# Crystal prediction of hard dumbbell particles through Monte Carlo simulations

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## Abstract

The prediction of crystal structures through the use of a NPT Monte Carlo simulation of hard dumbbell particles is reported. Fits are made to known extensions of the Carnahan starling equation of state to apply to nonsymmetric dumbbell particles within a low pressure range (P < 18). Rotator phases are observed for melting crystals. Recrystallisation is attempted on molten crystals by raising the pressure and applying a brownian motion to the particles. Bcc, fcc, and hcp crystalls are made using dumbbell like polynomial particles.

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# Chapter 1 Introduction

In this thesis the behaviour of hard dumbbell particles is studied by means of computer simulation. We start with Monte Carlo simulations of a system of hard spheres. When this has been accomplished we use dumbbell particles and by increasing the pressure we try to create crystalline structures from a collection of dumbbell particles with different size ratios between the two dumbbell halves. We hope to be able to use these results from computer simulations and predict stable crystalline structures of these particles. We also examine the Carnahan starling equations to make predictions about how a system will behave. For particles for which there is no Carnahan Starling equation of state we extend the equation of state so that it describes that particular particle system. We compare the behaviour of a system consisting of dumbbell particles with that of a 1:1 mixture of hard spheres. The crystal structures that have been created are melted by reducing the pressure and study the resulting rotator phases of different systems.

We also look at non-dumbbell particles. These particles consist of 4-6 hard spheres are also used to predict the stable crystal structures.

## Methods

#### 2.1 The Monte Carlo method

The Monte Carlo (MC) method can be used in a wide number of varieties. Using a Monte Carlo method means that you are sampling the Boltzmann distribution of possible outcomes of a measurement. A simulation of a measurement is made and of its outcome the Boltzmann weight is determined. Doing this many times and averaging over the outcomes will give us a result that approaches real life situations.

The Monte Carlo methods are used in many different scientific fields such as physics, chemistry or economics. Monte Carlo methods are even used to develop more realistic video games.

#### 2.2 The Monte Carlo simulation

In this thesis the MC simulation is a computer simulation that randomly moves particles in a volume to make predictions and approximations of real systems that usually cannot be derived exactly.

A 2-dimensional representation of a MC simulation is shown in figure 2.1. In this example we have 9 hard spheres  $(N_{part} = 9)$  in a 2 dimensional box. In each step of the simulation a random choice is made to either attempt a particle move or change the volume. On average one volume move is attempted every  $N_{part}$  particle moves.

#### 2.2.1 Particle moves

When a particle move is initiated, a random particle (P) is selected. A random vector  $(\vec{v})$  is generated where the value of  $|\vec{v}|$  may vary every particle move but typically does not get larger than the diameter of P. The particle is moved from its old location to the new location  $(\vec{x}(P) \rightarrow \vec{x}(P) + \vec{v})$ .

We employ periodic boundary conditions. Specifically, when a particle is moved we check if the new location is outside of the box. If so then we move it back into the box on the other side (move C in 2.1). We then check for overlap between particle P and all other particles in the box. The spheres interact with a hard sphere potential described by:



Figure 2.1: A simple 2 dimensional representation of a Monte Carlo simulation. A and C are allowed particle moves. B creates overlap and should be rejected

$$U_{hs}(r) = \begin{cases} \infty & \text{for } r < 2R\\ 0 & \text{for } r > 2R \end{cases}$$
(2.1)

,where R is the particle radius. This means they do not feel each other at a distance larger then twice their radius R.

The distance between P and the other particles is calculated. We have found overlap if one of the other particles is closer than 2R to P's new location(move B). If overlap is found the particle move is undone otherwise it can be accepted.

#### 2.2.2 Volume Moves

When a volume move is initiated a small random volume change is generated  $(\delta vol)$ . The old volume of the box $(V_{old})$  is calculated and used to determine the new volume  $V_{new} = V_{old} + \delta vol$ . A random dimension is then selected and the box size is changed to accommodate the newly determined volume. In the case where the x direction is selected we get:

$$X_{box}^{new} \to X_{box} + \frac{\delta_{vol}}{Y_{box}Z_{box}}$$

Where  $X_{box}$ ,  $Y_{box}$  and  $Z_{box}$  are the dimensions of the box. To check whether the configuration created by a volume move is physically reasonable, at the temperature and pressure we are working with, we compare the Boltzmann factor  $(e^{-\frac{E}{K_B T}})$  of the old and new configurations. In our NPT MC simulation this condition can be written like:

$$Rand > e^{-P\frac{(V_{new} - V_{old})}{\sigma^3} + N_{part} \times \log \frac{V_{new}}{V_{old}}}$$
(2.2)

