BACHELOR

Squeezing soft spheres into non-Bravais lattice structures

van Gool, T.

Award date:
2018

Squeezing soft spheres into non-Bravais lattice structures

T.v.gool 0911044
Supervisor: Wouter Ellenbroek

September 2018

Abstract

Some structures have desirable properties. One of the most wanted structures is the diamond structure, because of its photanic band gap. The optical allows some wavelengths to pass through while blocking others. This allows for manipulation and control over light. The diamond structure is usually made by self-assembly of expensive materials. However studies have shown that so called soft spheres allow to self-assemble at different volume fractions. The soft spheres have a repulsive harmonic potential which causes them to exert a force when squeezed. As the spheres becomes more squeezed they start to form different structures. A quick calculation on the lattice sums of some structures suggests that at a volume fraction the diamond structure has the lowest potential energy. In this report we are going to investigate the ground states of the soft spheres by simulating the primitive unit cell. We will find that other structures will emerge then we initially expected of out lattice sums. And we will find a deformed diamond structure. Our results suggest that the soft spheres with repulsive harmonic potential are able to form complex structures.

Introduction

Understanding how particles can self-assemble into structure is the subject of a lot of new studies. By studying this self-assembly we might be able to recreate desirable structures. The diamond structure is one of the most desired structures. This is because diamond can be structured to have a photonic band gap. The photonic band gap allows some wavelengths to pass to the crystal structure but blocks other wavelength. Which allows us to control and manipulated light.[1]

Particles with complicated potentials might be able to self-assemble into the diamond structure. However it is hard to find these potential and even harder to make the particles corresponding to them. Instead research has shown that soft particles, which interact via an inverse power potential, are able to form structures when pressured. These soft particles with an inverse power potential are easy and cheap to produce.

Studies have shown that there are changes in structure as the volume fraction(ϕ) of 2D Hertzian spheres is increased.[2] Different structures are also found for an increasing volume fraction of 3D Hertzian spheres. [3][4] It was shown that the expected FCC structure, which is the most efficient way to store spheres in a box, changed into a BCC structure at higher volume fractions. The structures of soft spheres are also investigated. This was done in 2D by Wouter G. Ellenbroek. He found that these spheres also changed structures and could also created complex structure. An example being a structure that seems to consist 5 particles that were repeated. In his research he also found that at certain volume fractions some structures might coexist which each other. Meaning that

both structure are present and separated by a grain boundary. [5].3D simulations confirm these first-order structure transitions. They also show that there is an area where the diamond structure seems to be favoured.[6]. Simple lattice sums of the potential energies of common structures confirms this further. Figure 1 , created by Wouter G. Ellenbroek [5], shows the potential energy of 5 structures, we will call them the standard structure throughout this report. In this graph the potential energy of the FCC structure is subtracted to highlight the differences better. We can clearly see that FCC has the lowest potential energy at low volume fractions, HCP has the same potential energy as FCC at the lower volume fractions,which will be explained later. For now we should focus on the fact that the BCC structure has a lower at a higher volume fraction, which is consistent with what we have seen in the Herztian and soft spheres in 3D. More importantly there is a area where the diamond structure has the lowest potential energy. This look promising, but it should be noted that only 5 structures were taken. This means that the diamond structure might not be the real ground state at this volume fraction.

The goal of this Bachelor End Project is to find what the ground states of the soft spheres at higher volume fractions are. Focus will lie around the area where the diamond structure has the lowest potential of the 5 standard structures. However instead of calculating the lattice sums of known structures, we will try to simulate the primitive unit cell of the ground state. The energy of the system is compared with the energy of the standard structure to see whether the standard structures have the lowest energy in the ground state or there are other structures that might emerge.

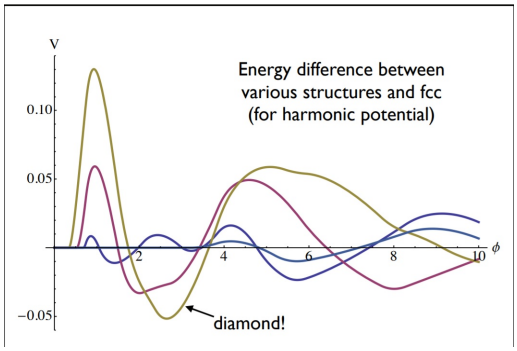

Figure 1: Energy difference between diamond(yellow), BCC(purple), sc(red), HCP(blue) and FCC(base line)[5].

Backgrounds

The energy of each simulated primitive unit cell will be compared with the energies of the standard structure. We will use the energy per particleϵ for this.

By using ϵ any number of particles can be put in the simulation box while still having the same energy reference. The standard structures also differ in particles in there primitive unit cell. However to explain these structure we will look at there lattice structure. Some of these structure are so called Bravais lattice structures. A Bravais lattice is a lattice which when repeated fill the whole structure and the orientation of each lattice point must be the same. This means the Bravais lattice structures are symmetric. The simplest example of this is taking a cube and putting a particle on each of the corners. This structure is called Simple cubic. A particle can be placed in the middle of this cube, note that the cube will still be symmetric implying this is also a Bravais lattice structure. This structure is called Body Centered Cubic(BCC). Face Centered Cubic(FCC) is created when addition particles are added to the face of the Simple Cubed structure. The FCC structure consist of hexagonal planes, which are the most effective manner to store circles in plane. Hexagonal planes are planes where each particle has 6 neighbors and the plane looks like alternating triangles. The term honeycomb lattice will also be used, the honeycomb lattice will consist of hexagonal. Some sources will name hexagonal and honeycomb lattices as being the same however throughout this project we will use stated definition for the 2 lattice planes. The hexagonal planes are not stacked directly on top of each other but are alternated with a ABCABC pattern where A,B and C are rotated, by doing so the structure is the most efficient manner to store spheres in a box. 74% of the box will be filled by the spheres. There is another way to structure the hexagonal planes on top of each other while still maintaining this store efficiency. This has an ABAB pattern. This structure is called ideal Hexagonal Close packed(HCP) and is a non-Bravais structure, because the orientation of the particle differs between the closes neighbors. Even thou HCP is non-Bravais it is still very similar to FCC, which can be seen in figure 1 as they have the same potential energy until a volume fraction around 3. The diamond structure has the base of FCC with an addition particle added at $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$. These additional particles makes the diamond structure non-Bravais as the lattice points don't have the same orientation anymore.

The soft spheres that will be used in this project will have an inverse power potential. This means that the spheres have a repulsive harmonic potential.[7]

$$V(r) = \begin{cases} \epsilon(1 - \frac{r}{\sigma})^2 & \text{for} \quad r \leq \sigma \\ 0 & \text{for} \quad r > \sigma \end{cases} \tag{1}$$

where σ is the diameter of the spheres. r is the distance between the centers of the spheres and ϵ, not to be confused with the energy per particle, is an energy constant. For simplicity ϵ is chosen to be 1. Because the soft spheres are only repulsive no force is exerted when the sphere is in relaxed/no compressed state.

The statistics of the soft spheres become interesting when the soft spheres are squeezed against each other. This happens when the volume fraction(ϕ) inside

the primitive unit cell is increased. The volume fraction is defined as:

$$\phi = \frac{n \cdot V_{\text{sphere}}}{V_{\text{cell}}} \tag{2}$$

where n is the number of particles inside the cell, V_{sphere} is the volume of soft sphere in a relaxed state and V_{cell} is the volume of the primitive unit cell. At higher volume fractions the spheres start to press harder against each other. They will exert a force onto each other. These forces will create an energy between the particles. We will define the energy per particle ϵ as half of each of the energy between the particle and each of its neighbors. Note that the particles them self don't have a energy but this energy per particle is created artificially by looking at the energy between the contact points of each particle. This ϵ can also be found by calculating the energy of the system and dividing it by the number of particles.

