in this research. The two temperatures that are most likely to contain an equilibrium cluster whose size is between 0 and 100 particles at the given conditions are $\Theta = 1.0$ and $\Theta = 0.9$. These two temperatures were isolated for further investigation to determine whether the minimums evident in the free energies at these temperatures were not the result of experimental error. Again, the plots of energy as a function of temperature were created for all cluster sizes and the fits for the positive, linear portions of these plots were obtained (**Figure 4-6**).

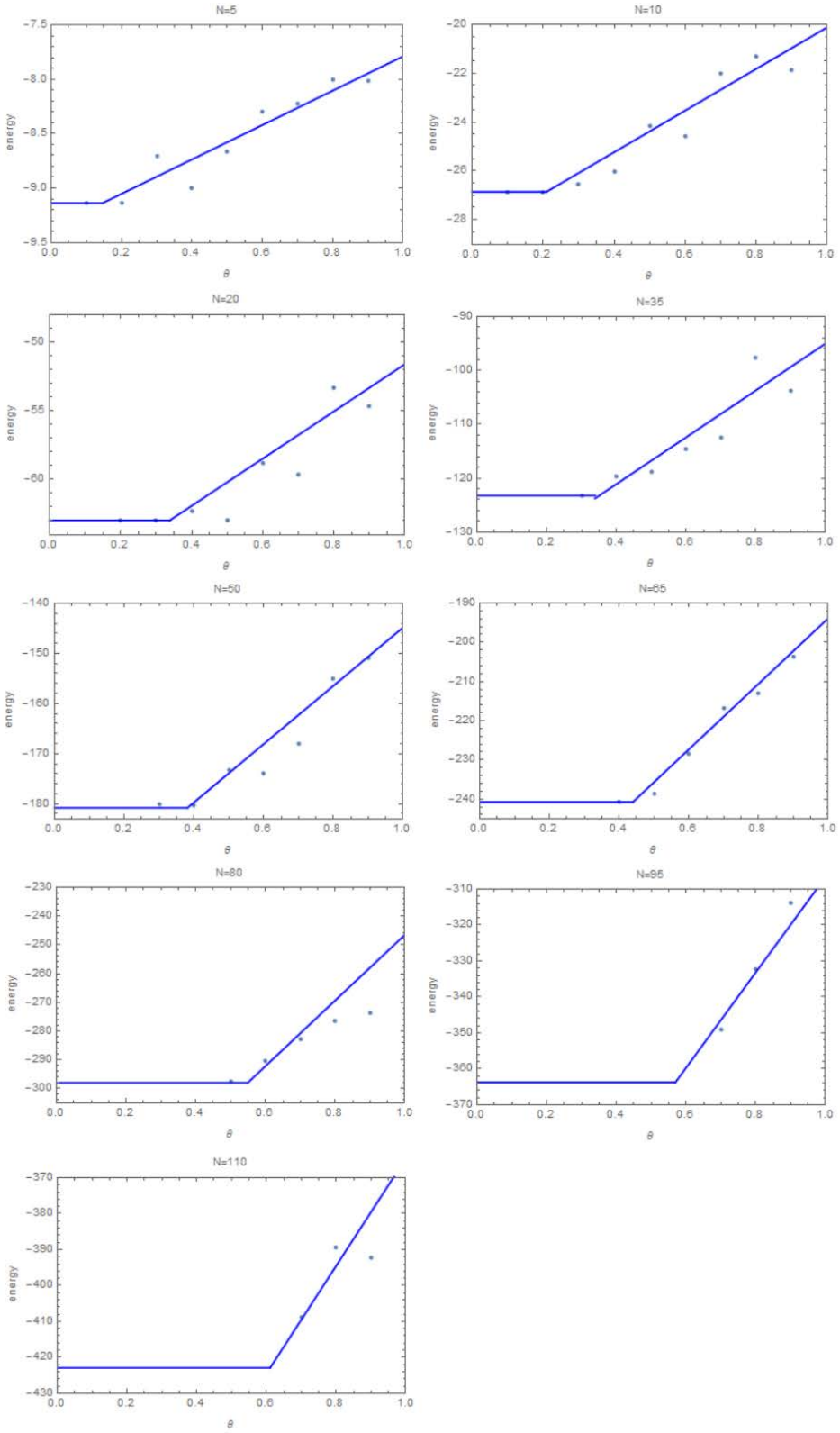

Figure 4-6. Results of simulations for cluster sizes ranging from 5-110 particles.