. Where P is a dimensionless pressure (or  $P = \beta p \sigma^3$ ) and Rand is a random real with a value between 0 and 1. When eq. 2.2 returns true the move is rejected and the box returns to it's original size. When the condition given by eq.2.2 is found to be false we move on with the repositioning of the particles in the new box. All of the particles get moved along with the volume change. If a box move of a size  $\delta x$  is made in the x direction:  $X_{box}^{new} \to X_{box} + \delta x$  then the coordinates of the particles are changed as well:  $x_{new} = x_{old} \frac{X_{box}^{new}}{X_{old}^{old}}$ . The volume is changed:  $V_{new} = V_{old} + \delta x Y_{box} Z_{box} = V_{old} + \delta_{vol}$ . Once the particles are redistributed over the volume we do an overlap check. This time not for a single particle but for all of them. If overlap is detected then the move is rolled back completely leaving the system in its original state

#### 2.2.3 Rotational moves

In the most common MC simulations particles are used that are rotationally symmetric. We also work with non symmetric particles that consist out of multiple hard spheres. These non-symmetric particles are not just represented by a location and a radius but we add an orientation vector  $(\vec{O})$  to the data set that we can use to rotate the particle in all directions. To perform the rotations quaternions are used. We do not give a complete explanation of how quaternions work but we do give a short overview. A random angle  $(0 \le \alpha \le \frac{\pi}{2})$  is generated as well as a vector on the unit sphere  $(\vec{k} = x, y, z)$ . A four dimensional vector is created by normalising  $\vec{k}, u$  with  $u = \cos \frac{\alpha}{2}$ . Then  $\vec{O}$  is rotated via the matrix multiplication  $\vec{O} \to \mathbf{R}\vec{O}$  with R given by

$$\mathbf{R} = \left\{ \begin{array}{cccc} x^2 + y^2 - z^2 - u^2 & 2yz - 2xu & 2xz + 2yu \\ 2xu + 2xz & x^2 - y^2 + z^2 - u^2 & 2zu - 2xy \\ 2xu - 2xz & 2xy + 2zu & x^2 - y^2 - z^2 + u^2 \end{array} \right\}$$
(2.3)

. After the particle has been rotated we check for overlap. If necessary we undo the rotation by replacing u by -u and redoing the matrix multiplication.

Another method that was tried involved picking a random vector on the unit sphere and rotating the dumbbell around it by a random angle smaller then  $\pi$ . Quaternion rotations where chosen as they don't rely on trigonometric equations which are processor heavy.

#### 2.2.4 Variable box shapes

In some situations we change the box shape as well as the volume. Volume moves are not made along the normal basis vectors  $\vec{e_1}, \vec{e_2}$  and  $\vec{e_3}$  (Basis A). To achieve a box with a non cubic shape we make basis transformations. This allows for a large degree of freedom in bounding box shapes and sizes.



Figure 2.2: vectors that span the box are no longer of standard size and direction. The Basis changes from A to B or  $\vec{e_1}, \vec{e_2}, \vec{e_3} \rightarrow \vec{V_1}, \vec{V_2}, \vec{V_3}$ . This allows non-cubic crystalls to form

The starting configuration is always in a cubic box spanned by the cartesian unit vectors. Now every time a volume move is called, a small random real is generated and added to a randomly picked entry of the basis matrix. The volume of the new box is then calculated and if the new volume is energetically viable (eq. 2.2 returns false) and does not create any overlap it is accepted.

One of the difficulties with a shape changing box is that it has the tendency to collapse ( $\vec{V_3}$  tends to end up in the plane spanned by  $\vec{V_1}$  and  $\vec{V_2}$ ). This is prohibited in the following way: If a move is made sending  $\vec{V_3} \rightarrow \vec{V_{3'}}$  then the angle between  $\vec{V_{3'}}$  and  $\vec{V_1} \times \vec{V_2}$  should be smaller then  $\frac{\pi}{4}$  or the move is not accepted.