The fact that the energy scales with the volume fraction and depends on the forces between the particle and their neighbors lies at the base of the structure transition. The structure of the spheres is described as the structure that arises when the centers of soft spheres are connected by artificial created bonds. Transitions between these structures can be best explained by looking at the transition between a hexagonal and squared 2D structure. The hexagonal structure is a better way to store the spheres as the least empty space needs to be used. As the volume fraction is increased and the spheres become more squeezed, the energy between each particles start to increase. This will also increase the ϵ. The extend to which this energy increases depends on which neighbors press against the spheres and how far the neighbors compress the sphere. For the hexagonal lattice this means that 6 neighbors press against the sphere with a force. For the squared lattice these are only 4 neighbors. But the neighbors will press harder against the sphere. The balance between these smaller but more forces and larger but less forces lies at the foundation of the structure transitions. Earlier studies show that the transitions in the structure are from the first order and have a coexistence region [5][6].

The primitive unit cell in which we put the particle in is a combination of vectors. These vectors define the size and shape of the box but do not interact with the particles at all. Instead of having interacting with the walls of the cell the particles will interact with themself as if having Period boundaries conditions at these walls. This way the primitive unit cell can easily replicated in all directions to create the structure. Because the primitive unit cell consist of vectors that can are created by the interaction between the particles the shape of this cell is not always just cubic but can have any shape.

Methods

The statics of the soft spheres will be implemented into a simulation. From these statics the ϵ can be calculated and also the structure can be visualy inspected. The standard structures can be recreated by forcing particles into the structures corresponding lattices. A volume fraction can be implemented using the diameter of the spheres. From equation 2 the formula for the diameter of the spheres is derived:

$$\sigma = \sqrt[3]{V_{\text{cell}}} \cdot \sqrt[3]{\frac{6\phi}{\pi \cdot n}} \tag{3}$$

n is here the number of atoms in a unit cell. V_{cell} is the volume of a unit cell. For the cubic structure(sc,bcc,fcc,diamond) this comes down to the size of the lattice cubed. The volume of the HCP unit cell is slightly different due to the hexagonal base. For ideal HCP $V_{\text{cell}} = a^3 \cdot \frac{\sqrt{3}}{4} \cdot 6 \cdot \sqrt{\frac{8}{3}}$ where a is the lattice length.

However as said in the introduction we do not known whether these standard give the lowest energy. Therefore we need to find the ground states by numerical minimization. This is done by simulating the primitive unit cell of the structure. The particles are put in a simulation box which will mimic the primitive unit cell. A minimizer iterates the coordinates of the particles within the box .[8] The particle coordinates are updated in order that the system moves towards a minimum and the minimization stops when certain conditions are met. These include the maximum number of iterations and the minimum in potential energy chance per iteration. During the minimization an external pressure is applied via external vectors. To keep the pressure constant within the simulation box the box is allowed to change size and shape. By changing the size and shape of the box the volume of the box can also be changed. This means that the external pressure that is applied to the box is a measure of the volume and consequently a measure of the volume density, according to equation 2. To sample the structures around the diamond structure a ϕ between 0 and 6 should be sufficient. This can seen in figure 1 where the area of the diamond structure lies between a volume fraction of 2 and 4. By taking investigation area which is doubled at each side it will let us also investigate other structures that might emerge.

The minimization works towards a local minimum inside the energy landscape of the system. However it does not take into account whether this is a local or the global minimum. To maximize chance that the system finds the global minimum an NPT simulation is done. The number of particles and pressure is kept constant throughout the simulation. The temperature within the simulation is slowly lowered, allowing the system to settle into a valley within the energy landscape, while simultaneously allowing the system to still escape this valley with kinetic energy if the found valley is not the lowest. Eventually the kinetic energy will be eliminated as the temperature moves towards zero. This slowly eliminating of the temperature is called simulated annealing. When the

temperature is close to zero the simulation is stopped and a minimization is done. This will bring the system into a local minimum which hopefully is the global minimum.

The dynamics of the system including the simulated annealing is solved by using Molecular Dynamics(MD) methods. MD methods focus on solving Newton's equations of a system. More on MD can be found in the book of Tao Pang.[9] The temperature is controlled using a Nosé-Hoover thermostat.[10] The MD equations calculated the position, velocity and acceleration of each particle during each time step.

The simulations are done in a MD program called LAMMPS.[11]. The system is loaded by creating a simulation box and placing particles randomly in this box. The interaction between the particles is specified. First a minimize is done. This is to create a nice initial configuration and prevents excessive heating during the MD simulation [12]. Then random velocities are implemented which are necessary to start the MD simulation. After the NPT simulation another minimization is done. This wouldn't be necessary if the temperature would go to absolute zero. Then the simulation would work as a minimize. However there is a low temperature and kinetic energy left after the MD simulation which should be eliminated to get the local minimum. The system is now hopefully in the global minimum and the corresponding structure could be investigated.

It should be noted that in this project we chose to do a separate simulation for each pressure point. Each pressure point had it own initial state that was not influenced by previous simulations. All simulations did use the same seed for initializing the system. Another method of doing the simulation would be to initialize a system and slowly increasing the ϕ. The ϵ would then be calculated throughout the simulation.

During the simulation snapshots of the system are saved in a dumpfile. This dumpfile contains the size and shape of the simulation box as well as the positions of all the spheres/atoms inside the box. The dump_file can be visualized with The Open Visualization Tool Ovito.[13] Ovito can visualize the particles inside the box and can also show how the structure evolves during the time-series of the simulation. Ovito can apply modification to the data. These modification do not change the simulated data but are used to do addition calculations on the data. Useful modification for this project are the Common neighbor analysis(CNA) option which identifies some structures. These structures include FCC, BCC, HCP and ISO. Diamond structures are found with a extended version of the CNA. In the extended version the second neighbors are also taken into account. This is done by identifying the nearest neighbors of a particle and then looking at the nearest neighbors of these particles. The coordination analysis modifier shows the radial distribution function of the data. "The radial distribution function measures the probability of finding an atom at distance r given that there is an atom at position 0" [**?**]. For perfect crystalline structures

the RDF should contain a sharp peaks in accordance with the nearest neighbors followed by a sharp peak at the second nearest neighbor distance and additional sharp peaks for particles that are further away .

Results

The energy difference between the 5 standard structures as depicted in figure 1 are the starting point of this project. Therefore we should start by getting the ϵ values of these structures within the parameters of our simulation. This is done by forcing the spheres into the structure as described in the methods. For ϕ ranging from 0 to 10 the ϵ of the 5 standard structures were calculated. The results can be found in figure 2. The ϵ of these structures start to rise from different points. E.G. the HCP and FCC structures ϵ is the longest zero and only starts to rise between a ϕ of 0.725 and 0.75. In fact all the structures start to have an energy at their packing efficiency. The packing efficiency gives the factor of volume of a unit cell that is occupied by the particles.[14] That the structures start to rise from this factor makes sense considering that the spheres need to be compressed in order to get a potential energy. After the maximum packing efficiency the connection between ϕ and ϵ is somewhat linear. When ϵ_{FCC} is subtracted from all curves, the difference between the curves becomes more visible. The created graph can be seen in figure 3. The graph looks exactly like the graph that was our starting point as depicted in Figure 1. And gives a baseline to compare the simulation data with.

Now that we have our baseline to compare our results with we can start the simulations. The first simulation that is done is with 2 particles in the simulation box. The plot of the volume fraction against the pressure is shown in figure 4. ϕ is calculated using equation 2 which can be found in the methods section. But V_{cell} is here replaced with the volume of the simulation box.

The first thing to note is that the graph does not cross the y-axis in the origin. The graph actually stops at 1000 pressure units. This was a choice as the simulation at zero pressure could cause the volume of the expand rapidly and cause the simulation to crash by having the deal with large forces. The volume fraction around zero pressure would probably lie around 0.74 as this is the packing efficiency of FCC, which is considered the most efficient way to store hard spheres in a cubic box. The initial size of the simulation box is chosen smaller than it would be at zero pressure. Therefor the box will always expand to the volume fraction of 0.74. If the initial ϕ would be smaller the box would not expand or shrink as the spheres inside the box would not be compressed and the pressure would already be zero. Which means that at zero pressure the ϕ can range from 0 to 0.74.