Table 4-4. Simulation parameters for Figure 4-6

Number of Particles	5-110
Temperature (θ)	0.0-1.0
Attraction	-2.0
Repulsion	10.0
Screening	1.0

After obtaining the fits for the positive, linear portion of these plots, the energies, entropies, and free energies per particle were plotted as a function of cluster size at $\Theta = 1.0$ and $\Theta = 0.9$, which can be seen in **Figure 4-7**, **Figure 4-8**, and **Figure 4-9**. The energy data was averaged over three separate trials to statistically remove as much error from the simulation results as possible.

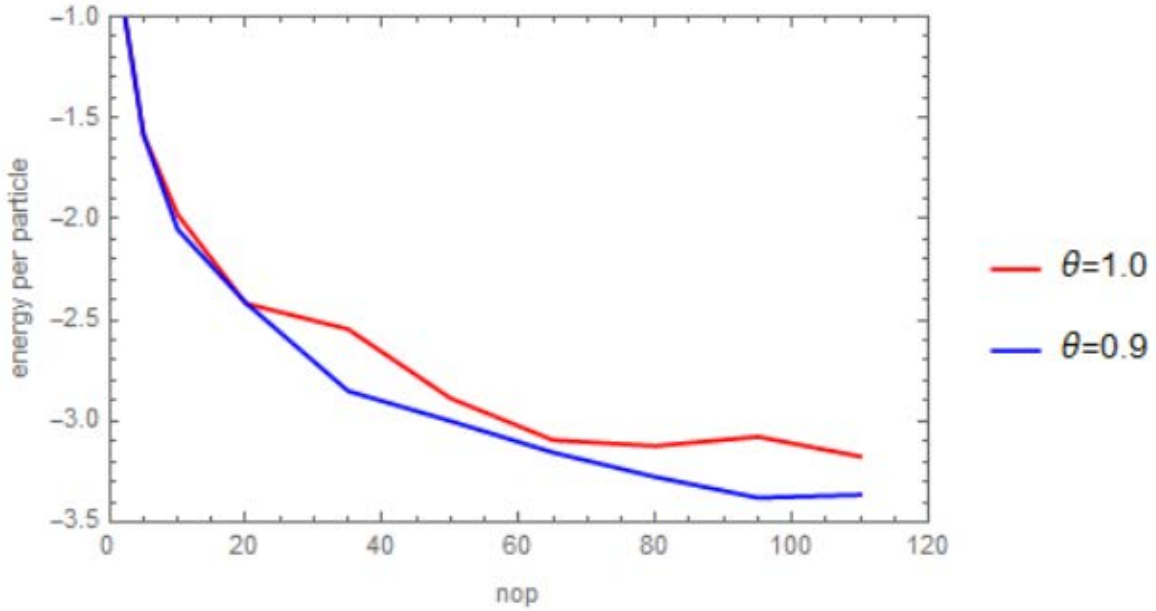

Figure 4-7. A plot of energy per particle as a function of cluster size at all experimental temperatures.