With the new set of basis vectors it is difficult (and expensive in computational time) to check if a particle is moved outside of the box. The particle coordinates are stored as cartesian coordinates with standard basis vectors. For a given particle move we need to check if the move is within the box. If it moves outside of the box the program must calculate where the particle will reenter the box. In a square box this is trivial. In the new non-cubic box the best option would be to change the basis of the particle coordinates  $(\vec{e_1}, \vec{e_2}, \vec{e_3}) \rightarrow (\vec{V_1}, \vec{V_2}, \vec{V_3})$   $(A \Rightarrow B)$ . If the new particle coordinates lie between 0 and 1 the particle is within the bounding box. If it was moved outside of the box 1 can be added or subtracted from that particular coordinate making the particle reenter on the other side. Now the 'out of the box' problem is solved. There is no more need to transform all of the particle coordinates at this point because all of the dumbbell coordinates remain unchanged in B.

The next problem is that of particle overlap. We cannot calculate the real space distance between two dumbbells using their coordinates in B. It is possible to calculate real space coordinates every time they are needed. It is easier to store the dumbbell coordinates in A as well as in B making them immediately available when needed. Storing a double set of coordinates is expensive but since the number of particles were using ( $\leq 4$ ) it is still not as heavy on the memory as the larger simulations.

#### 2.2.5 Cell lists

Cell lists are a method of making a MC simulation run faster. They do this by eliminating the need to do overlap checks when this is not necessary. Because we are working with many particle systems with different shapes that will be heavy on processing power we will use cell lists to speed up the simulation.

The box is divided into cells. These cells are as small as possible, but large enough so that a particle in one cell can only overlap with particles in a cell that is adjacent to the original cell. By keeping track of in which cell every particle is, we can perform an overlap check with those particles in the original cell and the cells that surround it. The cell lists create a lot of overhead and become effective for systems where  $N_{part} > 150$ . The runtime of a simulation without cell lists scales as  $t_{run} \sim N_{part}^2$  by adding cell lists we get  $t_{run} \sim N_{part} \ln(N_{part})$ .



Figure 2.3: On the left we need to check for overlap with all particles. On the right we use cell lists to loop only over the particles that are in the vicinity

# Basic hard sphere simulation

In this chapter we discuss a MC simulation for hard spheres. A basic Monte Carlo (MC) code is described that is used used as a starting point for the other more complex simulations that we need for the asymmetric particles. Slight alterations can be made to do a specific measurement, but the general workings of the program remains the same in all cases.

Throughout the course of the entire project NPT simulations were used. This means that during a simulation the number of particles(N) as well as the pressure(P) and temperature (T) were kept constant during runtime. The volume is allowed to change.

#### **3.1** Equation of state for hard spheres

The hard sphere (hs) system has been significantly examined in the past and analytical approximations are known. We start out with a basic system as it will be easy to compare the measured data with other results known to be correct. We examine the density at different pressures to test wether the results are correct for hard spheres. These densities are known from the Carnahan Starling equation of state for (fluid) hard sphere systems<sup>[5]</sup> given by:

$$P(\eta) = \eta \frac{6}{\pi} \frac{1 + \eta + \eta^2 - \eta^3}{1 - \eta^3},$$
(3.1)

where  $\eta$  is the packing fraction .This equation has been analytically obtained and is widely used and accepted as correctly describing a hard sphere fluid. A certain density  $\eta$  is linked to a certain pressure P. A plot of eq. 3.1 is shown in figure 3.3

#### **3.2** H.S. Monte Carlo simulation

For this simulation we used a large system of  $N_{part} = 200$  and a traditional square box. The first  $2 \times 10^5$  cycles of the simulation were be used to equilibrate the system. In fig. 3.2 we show the progression of the number density as a



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Figure 3.1: The Number density  $(\rho_N)$  will fluctuate during the equilibration period.

function of the length of the simulation (MC steps). From the plot we can see that after about  $1*10^5$  cycles the density stops increasing and starts to fluctuate around some mean value.

During the equilibration time of  $2 \times 10^5$  cycles the maximum particle and volume stepsizes are tuned to make sure a predetermined fraction of the attempted moves are accepted. After the equilibration stage the acceptance ratio for particle moves  $(r_{part} = \frac{accept}{reject})$  will be  $0.50 \pm 0.05$ . For the volume moves, the acceptance ratio  $r_{Vol}$  is tuned to be  $0.30 \pm 0.05$ . The fluctuations in the stepsize can be seen in figure 3.2.