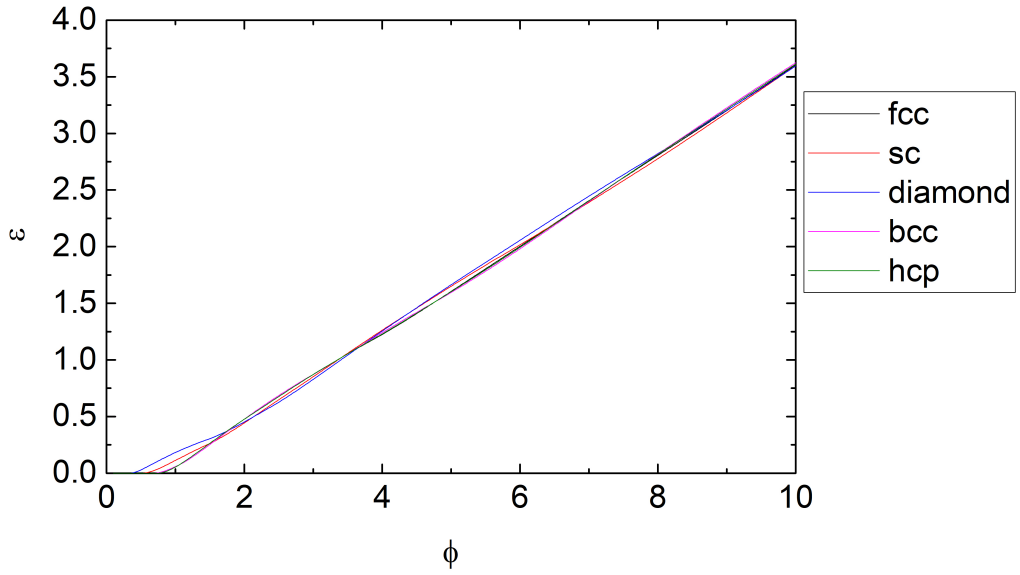

Figure 2: ϵ set out against the phi for the 5 standard structures. Being Face-Centered-Cubic(FCC),Simple cubic(SC),diamond,Body-Centered-Cubic(BCC) and Hexagonal-Close-Packed(HCP)

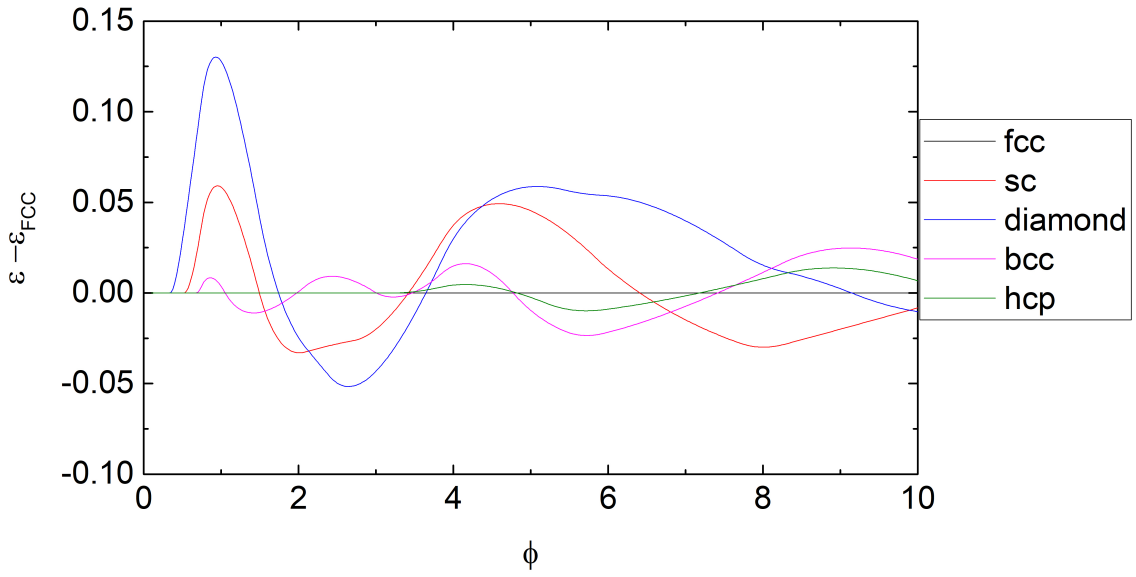

Figure 3: Energy per particle difference between diamond, BCC,SC,HCP and FCC with an offset of the values of FCC.

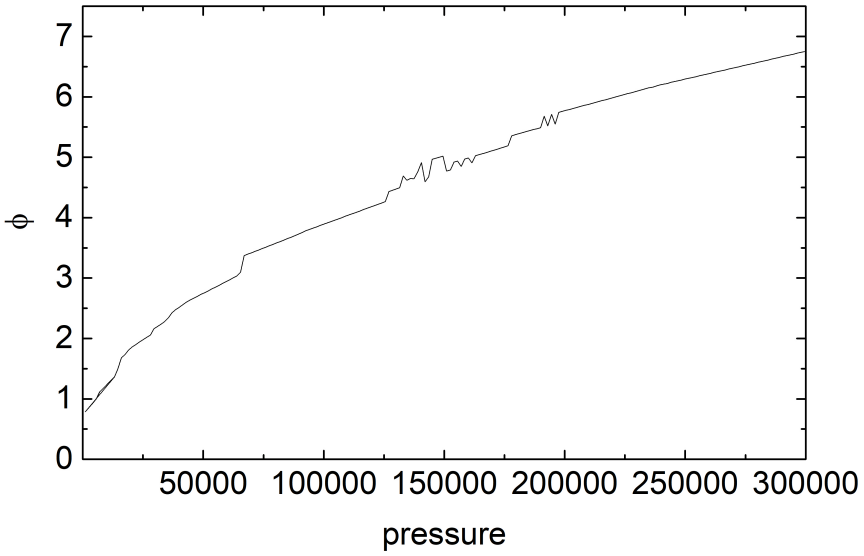

Figure 4: Pressure set out against the volume volume fraction ϕ for the 2 particles in the simulation box

The second remarkable thing is that there are jumps in the graph. Most notably at a pressure around 70000 the value of ϕ suddenly jumps from 3 to 3.5. These jumps represent a transition in structure, how and why these transitions happen is explained in the Backgrounds. The last thing to note about the graph is that the graph jumps between different branches at higher values of ϕ. This is due to different structures having at similar ϵ at the same ϕ. The simulation is not always able to find the global minimum of the system but might end up in a local minimum. Because we are only interested in the ground state we can disregarded the data points with a higher energy. Additional simulations are done where needed.

For the 2 particles simulation the ϵ is calculated. The ϵ against ϕ data points are added to the graph with the standard structures. To make the differences between ϵ more visible a value of $\beta\phi$ is subtracted for a suitable value of β. Each following graph in which ϵ is set out against ϕ will have this subtraction, unless it is stated differently. Figure 5 shows the standard structures with the added data points for the 2 particles in simulation box.

The data points are compared with the curves of the standard structures. At first the simulated points follows the expected structures. First a FCC and then BCC structure. After $\phi > 1.6$ the measurements start to differentiate

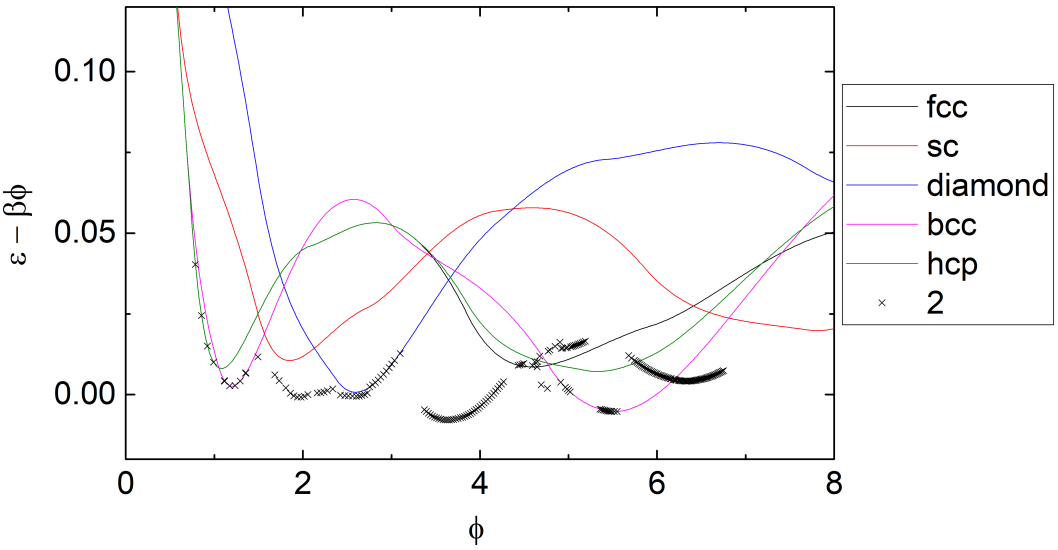

Figure 5: The ϵ of the standard structure and the measured values of 2 particles in the simulation box set out against there respective volume densities. The data is subtracted by the gradient β of the graph.