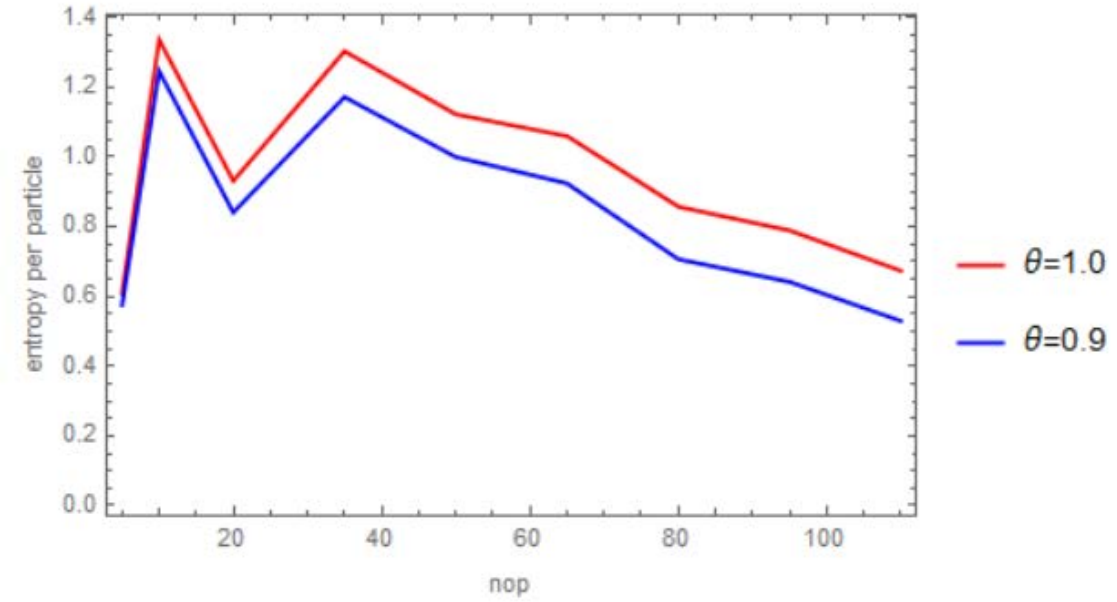

Figure 4-8. A plot of entropy per particle as a function of cluster size at all experimental temperatures.

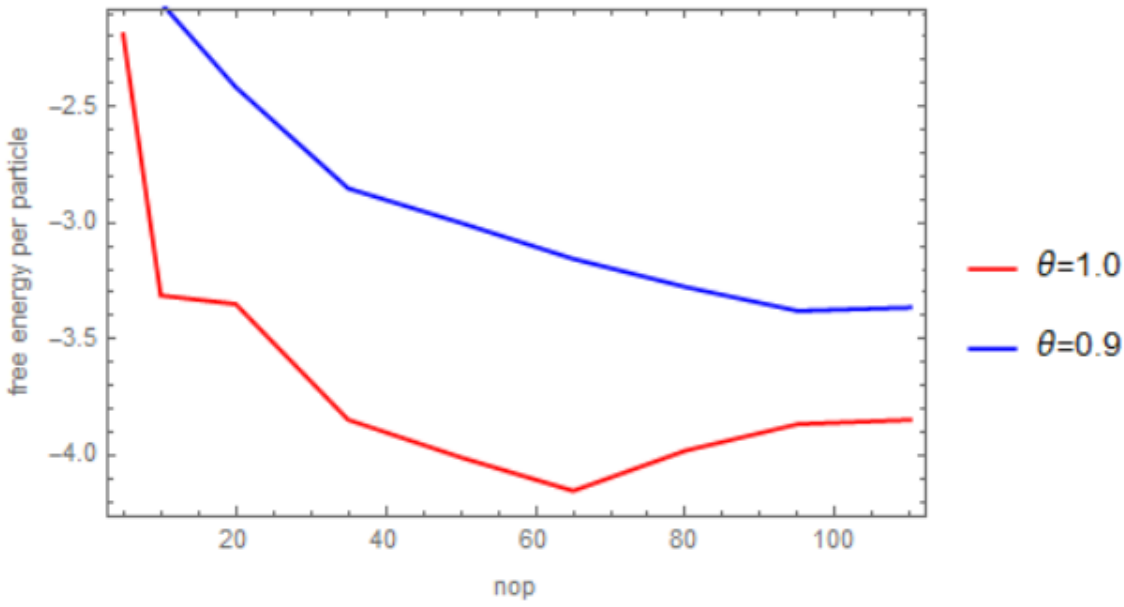

Figure 4-9. A plot of free energy per particle as a function of cluster size at all experimental temperatures.

Table 4-5. Simulation parameters for Figure 4-7, Figure 4-8, Figure 4-9

Number of Particles	27
Temperature (θ)	0.0-1.0
Attraction	-2.0
Repulsion	10.0
Screening	1.0

Chapter 5

Discussion

The data gathered in the experiment provided a lot of valuable insight into the capabilities and scope of the simulation. Using the results of the experiment, a clear path forward can be established for future experimentation with this simulation to learn more about the behavior of reversible clusters.

The general trends that were observed in the simulations upheld many long-standing axioms of molecular thermodynamic theory. In **Figure 5-1**, the trend that can be observed is an inverse relationship in between the cluster size and energy.