After the equilibration cycles are completed the MC sampling begins. During this part we measure the number density of the system. The maximum volume and particle stepsizes are kept constant during this stage. The length of the MC sampling is generally, but not necessarily, the same as the equilibration. After the MC cycles are finished the data is saved.

After a Monte Carlo simulation of the system has completed to run at a pressure P we take the resulting configuration and use it to start a new simulation at higher pressure. Doing this for  $P = \beta p \sigma^3 = 1, 2, 3, ..., 19, 20$  we can save a lot of equilibration time because the system is at equilibrium for the previous (slightly lower) pressure<sup>1</sup>.

#### 3.3 Results for hard spheres

Our original configuration, displayed in fig. 3.3, melts immediately at small P as soon as we start the simulation. If we then slowly increase the pressure, the system will freeze at P > 12 (see fig. 3.3). This is consistent with the value presented by Frenkel and Smit<sup>[4]</sup> who tell us that for the hard spheres there is bulk coexistence of solid and liquid at P = 11.70

 $<sup>^{1}</sup>$ It is important to understand that the pressure during the simulation is always constant (NPT). It is when a simulation is complete that we increase the pressure



Figure 3.2: Acceptance ratio for the particle moves(orange) and the volume moves(green). The the stepsizes are changed during equilibration. If too many moves are accepted the moves are made bigger and vice versa.

By slowly increasing the pressure we can go from a starting configuration seen in fig. 3.3 at P = 0 to the end configuration at P = 29 from fig. 3.3. At pressures lower than 12 we have a fluid that is seen in the first picture of fig. 3.3 that at higher pressures the system freezes.

The density we observe at each pressure is compared to values given by the Carnahan starling equation of state (eq. 3.1)) where  $\eta$  denotes the packing fraction. If we plot this equation along with the pressures found in the simulations we obtain fig. 3.3 which confirms the measured data. At a pressure of about 13 the density starts to deviate from the predicted value from the Carnahan Starling equation for a hard sphere fluid. This means that the system is crystalline (in some regions) and eq. 3.1 does not hold anymore.



Figure 3.3: A typical start configuration of  $N_{part} = 250$  hard spheres for P = 0



Figure 3.4: The same hard sphere system as in fig. 3.3 now at P = 3 (a). It is much denser but there are no crystal symmetries visible. At P=13 (b) the system starts to crystallise and at P=29 (c) the system is almost completely crystalline (FCC)



Figure 3.5: A Plot of the Carnahan Starling equation (solid line) for hard spheres in a fluid state (3.1) along with the simulation results (circles). There is a sudden shift in packing fraction obtained from the simulations (around P = 15) due to crystallisation.

## Simple Dumbbells

Previously the hard spheres were represented by their coordinates in space and their radius. The dumbbells in the following chapters will also be represented by their location and radius but an extra vector is added that will store the orientation of the particle. This means a large increase of memory usage of the simulation program. The rotations are made around the centre of mass (B in fig 4). Variations were tried where rotations were made at A or D but these were inefficient for certain sizes ratios( $\frac{\sigma_L}{\sigma_s}$ ). If we rotate around A and  $\sigma_L \simeq \sigma_s$  then such a long tail will prohibit many rotational moves. The same is true when we rotate around c if  $\sigma_L \ll \sigma_s$ 

All of the extra calculations that need to be made due to the dumbbell shape of the particles make for a noticeable increase in runtime.

#### 4.1 Equation of state for dumbbells

Similarly as for the H.S. simulations described in the previous chapter, we compare the equation of state we determine numerically with an analytical equation of state. The equation of state for dumbbell fluids was derived by Tildesley et



Figure 4.1: The location and orientation of the dumbbell is stored. In this chapter we use simple dumbbells with  $\sigma_1 = \sigma_2$ 

 $al^{[1]}$  and is given by:

$$\frac{P}{\rho kT} = \frac{1 + F(l^*)\eta + G(l^*)\eta^2 - H(l^*)\eta^3}{(1 - \eta)^3}.$$
(4.1)