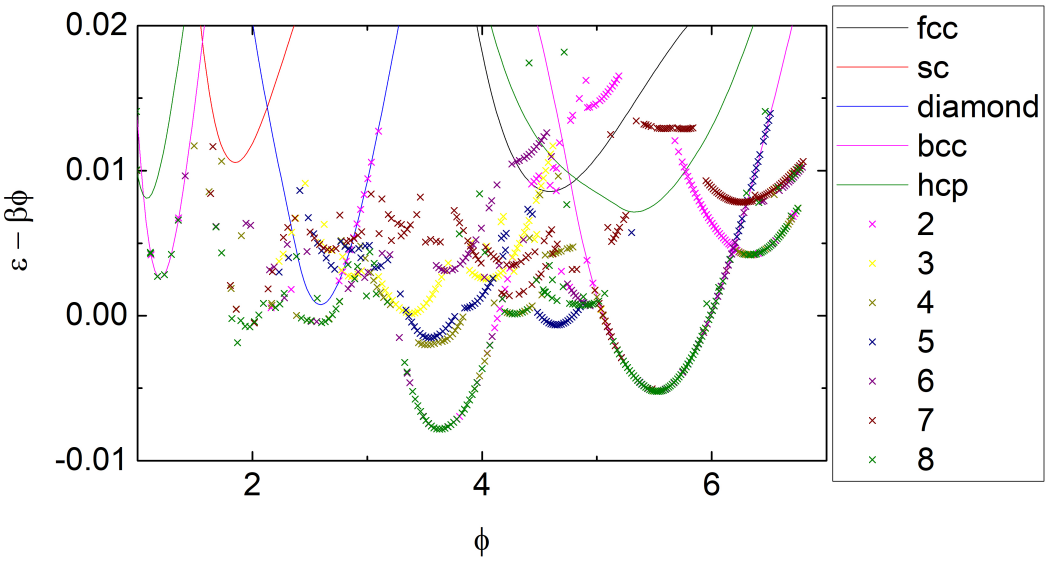

Figure 6: The ϵ of the standard structure and the measured values of 2 to 8 particles in the simulation box set out against there respective volume densities.

from the original graph. Instead of the simple cubic structure another curve is found. Around the diamond structure the measured values lie a little bit lower before following the diamond curve. Then the measured values jump towards another unidentified curve. From ϕ around 4.5 and onwards the simulations seemed to have trouble finding the lowest ϵ structures. This can be due to the fact during the simulation the system moves towards a local minimum, which does not correspond with the global minimum, but cannot escape from this minimum . But could also be due to the structures having a primitive cell of which the shape and size is harder to simulate with only 2 particles. BCC is an example of such a structure, which becomes also apparent from figure 5 as only a few points lie on the BCC curve while the BCC curves clearly has the lowest ϵ.

Because the 2 particle simulation had some trouble finding the lowest structure, additional measurements were done with more particles in the simulation box. This should eliminate most inconsistencies and could also uncover more complicated structures in which more than 2 particles are needed inside the primitive cell. The results are in figure 6.

The measured data points do not all have the same ϵ at a certain ϕ. Apparently the number of particles inside the simulation box does have an impact on the ϵ. Some structures require a particular number of particles to be constructed. Most structures require 2 particles in their primitive cell to be constructed. Be-

cause 3,5 and 7 cannot make multiple complete primitive cells they tend to be imperfect and have a higher energy. This is seen on multiple curves where 2,4,6 and 8 particles have the same energy. Their ϵ is lower than that of the other measurements. Also it can be seen that at the higher volume fractions most particles follow the BCC curve. BCC only requires 1 particle in the unit cell. This differs greatly from the 2 particle line. Before the BCC curve there is also a zone where smaller structure curves are detected. Here the 5 particle measurement is the lowest. Apart from these differences at higher volume fraction it seems that the lowest energy are the same as described above during the 2 particle measurement.

The goal of this project is to investigate which structures arise and whether the diamond structure can be found. A good place to start is the area where the data points lie close to the valley of the diamond curve lies. This is at a ϕ between 2.3 and 3. A zoomed in version of this area can be found in figure 7. Additional measurements of 2 particles are done to get a better idea of the curve, these are called the detailed data points. It is clear that the simulated curve lies just below the diamond curve. We use Ovito to look at snapshots of the simulation. The Ovito snapshot corresponding to a point at a ϕ of 2.6 on the energy curve is found figure 8. Note that in these snapshots the centers of the soft spheres are drawn and interconnected with bond , this is how we defined the structure of the soft spheres in the Backgrounds. In reality the spheres overlap but drawing this would make us unable to visualy distiquist the structure. The structure looks like diamond. However the identify diamond structure function does not recognize this structure as being diamond. A point that is identified as diamond lies on the diamond curve at a ϕ of 2.8. This snapshot of this point is shown in 9 to compare the unkwown structure with.

Visually comparing the 2 structures it looks like the structure have similar orientations. However the hexagons of the diamond structure look more perfect. All the angles look the same while the simulated structure seems to have a more deformed hexagons, we will call this structure deformed diamond. The deformation also means that the nearest second nearest neighbor length differ. In figure 10 both RDF of the structure are given. From this graph we can see that the ratio between the first and second nearest neighbors differs. Also the nearest neighbor lengths differ, this is partly due to the increase in volume fraction but also due to the deformation of the structure. For a diamond structure the ratio between the nearest neighbor distance and the second nearest neighbor distance should be $2\frac{\sqrt{2}}{\sqrt{3}} \approx 1.633$. This ratio is also found in figure 9 as the nearest neighbor length is just below 1 while the second nearest neighbor-length is just above 1.6. For the deformed diamond structure this ratio is 1.31356 with the nearest neighbor at 1.069 and the second nearest neighbor at 1.404. During the whole curve the ratio varies from 1.3 to 1.4. The deformation is also noticeable when looking at the primitive unit cell of the structures. For diamond all faces of the primitive unit cell are equal, while for the deformed diamond the primitive unit

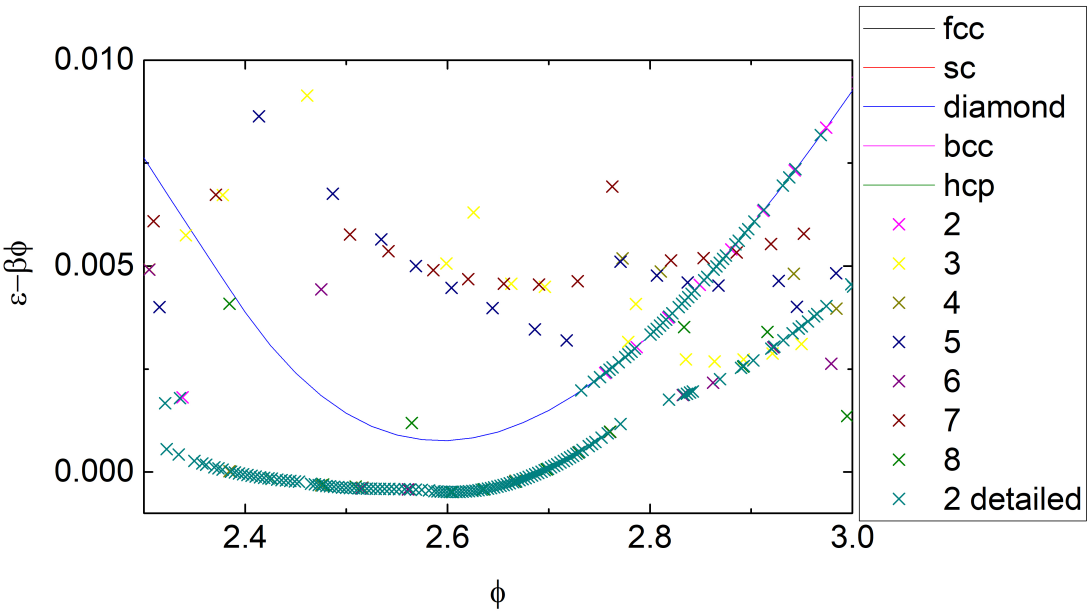

Figure 7: Zoomed in ϵ set out against the volume volume fraction around the lowest diamond curve. Including a more detailed measurement of 2 particles in the simulation box