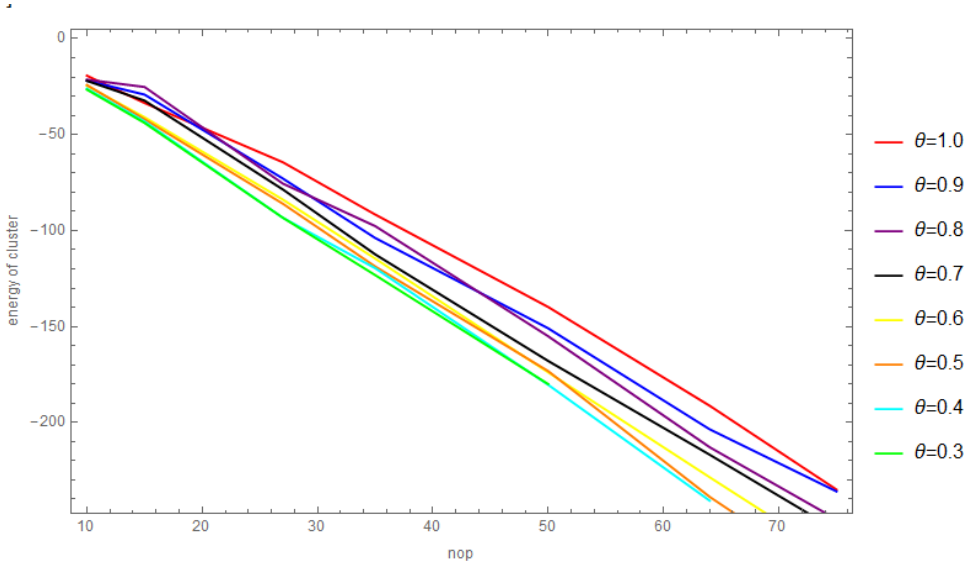

Figure 5-1. As the size of the cluster increases, the corresponding energy of the cluster decreases.

Table 5-1. Simulation parameters for Figure 5-1

Number of Particles	5-110
Temperature (θ)	0.3-1.0
Attraction	-2.0
Repulsion	10.0
Screening	1.0

This trend is expected, as an increase in the number of particles increases the magnitude of attractive interaction in the cluster. Attractive interactions were defined in the energy model to represent negative energy, so it makes sense that as the number of attractive interactions increases, the energy of the particle decreases. This phenomenon manifests itself in a physically obvious manner when considering an irreversible cluster of colloids. According to the energy model used in the simulation, as the strength of the attraction increases, the energy of the cluster decreases. It is also known that for reversible colloids, gelation is approached as the strength of the attraction increases.[6] This suggests that the energy of a reversible cluster decreases until it reaches a minimum value, at which point the colloid becomes a gel (**Figure 5-2**).

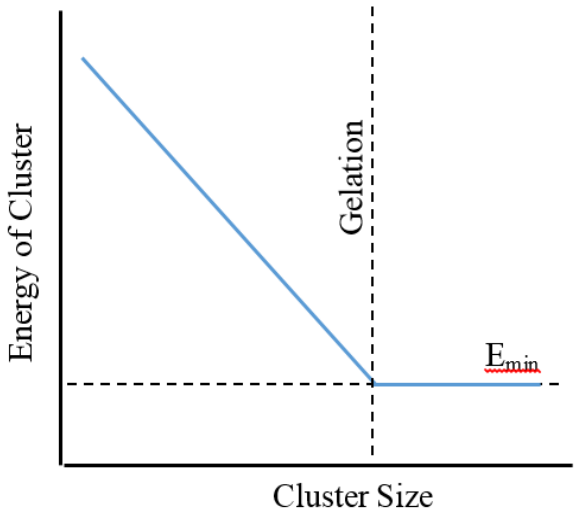

Figure 5-2. The energy of a reversible cluster decreases until it reaches a minimum value, at which point it forms a gel.

Another trend observed in the data collected from the simulations is that as the temperature decreases, the energy of a cluster with a defined size will subsequently decrease (**Figure 5-3**).

[6] Puertas, Antonio M., Matthias Fuchs, and Michael E. Cates. "Comparative Simulation Study of Colloidal Gels And Glasses." Physical Review Letters 88.9 (2002): n. pag. Web.