Where F,G and H are polynomial functions of  $l^*$  which is the elongation of the dumbbells (or the distance between the two hard spheres that form it). When the two dumbbell spheres overlap completely  $l^*=0$  and eq. 4.1 reduces to eq. 3.1. Tildesley used overlapping dumbbells of equal diameters( $\sigma$ ) and a varying distance (l) between the centres of the particles such that  $l^* = \frac{l}{\sigma}$ . Since our dumbbell particles are touching at the surface we have  $l^* = 1$  for  $\sigma_1 = \sigma_2 = 1$ . It has been shown<sup>[1]</sup> by means of simulations that F,G and K can be represented by:

$$F(l^*) = 1 + Ul^* + Vl^{*3}, (4.2)$$

$$G(l^*) = 1 + Wl^* + Xl^{*3}, (4.3)$$

$$H(l^*) = 1 + Yl^* + Zl^{*3}.$$
(4.4)

In the situation where  $l^* = 1$  and the radii of the dumbbell spheres are equal the values U,V,W,X,Y and Z are known and can be used to determine the density as a function of pressure for a dumbbell system with symmetric dumbbells.

#### 4.2 Simple dumbbell results

A simulation is performed with a system of 200 dumbbell particles in a square box for P = 5, 6, ..., 49, 50. Cell lists are used to decrease runtime. The predictions made with equation 4.1 are compared with the measured densities in figure 4.2. The theoretical predictions confirm the data in the left region of the plot but at a pressure of about 24 there is crystallisation of (part of) the system. Some snapshots of the system seen in figures 4.3 to 4.5 show the critical points in the crystallisation process.



Figure 4.2: The equation of state confirms the measured densities. There is crystallisation visible in this plot around P = 23.



Figure 4.3: At P = 18 the system is still in a dense fluid state.



Figure 4.4: At P = 23 some symmetries are visible. Crystallisation has started



Figure 4.5: This is the system at a pressure of 4000 which is the result of a big pressure step that is taken at the end of the simulation. This large step makes the system as dense as possible. In the lower left part of the image we can still see a fluid but the major part of the system is frozen.

## **Crystal structures**

Until now all of the presented results have come from large systems. The focus has been on the equation of state and in order to get good data on these variables we needed large systems of  $N_{part} \ge 200$ . We have seen crystallisation happen in (parts of)the large systems but it did not happen uniformly throughout the entire system. If we want to see uniform crystallisation we will need to look at smaller systems. Small systems of  $N_{part} = 2, 3, 4$  will crystallise easier and uniformly.

#### 5.1 Binary crystals

Because we want to see a large variety of crystals we will look at different size ratios  $(r = \frac{\sigma_s}{\sigma_L} = 0.3, 0.4, ..., 0.8, 0.9)$  and look at the resulting systems at high pressure and search for symmetries and known crystal structures. The crystal structures we might expect to see based on work done with binary hard sphere mixtures<sup>[2]</sup> with size ratios corresponding with the ones that are used are that of:

- NaCl
- CsCl
- $\alpha IrV$
- $\gamma$ CuTi
- $\bullet \ {\rm CrB}$

These solids will all form in binary systems with size ratios between 0.3 and 0.9 which is the range in which we were working.

#### 5.2 Crystal synthesis

The small simulations are performed without cell lists. The boxshape is variable as explained in section 2.2.4. In figures 5.2 to 5.2 some examples are shown of the crystal structures that where found and identified.



Figure 5.1: NaCl.  $P=4000, N_{part} = 2, r = 0.4$ 



Figure 5.2: CsCl.  $P=4000, N_{part} = 2, r = 0.8$ 



Figure 5.3:  $\alpha IrV. P=4000, N_{part} = 2, r = 0.9$ 



Figure 5.4:  $\gamma \mathit{CuTi.}$  P=4000,  $N_{part}=2,\,r=0.8$ 



Figure 5.5: NaCl.  $P=4000, N_{part} = 2, r = 0.6$ 

All of the crystals we were expecting to see were present. Multiple runs of the program were made at each size ratio and system size. Results from identical runs (but different random seeds) varied. With a two dumbbell system with a size ratio of 0.9 we have seen CrB, CsCl,  $\alpha$ IrV and  $\gamma$ CuTi being formed. The results of the 2,3 and 4 dumbbell simulations are shown in Table I-III. The high number of uncrystalline and unidentified results from the 3 and 4 dumbbell simulations is caused by the difficulty of a large system to crystallise.