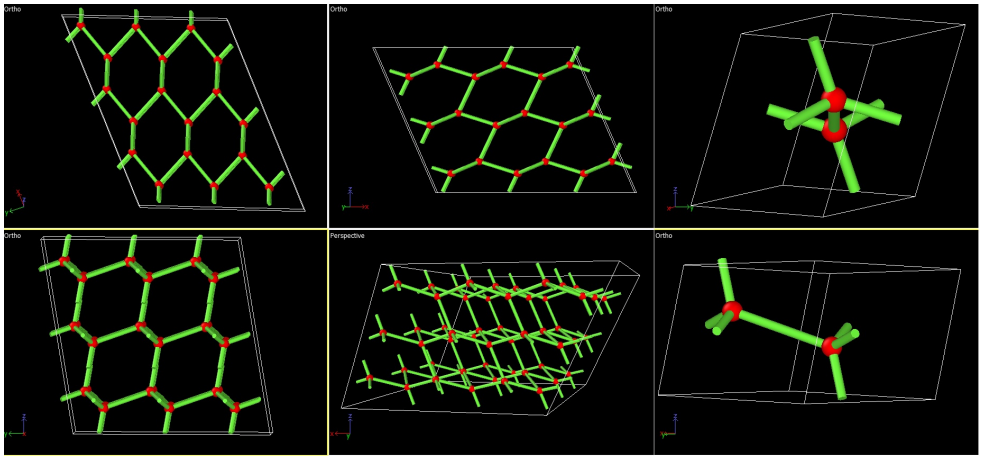

Figure 8: The structure found at a ϕ of 2.6 visualized with Ovito. From left to right and top to bottom: the structure as watched from the top; from the front; the simulation cell with 2 particles; from the left; a perspective view and lastly the simulation box from another angle.

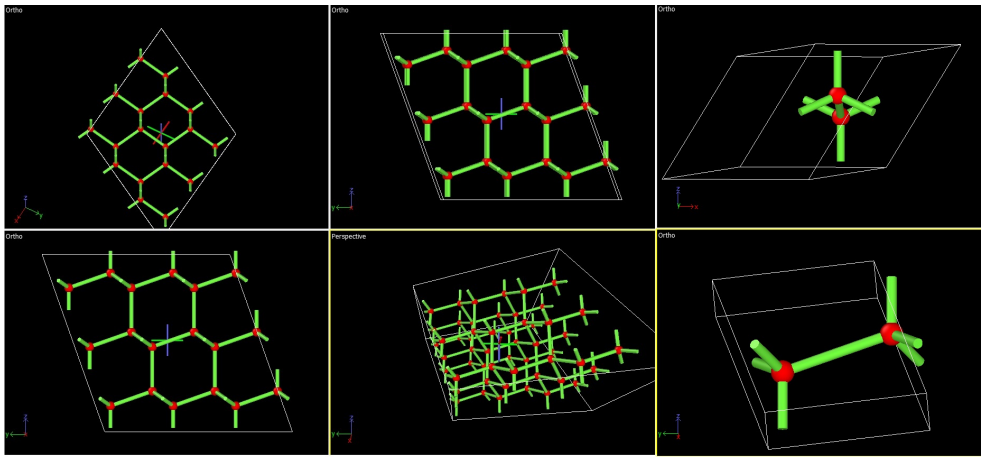

Figure 9: The diamond structure found at a ϕ of 2.8 visualized with Ovito. From left to right and top to bottom: the structure as watched from the top; from the front; the simulation cell with 2 particles; from the left; a perspective view and lastly the simulation box from another angle.

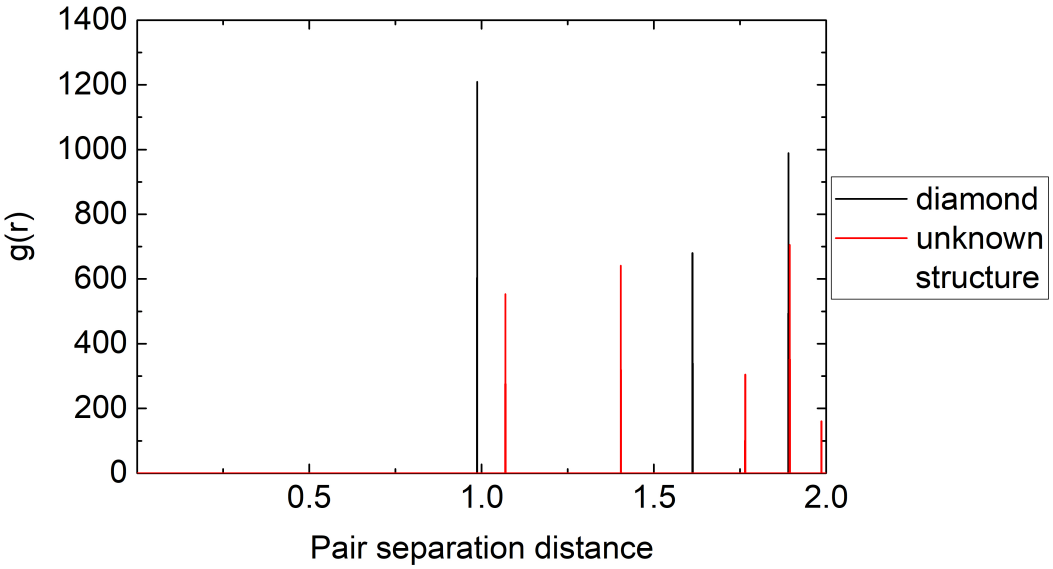

Figure 10: The Radial distribution function of both the diamond(black) and unknown structure(red) that are shown in figure 9 and 8.

cell is more rectangular.

How the diamond structure can be deformed while still keeping its general orientation and all nearest neighbors having the same bond length can be explained by Guest modes. A Guest mode is a deformation of the structures unit cell in which the nearest neighbor length does not change.[15] Regarding the diamond structure the guest modes are easy to count with Maxwell's constrain counting method. For diamond there is 1 more constrain then degrees of freedom. However because a NPT simulation is done the box adds another 6 degrees of freedom to the Guest modes making it possible to have at least 5 parameters with which Guest modes can be created. The found structure is a Guest mode of diamond. How the parameters of the diamond structure are adjusted to create this the simulated structure can be calculated. However because the first with second neighbors ratio varies and the curve looks very flat it is expected that this minimum curve is a combination of multiple curves of the Guest modes. Calculating these Guest modes with the 5 parameters goes beyond the scope of this BEP.