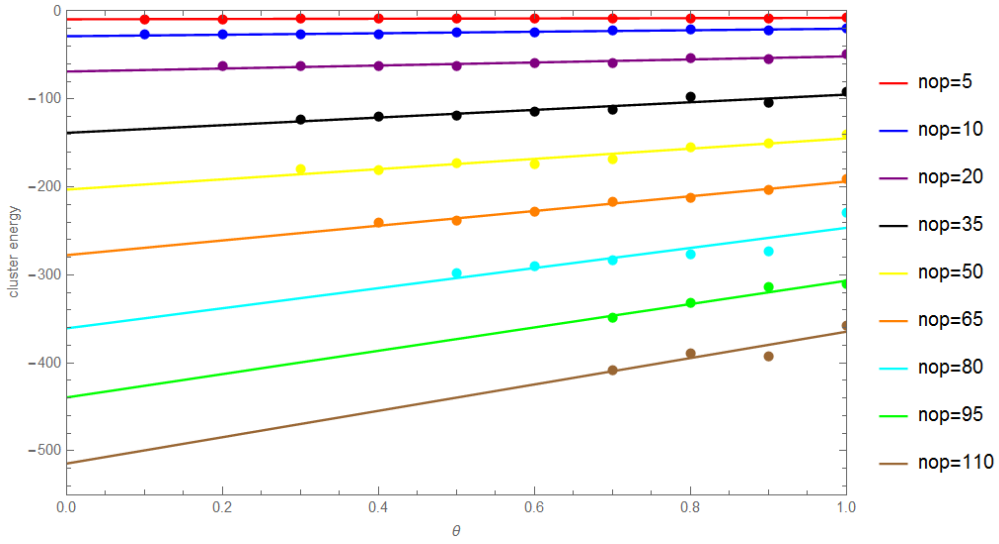

Figure 5-3. Plots of cluster energy as a function of dimensionless temperature. The energy of the cluster increases with the temperature.

Table 5-2. Simulation parameters for Figure 5-3

Number of Particles	5-110
Temperature (θ)	0.3-1.0
Attraction	-2.0
Repulsion	10.0
Screening	1.0

This trend is expected because as the temperature decreases, the probability that the simulation accepts a new conformation using the Metropolis Algorithm also decreases. If the simulation is less likely to accept new conformations, the cluster's structure will favor a spherical structure, or in the case of the simulation, a cubic structure. This cluster shape is the lowest energy structural conformation as it maximizes the negative effect on energy by attractive forces and minimizes the positive effect on energy by repulsive forces. For this reason, it is not surprising that the energy of the cluster will decrease with temperature.

The last trend observed in the results of the simulation that supports established theory is an asymptotic decrease in the per particle thermodynamic properties as the cluster size is increases. This trend is expected because as the size of the cluster increases, the thermodynamic decrease at a slower rate than the cluster size is able to grow. This results in the thermodynamics approaching a minimum value at very large cluster sizes.

The results of the experiment indicate that the simulation corresponds to thermodynamic theory, which suggests that the simulation of the reversible colloidal clusters using the Monte-Carlo method was successful. Additionally, the data collected seems to suggest the possibility that a minimum exists given the experimental conditions of this research. However, given significant noise observed in the data, these apparent minimums could not be confirmed to be an indication of an equilibrium structural conformation.

The noise in the data is most apparent when looking at the variability in the energy distributions of small clusters at low temperatures (**Figure 5-4**).