Tal	bl	$\mathbf{e}$	Ι

			Tab	101					
$N_{part} = 2$									
r	0	1	2	3	4	5	6	7	8
0.3	NaCl	NaCl		NaCl		NaCl	NaCl	NaCl	
0.4		NaCl		NaCl	NaCl	NaCl			
0.5	CrB	CrB	CrB	CrB	NaCl	CrB	CrB	CrB	CrB
0.6	CrB	CrB	CrB	CrB	CsCl		CrB	CrB	
0.7		CrB	CrB		CrB				
0.8	CsCl	CsCl	$\gamma$ CuTi	CrB	CsCl	CsCl	CrB	CsCl	
0.9	CrB	$\alpha$ IrV	CsCl		$\alpha IrV$	$\gamma$ CuTi	CrB	CrB	

$N_{part} = 3$										
r	0	1	2	3	4	5	6	7	8	9
0.3	NaCl					NaCl			NaCl	
0.4	NaCl						NaCl	NaCl		
0.5										
0.6										
0.7	CsCl	CsCl	CsCl		CsCl					
0.8	CsCl		CsCl	$\alpha IrV$	$\alpha IrV$					
0.9							CsCl			

Table	Π

Table III										
$N_{part} = 4$										
r	0	1	2	3	4	5	6	7	8	9
0.3					NaCl	NaCl				
0.4			NaCl				NaCl		NaCl	
0.5	CrB				CrB			CrB	CrB	
0.6	CrB				CrB	CrB			CsCl	
0.7						$\gamma$ CuTi	CsCl		CsCl	
0.8	$\gamma$ CuTi	$\alpha$ IrV							$\alpha$ IrV	
0.9	$\gamma$ CuTi	$\gamma$ CuTi							$\alpha$ IrV	

It is important to achieve a close packing for these crystals. The space filling curve is shown in 5.2. Comparing the results to that of the same measurement for a AB hard-sphere mixture<sup>[2]</sup> we can conclude that similar (but a less dense) filling is achieved with a dumbbell system. Longer measurements at smaller size ratio intervals may yield closer packed results.



Figure 5.6: (a) The space filling curve for the obtained crystal structures with dumbbells. (b) Space filling curves for the same crystal structures with hard spheres made by L. Filion and M. Dijkstra<sup>[2]</sup>

#### 5.3 Fit to the equation of state

For all of the size ratios we have also performed a large simulation with 250 dumbbells in a square box. From these simulations we get the densities of those systems. The orange points in the figures in 5.3 show the density of the system when we slowly increase the pressure in the system. We fit equation 4.1 to the data that was taken to get approximated values for U, V, W, X, Y and Z for systems with  $\sigma_L \neq \sigma_s$ . If there is a point in the data which indicates (part) of the system has crystallised then the fit is made to the data before that particular point. This can is most appearant in the first plot of Fig. 5.3 where an obvious deviation between the data and fit occurs. Since all of the systems become crystalline at some pressure  $P \leq 20$  this gives us quite a narrow band of data to fit the equation of state to. This unfortunately results in a approximation that is not reliable for higher pressures. The values shown in table IV are useful only for low to medium high pressures ( $P \leq 18$ ).

TABLE IV

r	0.2	0.3	0.4	0.5	0.6	0.7	
U	-0.549251	-0.045433	0.212948	0.404096	0.0686448	0.048433	
V	-1.5257	-0.107534	0.434587	0.718393	0.00107258	0.0670353	
W	-11.6136	-11.6067	-10.0402	-8.27949	-0.00702141	-1.31118	
Х	-3.0757	-3.43399	-3.28315	-2.87658	-0.246037	0.771064	
Υ	-4.18089	-4.90383	-4.9197	-4.65721	-0.44937	-0.94733	
$\mathbf{Z}$	-8.54362	-8.12778	-6.7003	-5.11391	-0.00384433	1.06722	
r	0.8	0.9					
U	0.76361	-2.77823					
V	0.942729	-3.07837					
W	-1.09516	18.5367					
Х	1.45891	18.8495					
Υ	-0.887081	16.7294					
Ζ	1.80113	20.8859					



Figure 5.7: The density plots for r = 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9. Orange data was taken during pressure increase. Purple data is the decrease(or melting) of the system. The solid curve shows a fit of the data points where the system is still fluid.

CHAPTER 5. CRYSTAL STRUCTURES

## Crystal melting

Using the crystal structures obtained in Chapter 5 we now look at how these structures behave when they are slowly melting. We place copies of the crystal coordinates we found in the previous section next to each other until we have a large crystalline system of exactly N = 200. This large crystalline system is now put through the MC routine starting at a high pressure and decreasing it by steps of 1 (P = 30, 29, ...). We are interested in seeing how and where it melts. Due to the fact that we build a large system from non-cubic crystals the box we use is also non-cubic. Cell lists are used.