Before and after the discussed diamond area it seems that there are also structure curves that might be interesting. The area before the diamond starts when the energy minimum stops following the expected bcc curve and stops at the de-

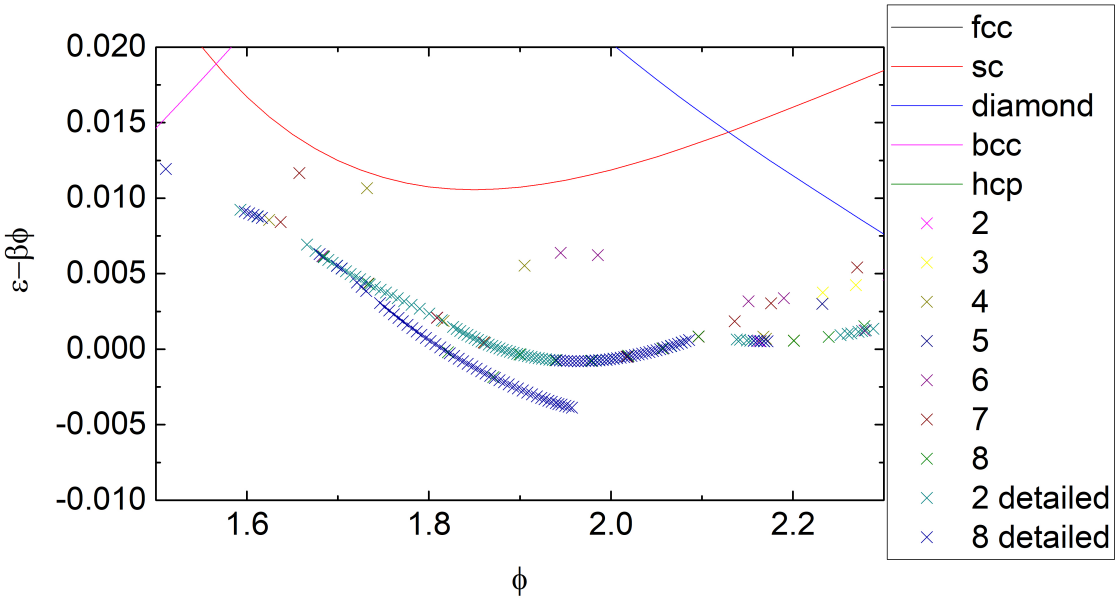

Figure 11: Zoomed in ϵ set out against the volume volume fraction ranging from a ϕ of 1.5 to 2.3. Including a more detailed measurement of 2 and 8 particles in the simulation box.

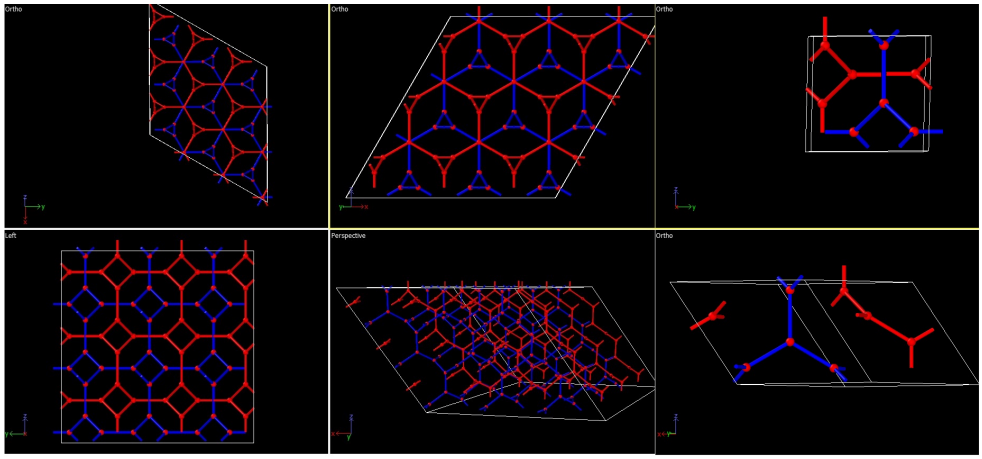

Figure 12: The structure found at a ϕ of 1.93 and 8 particles in the simulation box visualized with Ovito. From left to right and top to bottom: the structure as watched from the top; from the front; the simulation cell with 2 particles; from the left; a perspective view and lastly the simulation box from another angle.

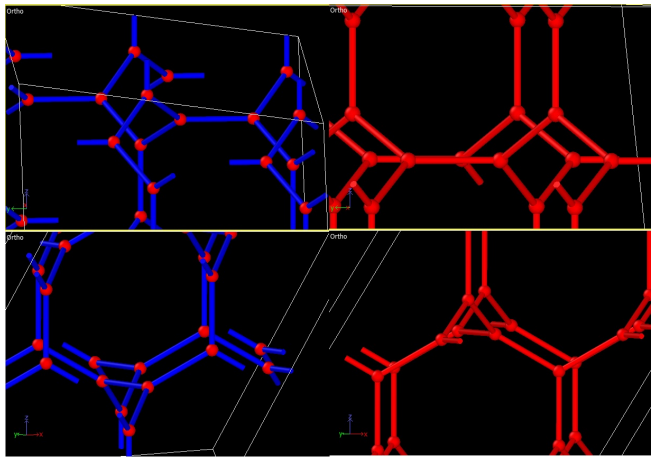

Figure 13: More detailed section of the structure found at a ϕ of 1.93. The 2 clusters are depicted separately.

formed diamond structure. This lies between a ϕ of 1.5 and 2.3. Again addition measurement are done with 2 particles. Also additional measurements are done with 8 particles. The cause of this is a measurement point of 8 particles which looks it is not on the curve but does have the lowest energy. The corresponding graph is shown in figure 11.

The data point of 2 particles clearly show a curve. The data points of 8 particles show a different pattern. At first the points follow a curve. Just before a ϕ of 2 the data points jump and start following the curve of 2 particles. Figure 12 shows the structure that is found at a ϕ of 1.93 and with 8 particles in the primitive unit cell. This is just before the 8 particle data point jump to the 2 particle curve.

The structure is well-defined as the nearest neighbors have the same bond length. Each particle has 3 nearest neighbors. When the nearest neighbor bonds are drawn we see that 2 clusters of structures emerges. Both cluster are coloured in the Ovito snapshot. Each cluster has 4 particles in it, both structure look familiar however by taking a closer look which can be see in figure 13 were it shows that the structures are rotated in orientation. This allows the structure to weave into each other. We can also see that the faces of the primitive unit cell are equal. We have not been able to find earlier reports of this structure before. For now we will call the structure the cluster structure. Throughout the curve of the cluster structure the bond length of the nearest neighbors is not on every point equal. At some points the bond lengths slightly differs. This is seen in the RDF as multiple small peaks very close to each other. This could imply some instability in the structure and help explain the sudden drop towards another structure. As the 2 cluster might interfere to much with each other and destroy the structure.

The 2 particle curve should contain a simpler structure because it can be made with 2 particles in the primitive cell. Figure 14 shows the structure around a ϕ of 2 for 2 particles in the simulation box. The first thing to note about this structure is that both the nearest and second nearest neighbors are connected to create this structure. When only the nearest neighbors are plotted the some parallel lines are created. A hexagonal plane is seen from the top. The hexagonal planes are stacked directly above each other. This is odd considering FCC and HCP would alternate the planes to create a favourable packing fraction. By stacking the planes on top of each other the side form rectangles. This structure is called simple hexagonal lattice.[16] The ratio of the distance between the first and second neighbors, which defines the ratio of the rectangles, changes during the curve. The ratio starts at 1.387 and stops around 1.655. Note that this lies close to the ratio of diamond and the transition to a diamond lattice would make sense would it not be for the deformed diamond.

After the deformed diamond another curve seems to emerge. This curve cover the ground state between a ϕ of 3 and 4.5. Figure 15 shows this area. The

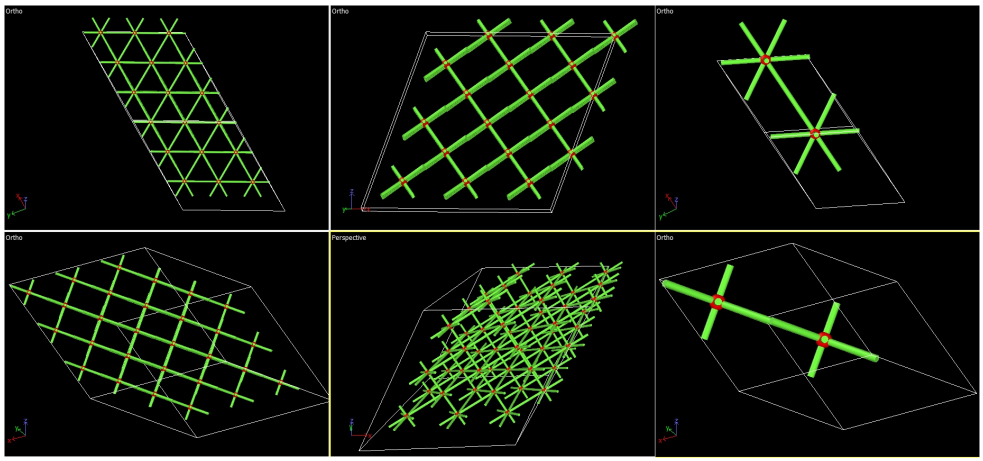

Figure 14: The structure found at a ϕ of 2 and 2 particles in the simulation box visualized with Ovito. From left to right and top to bottom: the structure as watched from the top; from the front; the simulation cell with 2 particles; from the left; a perspective view and lastly the simulation box from another angle.