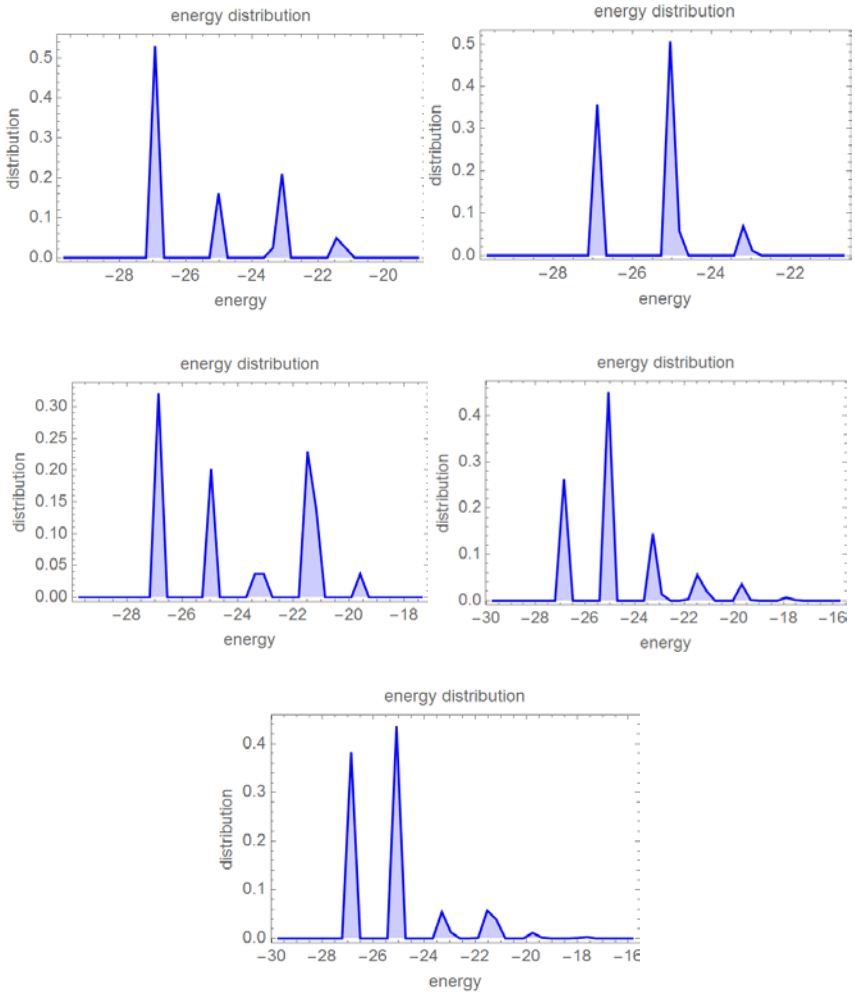

Figure 5-4. Energy distribution for 5 runs of the simulation at constant conditions.

Table 5-3. Simulation parameters for Figure 5-4

Number of Particles	27
Temperature (θ)	0.0-1.0
Attraction	-2.0
Repulsion	10.0
Screening	1.0

From these energy distributions, it is difficult to predict the actual average energy of this cluster of particles given the experimental conditions. These energy distribution were created using the same

number of simulation iterations as was used in the research for a cluster of the same size. This indicates that despite doing multiple trials in the research, the total number of iterations did not provide enough samples to obtain an accurate value for average energy of a cluster. If the values for energy are not accurate, then this error propagates in subsequent calculations. This means that the error is likely to be so significant by the time the free energy is calculated that the apparent minimum values may be an artifact of the noise in the data. Adjusting for the noise in the data would require a much more rigorous sampling method that is beyond the scope of this research. Despite this minor shortcoming, the research proved the feasibility of the model as an accurate representation of a reversible cluster of colloidal particles.

Future research should focus on two major areas. The first area that needs to be explored are the sampling conditions. It is possible that the sampling conditions used in this research would never yield a minimum free energy value for the cluster sizes sampled. Sensitivity studies need to be conducted to determine if the sampling parameters are appropriate for the cluster sizes sampled. This means adjusting the attraction, repulsion, and screening parameters of the simulation. A methodology will need to be developed to determine if a set of parameters is likely to yield a minimum value.

Once it is determined which parameters will yield a minimum value of free energy, the sampling method using these parameters will have to be rigorous. This means increasing the number of iterations for every cluster by at least one order of magnitude for the smaller particles and for particles at low temperatures. If enough samples are gathered and averaged, there can be more confidence that any apparent minimums are a true indication of an equilibrium structure.

Chapter 6

Conclusion

Overall the experiment was a conditional success, as the simulation successfully modeled the behavior of a reversible aggregation of colloidal particles. The results of the model agree with prevailing molecular thermodynamic theory, which supports this simulation's viability as an accurate representation of this system. Additionally, apparent minimums in the free energy of a reversible colloidal cluster was observed during simulations. However, these apparent minimums were not confirmed to be an indication of an equilibrium conformation due to significant noise in the data.

For future work, the simulation should be used to test different parameters in order to determine whether different conditions would increase the likelihood of observing an equilibrium conformation of a reversible colloidal aggregations. It is difficult to pinpoint the exact parameters that would yield an equilibrium conformation of a colloidal cluster, because research was conducted in a simulation environment that depends on five different parameters. Furthermore, when certain parameters are identified as ideal for the observation of an equilibrium conformation, then a very rigorous sampling methodology should be employed to ensure that any apparent minimums in free energy can be confirmed to be equilibrium conformations of a reversible aggregation of colloidal particles.

BIBLIOGRAPHY

Bentz, J., and S. Nir. "Aggregation of Colloidal Particles Modeled as a Dynamical Process." *Proceedings of the National Academy of Sciences* 78.3 (1981): 1634-637. Web.