#### 6.1 Rotator phases

As we lower the pressure in the system it becomes less dense and eventually the perfect crystal we started with melts. In a traditional binary system the smaller particles are expected to melt before the large particles. Fig. 6.1 shows an image where the larger particles are still placed on a square lattice but the smaller particles are free to move around(the dumbells are rotating in their place).

It is expected to only see a rotator phase for dumbbell systems with a small size ratio. The smaller secondary particles will move around easier without



Figure 6.1: In the rotator phase the large part of the dumbbells are still crystalline while the small ones are melted.



Figure 6.2: Three stages from the process of melting a NaCl crystal(r = 0.4). (a) Start at P=30 with a perfect NaCl crystal. (b) Shows the system in a rotator phase(P = 25). The larger spheres are still crystalline but the small spheres are melted. (c) The system has become fluid at a pressure of 19.(The particles are shrunk to improve the view into the system)

creating overlaps. Some images of melting crystals are shown in figs. 6.1, 6.1 and 6.1. The rotator phase seen in the NaCl system is prominently present. The smaller parts of the dumbbell particles melt at P = 27 and are later followed by the larger spheres at P = 21. The  $\gamma$ CuTi and CrB systems with respective size ratios of 0.8 and 0.6 do not show any hint of a rotator phase. At a pressure of 14 we still have a sloppy  $\gamma$ CuTi crystal which is completely melted at 13. The same happens with CrB going from  $P = 19 \rightarrow 18$ . It is not surprising that the same happens when we melt a bcc system (not pictured) consisting of dumbbell particles with a size ratio of 1. The bcc system stays crystalline until it reaches a pressure of 8 where it becomes a fluid.

We see that an increase in size ratio leads to a lower melting pressure which is not surprising. It is also apparent that as expected only systems with a small size ratio show a lengthy rotator phase.

#### 6.2 Recrystallisation

The large systems we have worked with before had tendencies to freeze without forming a crystal. It was attempted to form crystals using the completely fluid systems from the last section and slowly increase the pressure. We still have  $N_{part} = 200$  and a starting pressure (P) just below the melting pressure for the particular crystal we are trying to recrystallise. If the system we are working with used to be a NaCl type crystal we take use P=17, 18, 19, ..., 30. We gave



Figure 6.3: The CrB crystal (r=0.6) does not go through a rotator phase as it melts. In (a) we see a ordered crystalline system at a pressure of 19. (b) Shows the same system at p = 18 it has completely melted.



Figure 6.4: The  $\gamma$  CuTi crystal (r=0.8) does not go through a rotator phase as it melts. In (a) we see a ordered crystalline system at a pressure of 14. (b) Shows the same system at p = 13 it has completely melted.

the particles a brownian like motion by limiting the stepsizes by a small value of  $0.01R_{part}$  for particle and volume steps that remained unchanged during the entire simulation of  $4 \times 10^5$ . Other parameters where equal to that of the previous section. By increasing the pressure on the system and keeping the stepsizes small we hoped to recreate the crystall structures that were melted. Unfortunately this did not work. All of systems with size ratio's between 0.3-0.9 froze without forming a crystall.

## Colloidal cluster particles

In this chapter we extend our method for predicting crystal structures to systems consisting of small colloidal clusters. These types of clusters have been created and are studied by Manoharan, Elsesser and Pine<sup>[3]</sup>. By using a location and orientation method to represent particles in our code it is possible to take any particle consisting of a number of hard spheres and use it in a MC simulation. In this chapter only a few examples will be used which are shown in figure 7. These shapes consist of colloids of equal radii but different radii could be used if nescessary.

#### 7.1 Equation of state for C.C. particles

As with the dumbbell particles we perform MC simulations (with cell lists) on a large system of  $N_{part} = 100$  in a cubic box and look at the systems densities for different pressures. The reason we only use 100 particles instead of the usual 200 is because of the memory usage and computational time increase that comes with the usage of particles consisting of 4 or 5 hard spheres. For these large systems we do not have an equation of state to tell us how they should behave. This perhaps makes this section title misleading.

Only the octahedron system becomes crystalline (fig. 7.1) and does so quite nicely. The other systems remain fluid within this pressure range.