minimum curve consist of data points from only the 2,4,6 and 8 measurements. This means that the structure can be made by having 2 particles in the primitive structure. The structure at a ϕ of 3.46 is shown in figure 16. From the top down the structure contains a honeycomb structure. The hexagons with this honeycomb appear to have the same angles at every corner. The sides of the structure contain a hexagonal lattice. Which are stacked alternating to create the honeycomb structure seen from the top. The alternating of the hexagonal planes is known as the HCP structure. [16]

We have seen the ideal HCP structure before as on of the standard structure. However HCP is actually a collection of structures with the same symmetry group. The HCP structure has 2 independent variables which span these structures. These are known as a and c. a is the distance between the particles in the hexagons plane. And c is the distance between a particle and the particle directly above it in the $\vec{z}$ direction. The ideal HCP curve has a $\frac{c}{a}$ ratio of $\sqrt{\frac{8}{3}}$. This is the variant which gives HCP it's name of Hexagonal close-packed. Because it has the same atomic packing factor as FCC. The simulated HCP structure has a different $\frac{c}{a}$ ratio. This special version of HCP has 8 nearest neighbors instead of the 6 neighbors HCP normally has. This is because the structure is pressed down until the normally second nearest neighbors have the same length as the nearest neighbor. From this the $\frac{c}{a}$ ratio is easily be calculated to be $\frac{2}{3}$. This ratio starts at $\frac{2}{3}$ but changes slightly along the curve. Which is seen as the nearest neighbor length start to differ slightly. And the HCP structure becomes even more compressed.

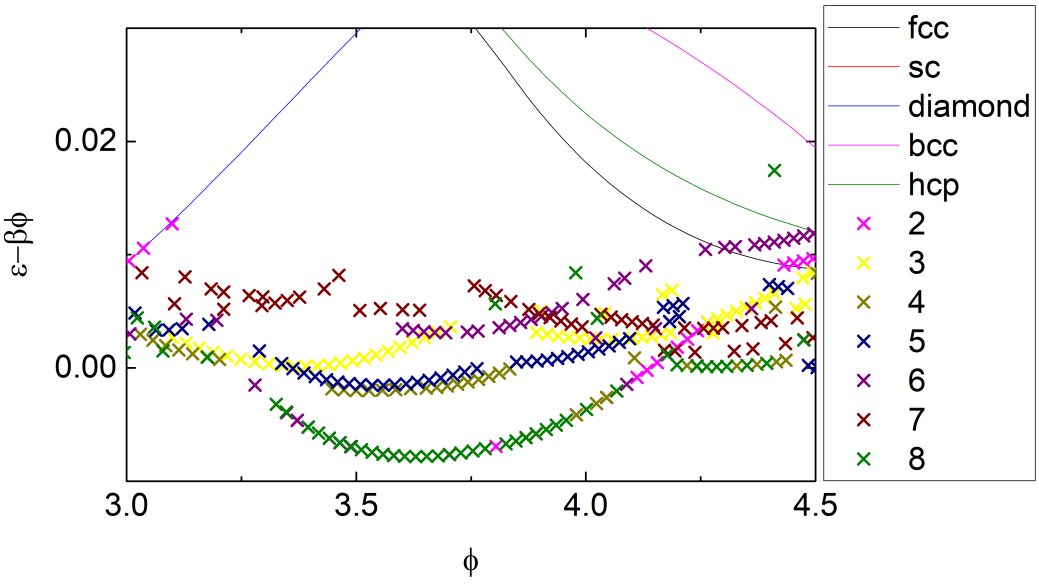

Figure 15: Zoomed in ϵ set out against the volume volume fraction around the curve found at a volume volume fraction between 3 and 4.5

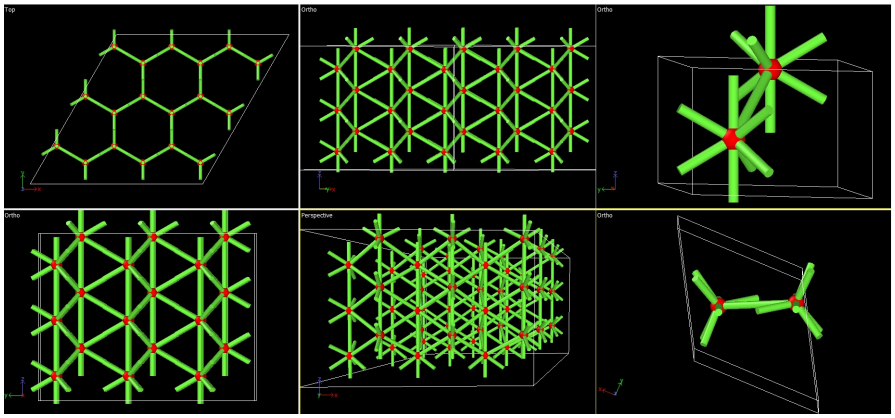

Figure 16: The structure found at a ϕ of 3.46 and 2 particles in the simulation box visualized with Ovito. From left to right and top to bottom: the structure as watched from the top; from the front; the simulation cell with 2 particles; from the left; a perspective view and lastly the simulation box from another angle.

The HCP with a $\frac{c}{a}$ ratio of $\frac{2}{3}$ (HCP2/3) lattice sum is also be calculated as is done with the 5 standard structure. The particles are forces into the HCP2/3 structure and the ϵ of this structure is measured. The values of the HCP2/3 can be drawn as an extra curve in figure 15. The line goes through the curve with a slight difference after the valley of the curve. With this confirmed the curve can be added to ϵ curve of the 5 standard structures. The new ϵ graph can be found in figure 17.

At higher densities we find the area where multiple energy curves arise, most

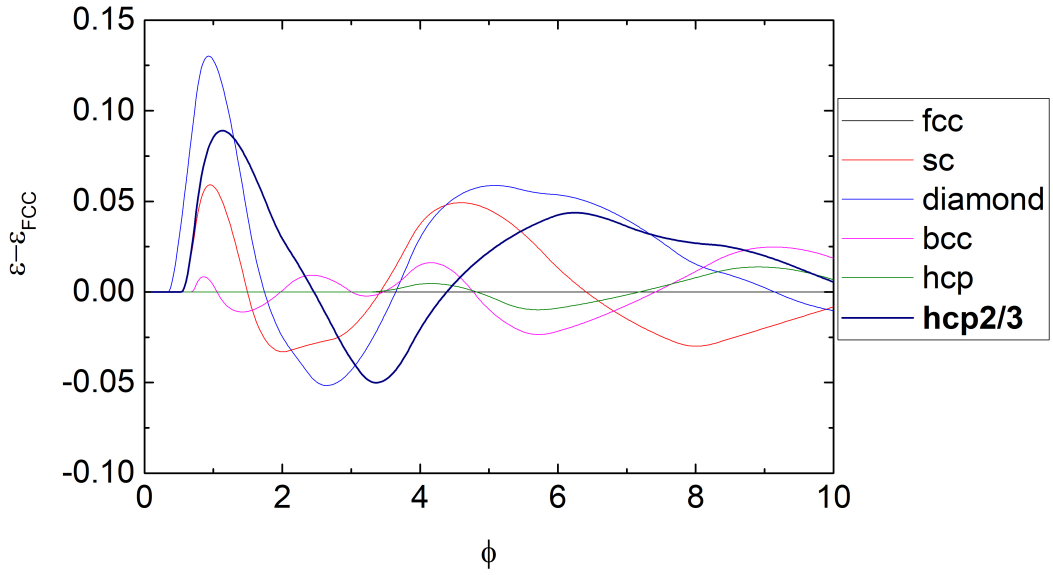

Figure 17: Energy per particle difference between diamond, BCC, SC,HCP,HCP2/3 and FCC. The value of ϵ_{FCC} is subtracted from the values.

notably one which consist of 5 particles in the primitive unit cell. However looking at this structures it seems that these structures are very complicated as no bond length is the same. This makes it hard to identify or even say something use full about these structures. In this project we will neglect these structures and call the structures within this area with multiple energy curves unidentified. Most of the last data points before a ϕ of 6 lie on the BCC curve and the structure of these data points are indeed confirmed to be BCC.