Bordi, F., C. Cametti, C. Marianecci, and S. Sennato. "Equilibrium Particle Aggregates in Attractive Colloidal Suspensions." *Journal of Physics: Condensed Matter* 17.45 (2005): n. pag. Web.

Law, B. M., J.-M. Petit, and D. Beysens. "Adsorption-induced Reversible Colloidal Aggregation." *Physical Review E* 57.5 (1998): 5782-794. Web.

Lotfizadeh, Saba, Hassan Aljama, Dan Reilly, and Themis Matsoukas. "Formation of Reversible Clusters with Controlled Degree of Aggregation." *Langmuir* 32.19 (2016): 4862-867. Web.

Morales, Victor, Juan A. Anta, and Santiago Lago. "Integral Equation Prediction of Reversible Coagulation in Charged Colloidal Suspensions." *Langmuir* 19.2 (2003): 475-82. Web.

Puertas, Antonio M., Matthias Fuchs, and Michael E. Cates. "Comparative Simulation Study of Colloidal Gels And Glasses." *Physical Review Letters* 88.9 (2002): n. pag. Web.

Alan Okan Johnson

alan.o.johns@gmail.com|Allentown, PA

EDUCATION

The Pennsylvania State University — **University Park, PA**
Schreyer Honors College — *Expected May 2017*
B.S. Chemical Engineering
Cumulative GPA:

Thesis Research — **University Park, PA**
Colloidal Research Group — *Jan. 2016 – Present*

- Utilizing innovative computational methods to simulate reversible aggregations of colloidal particles
- Revising Mathematica workbooks that use graph theory to calculate energies of particle arrangements

EXPERIENCE

ExxonMobil Chemical Company — **Houston, TX**
Supply Chain Intern — *May 2016 – Aug. 2016*

- Conducted case study on warehouse optimization to accommodate projected 2000 ft^2 required for 2018
- Advised against a $2.5M warehouse expansion project by proposing cost-effective alternative solutions
- Implemented IntelaTrac barcoding system to reduce quality incidents that cost the business $250K in 2015
- Expanded IntelaTrac barcoding system to establish means for inventory tracking and goods receipt to SAP

Procter & Gamble — **Scranton, PA**
Energy & Water Treatment Intern — *May 2015 – Aug. 2015*

- Led testing and implementation of a chemical that saved $114K/year in plant's water treatment process
- Discovered and eliminated fresh water losses in plant's wash down system by over 250K gallons/day
- Developed operation strategy for plant's gas turbine air chillers to optimize performance in summer months

BP Ultimate Field Trip Competition — **Houston, TX**
Team Organizer — *Oct. 2014 – Apr. 2015*

- Developed an innovative method that reduced water usage in the hydraulic fracturing method by 95%
- Earned first place at the campus-wide competition at the Pennsylvania State University
- Presented innovative hydraulic fracturing method to BP executives at the national finals

LEADERSHIP

Teaching Assistant — **University Park, PA**
Chemical Reaction Engineering — *Aug. 2016 – Jan. 2016*

- Taught several lectures covering key chemical reactor design concepts to a class of 80 students
- Communicated effectively to address student questions regarding class material
- Organized collection of class data to demonstrate that the class met ABET accreditation requirements

Pi Kappa Phi Fraternity — **State College, PA**
Vice President — *Jan. 2014 – Dec. 2014*

- Directed all efforts to recruit potential members resulting in a 30% increase in membership in 2014
- Logged member's housing points and served as the head of all communications for the fraternity
- Budgeted $40K for house projects and fundraising events with the fraternity's treasurer
- Collaborated with THON chairs to organize fundraising events to raise money pediatric cancer

VOLUNTEER

Leonhard Center Scholars Program — **University Park, PA**
Student Representative — *Aug. 2013 – Present*

- Improved engineering education by providing input on issues related to teaching and learning
- Assisted in the set-up of the engineering career fair and various other recruitment events

Boy Scouts of America — **Allentown, PA**
Eagle Scout — *Mar. 2006 – Apr. 2014*

- Led the planning, fundraising, and execution of a service project requiring 800+ hours of labor

ACTIVITIES & SKILLS

Languages: Proficient in Spanish
Activities: Schreyer Consulting Group, Penn State Debate Society
Computer Skills: Microsoft Excel, Mathematica, SAP, AutoCAD, Tableau, Autodesk Inventor, SolidWorks, and RGUI