#### 7.2 Colloidal cluster crystals

As in chapter 5 we perform MC simulations on a small number of particles  $(N_{part} = 2)$  to look for possible crystal structures. Basis transformations are used as volume moves. We look at the two particle system by visualising some of their nearest neighbours from surrounding boxes making it easier to identify crystal structures. The images shown in this section use shrunken spheres to improve visability of lower lying crystal layers. We will examine the systems as if they consisted out of individual hard spheres.

Due to the limited number of simulations that were made for these colloidal cluster particle systems<sup>1</sup> we can not use the results to draw qualitative conclusions

 $<sup>^1\</sup>mathrm{The}$  runtime of the simulation proved to be too long to perform a large number of simulations. 3 where made.



Figure 7.1: The shapes that where where put through the MC program. (a) tetrahedron. (b) octahedron. (c) pyramid. (d) dipyramid



Figure 7.2: Some of the colloidal cluster particles made by Manoharan, Elsesser and Pine<sup>[3]</sup> some of which (the three particles on the top right) have been simulated



Figure 7.3: The number densities for a small range of pressures for (a) tetrahedron, (b) octahedron, (c) pyramid and (d) dipyramid. All in a square box containing 100 particles. We see a large and sudden density increase in the tetrahedron system where crystallization occurs this crystalline system can be seen in fig. 7.1.



Figure 7.4: The octahedron system has formed a hexagonal crystal structure.



Figure 7.5: bcc (a) and hcp (b) structured crystals formed from octahedron shaped particles.



Figure 7.6: fcc (a) and hcp (b) structured crystals formed from tetrahedron shaped particles.

from these measurements. The octahedron shaped particles were found to form bcc and hcp crystals (fig. 7.2) of which the bcc system had the closest packing. With the tetrahedron particles fcc and hcp crystals were formed(fig. 7.2) with fcc having the closer packing. Face centered cubic was also formed with the pyramid shaped particles. The pyramids have also formed some unidentified structures which are not shown. An interesting result is that of the dipyramid system. It formed the same unidentified crystal (fig. 7.2) structure every time.



Figure 7.7: Dipyramids formed a particularly strange crystal.

# Chapter 8 Conclusion

In this conclusion we will discuss our results and we will also give recommendations on future work in the area of dumbbell MC simulations. The main goal of this masters project was to investigate the behaviour of a variety of dumbbell particles and more complex colloidal cluster particles through computer simulation. Earlier results in this field have been confirmed and expanded where possible making this research's main objective achieved.

One of the more important results was that we were able to show that the behaviour of a dumbbell based system is similar to that of a binary mixture of hard spheres with identical size ratios. The crystals that formed with the hard sphere mixtures<sup>[2]</sup> are the same as the ones we have found for the dumbbell systems. We also found that the space filling curves for the crystals are very similar (fig. 5.2) which was not necessarily expected.

The fits to the equation of state is an importand result that can be used in further research. It should be noted that, as mentioned in Chapter 5, these fits are only made for a fluid in the lower pressure regions.

#### 8.1 Recommendations

To improve the results obtained in this project some improvements could be made that were not made by the author due to time limitations. The stepsize of the size ratios in the dumbbells that where used to create the crystal structures in Chapter 5 could be made smaller. The space filling curves from fig. 5.2 would be a lot more informative if they where based on more data points. If possible a stepsize of 0.25 would give better results. In the same chapter it would have been good to do more runs for each separate system leading to more crystalline results and possibly a higher packing fraction.

In Chapter 6, where we look for rotator phases in the crystals that were created earlier, only a small subset of the results was used. This demonstrated that rotator phases happened for the smaller size ratios but to draw qualitative conclusions about when and where they happen more measurements need to be performed.

The non dumbbell particles from chapter 7 require further research. A larger colloid placed in the centre of these particles will change the shape into another one that is also physically interesting to examine.

Overall it can be said that, by making the computer program that we used more efficient, more measurements can be made over a larger span of pressures. This will improve the results that were found.

## References

- 1. D.J. Tildesley, 1980, Molecular Physics, 41,85-94
- 2. L. Filion and M. Dijkstra, 2009, Physical review, 79
- 3. V.N. Manoharan, M.T. Elsesser, D.J. Pine, 2003, Science, 301, 483-487
- 4. Frenkel, Smit, 2002, Understanding Molecular Simulation
- K.F. Starling, K Carnahan, 1969, The journal of chemical physics, 51, 635-636