There are some areas where no data points are present. These are for example just after the deformed diamond structure around a ϕ of 2.7 and around a ϕ of 1.5. These areas are not reached by the data points because of the jumps in

ϕ. We cannot say what happens around these points but it highly suggest that there are some transition areas here where structures might coexist.

Discussion

The goal of this project was to find the structures that emerge when soft spheres are at there ground state at different volume fractions. At low volume fraction the system had the expected structures of FCC and BCC. At a ϕ of 1.5 different structures arose. A clustered structure with 8 particles in its primitive unit cell was found first. This structure collapsed and turn into a structure that seemed to be a simple hexagonal lattice, which can be made with 2 particle in the primitive cell. After this structure a deformed diamond structure was found. The deformed diamond differs from diamond in the fact that the ratio between the first and second nearest neighbors is smaller. After the deformed diamond a HCP structure was found. This structure was special because had a $\frac{c}{a}$ of $\frac{2}{3}$. Which is also recreated and added to the standard structures as shown in figure 17. Next the structures became unidentified before finally returning towards a BCC structure. The found structure are shown in the structure diagram in figure 18.

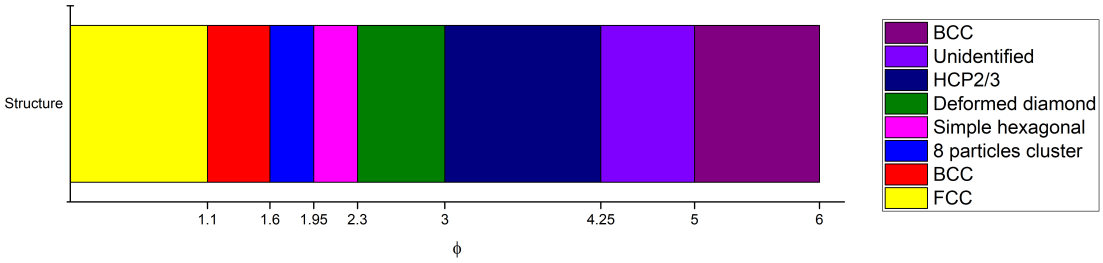

Figure 18: The found structures at there corresponding volume fractions

If we compare our found structures with the existing literature we find that our findings lie close to those of Zhu and Lu [6]. They also found that the curves of FCC and BCC are followed, an area with a hexagonal structure was also found by them which is consistent with our results, furthermore the ratio the found of $\frac{c}{a}$ ratio of 0.61 is consistent with 1 over the ratio of the bonds in our rectangles which lies between 1.387 and 1.688. After the HCP structure they found a diamond structure, however no remarks were placed about the deformation of their diamond suggesting that there diamond structure was perfect instead of our deformed diamond. Higher volume fractions are not simulated by then so we cannot say whether they would also have found the HCP2/3 structure. Our 8 particle cluster structure or something similar was also not found by them. They found also 2 other structure that are not found by our simulations, possibly because these structures are found at the transition zones. Our results also

show other structures than simulations with the Herztian spheres, suggesting that small changes in the potential can make big differences in the found structure.

The structures that are found for the ground state curves were not perfect. Often the structure had little changes between some ratios while following this curve. For the simple hexagonal structure this change was rather big as the ratio between the nearest and second nearest neighbor changed from 1.4 to 1.65. This change was also visible in the deformed diamond. The HCP2/3 seemed more constant but the HCP2/3 structure did become even more compressed as the volume fraction was increased. These small differences in structure could be explained by the structure slowly transition into another structure. This will not be the same as the transition areas but one structure slowly changes until it reached the transition area where it will change more rapidly into the other structure. The transition zone them self can be further investigated by doing a large scale MD simulation, here more particles are simulated to allow the system to go into a state of coexistence where multiple structures are formed. By simulation the primitive unit cell like we have done only 1 structure can be simulated.

The search for the structures started because some structure had use full properties. For example the optical band gap of the diamond structure. Whether the found deformed diamond also has a band gap and this band gap is optically favourable needs to be investigated. For this is would also be interesting to investigate with which Guest modes the deformed structure is created. The properties of the HCP2/3 structure are also unknown. The structure might get some extra interesting properties due to nearest neighbors being increased to 8 instead of 6. The use fullness of the found structures could be investigated.

It should also be noted that we searched for ground states. This meant that we set the temperature of system to zero. The stability of the found structures at higher temperatures is not investigated and the structures that we have found might not be stable and collapse. We also don't know if we can create the soft spheres with the implemented potential or a small adaptation to it. However star polymers could probably be made that the interact like our soft spheres and might even allow some small adjustments to the potential. This would imply a cheap way to create structures.

For now it is impossible to say whether making structures with soft spheres is beneficial. What can be concluded from this project however is that, even with a simple potential, as the repulsive harmonic potential, complex structure can be created. These structures will changes as the volume fraction and pressure is increased. Small adaptations to the potential could result in different structures. As is shown with for example Hertzian spheres [3][4]. Which differ from soft spheres by having a exponent of $\frac{5}{2}$ instead of 2. These simple potentials could be the key to creating specific structures cheaply.

Conclusion

To summarize, calculations of the ground states of soft spheres with at a certain volume fraction were done by simulating the primitive unit cell. A structure can be created from this primitive unit cell, which hopefully had some beneficial properties. The found structures were compared with the lattice sums of some known structures. The simulating structures differed from the known structures resulting in some interesting structures. These structures are a 8 particle cluster structure, a simple hexagonal structure, deformed diamond and the HCP2/3 structures. All these structures have some differences with known structures, except for the cluster structure which does not look like any known structure. These differences make it hard to assign any properties to the structures. What we can learn from the found results is that particles with a simple potential,which in essence works with only length scale, can create complex 3D structure. This means that the soft spheres could be the key to create complex structures more easily.

References

[1] Martin Maldovan and Edwin L. Thomas. Diamond-structured photonic crystals. *Nature Materials*, 3:593 EP –, Sep 2004.

[2] William L. Miller and Angelo Cacciuto. Two-dimensional packing of soft particles and the soft generalized thomson problem. *Soft Matter*, 7:7552–7559, 2011.

[3] Santi Prestipino, Franz Saija, and Gianpietro Malescio. The zero-temperature phase diagram of soft-repulsive particle fluids. *Soft Matter*, 5:2795–2803, 2009.

[4] Josep C. Pàmies, Angelo Cacciuto, and Daan Frenkel. Phase diagram of hertzian spheres. *The Journal of Chemical Physics*, 131(4):044514, 2009.

[5] Wouter G. Ellenbroek. Zooming in on soft "spheres". *Unpublished*.

[6] You-Liang Zhu and Zhong-Yuan Lu. Phase diagram of spherical particles interacted with harmonic repulsions. *The Journal of Chemical Physics*, 134(4):044903, 2011.

[7] SklogWiki. Soft sphere potential, sep 2018. http://www.sklogwiki.org/SklogWiki/index.php/Soft$_s phere_p otential$.

[8] LAMMPS. minimize command, 5 sep 2018. https://lammps.sandia.gov/doc/minimize.html.

[9] Tao Pang. *An introduction to Computational physics*. Cambridge University Press, 2006.

[10] Victor Ruhle. Berendsen and nose-hoover thermostats. 2007.

[11] LAMMPS. Lammps molecular dynamics simulator, sep 2018. https://lammps.sandia.gov/.

[12] Multiple. Is energy minimization really needed for a typical md simulation?, 2015. https://www.researchgate.net/post/Is$_e nergy_m inimization_r eally_n eeded_f or_a t ypical_M D_s imulation$2.

[13] Ovito. Ovito the open visualization tool, sep 2018. https://ovito.org/.

[14] ExcellUp. Solid state, sep 2018. https://www.excellup.com/class$_1$2/$chemistry_1$2/$SolidState$1.$aspx$.

[15] S.D Guest and J.W Hutchinson. On the determinacy of repetitive structures. 51:383–391, 03 2003.

[16] Universität Wien. Crystal lattice structures, 2008.