PHASE TRANSITIONS IN THE PLANAR HARD TRIANGLE SYSTEM

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SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR

THE DEGREE OF MASTER OF SCIENCE IN PHYSICS

AT

ADDIS ABABA UNIVERSITY, ADDIS ABABA, ETHIOPIA

FEBRUARY, 2020

ADDIS ABABA UNIVERSITY

COLLEGE OF NATURAL SCIENCES

DEPARTMENT OF PHYSICS

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Dated: February 2020

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Degree: M.Sc.

Convocation: February

Year: 2020

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Abstract

A 2D liquid crystal system composed of hard particles shows phase transitions as the pressure of the system varies. This fact was confirmed by different works done on 2D liquid crystal system different shapes. These works done on hard particles of different shapes confirmed that particles of different shapes show phase transition at different packing fractions. By understanding this idea, we are interested to study the phase transition of a system composed of hard triangles. We have considered NPT system with different number of particles and used Monte Carlo method to study the phase transition of the system. To study the phase transitions, we have considered the pressure, the radial distribution function and the mean square displacement of the particles at different packing fractions. All of these results have shown as there is phase transition at $\phi \approx 0.6$ and $\phi \approx 0.9$. The packing fraction at which the phase transition occurred didn't vary with size of the system which shown the phases are stable at the thermodynamic limit. As shown by previous work, if there is complete isotropic phase, the tetratic order parameter $s_4 = 0$ [20] but in our case the minimum value of tetratic order parameter was $s_4 \approx 0.41$ which shows the non-existence of complete isotropic phase for hard triangles. For a system of hard triangles, the phases observed during the phase transitions are: isotropic phase(when $\phi < 0.6$), tetratic phase (when $0.6 < \phi < 0.9$) and solid phase (when $\phi > 0.9$), and the plastic crystal wasn't observed.

Acknowledgments

First of all I want to give thank for my God for his help from the beginning to the end of this work. I would like to express my sincere thanks to my advisor and instructor Dr Tatek Yirgou for his guidance, assistance, supervision and contribution of valuable suggestions. His scientific excitement, integral view on research and overly enthusiasm, has made a deep impression on me. I would like to thank to all my friends for providing encouragement and support

Chapter 1

Introduction

A 2D liquid crystal system composed of hard particles shows phase transitions as the volume and/or the temperature of the system varies. This fact was confirmed by different works done on 2D liquid crystal system composed different shapes. One of these works was done by Wojciechowski et al on hard rectangles [27] in which they studied the phase transition of an NPT system composed of hard rectangular particles by using Monte Carlo method. By using computer simulation, they shown as there were phase transition from isotropic to tetratic phase (long range orientational order but short range translational order) at $\phi \approx 0.68$. The transition between the tetratic phase and isotropic fluid is either continuous (cusp-like) or weakly first order but they were unable to say anything about the stability of the tetratic phase at the thermodynamic limit. Similarly, Aleksandar et al [8] studied the phase transitions for an NVT system of hard dominos. In their work, they used Monte Carlo method to simulate the system in their consideration and observed as there is isotropic tetratic phase transitions at $\phi = 0.7$ and tetratic-square crystal at $\phi = 0.8$ and they have concluded that the tetratic phase of the system is stable. The phase transition in hard spheres was studied by different scholars [19, 1]. In a work by Ander et al [1], they used Molecular Dynamics method to simulate a system of hard sphere and shown as there is first order phase transition in the hard sphere system at packing fraction $\phi = 0.675$. Ryzhov et al have also studied the phase transition of hard sphere system and observed liquid phase transition and second phase transition corresponding to the liquid-gas transformation. In simulating all these hard particles and particles of other shapes, the hard particle model was used in different studies. As an example, for a system composed of hard spheres [15, 3], hard rectangles [14, 27, 8], hard rods [24, 23] and hard disks [10] they used hard particle model to simulate the systems. By knowing the phase transitions in 2D liquid crystal system of different shapes and following the recommendation given by Wojciechowski et al [27], we were initiated to study the phase transitions in a 2D liquid crystal system with triangular shaped particles.

In this work, we have studied the phase transitions of a 2D liquid crystal system composed of hard triangles by using Monte Carlo method. To simulate this system, we have used the concept of hard sphere model and related the concept of this model. We have used the hard triangle model in code written to perform expansion and compression of the NPT system we are considering. To observe the phase transitions, we have used reduced pressure (P/NKT), orientational order parameter and mean square displacement of the particles, and observed some results including the variation of pressure with the packing fraction which leads to the phase transitions which shown cusp near $\phi = 0.6$ and

change of slope near $\phi = 0.9$ as an indicator of isotropic-tetratic phase transition and tetratic-solid phase transitions respectively. To study the phase transitions, we haven't used only the relation between the packing fraction and reduced pressure rather we have also considered tetratic order parameter which almost doesn't vary with the variation of packing fraction for isotropic phase and solid phase but shows an exponential increase in the tetratic phase. Although tetratic phase is observed at intermediate densities, complete isotropic phase was not occurred. The minimum value for the tetratic order for hard equilateral triangles is $S_4 \approx 0.41$ which shows the non-existence of complete isotropic phase because of S_4 is equal to zero for complete isotropic phase [20]. We have also seen the radial distribution function which shown the particles have no translational ordering in the isotropic phase while the system has translational ordering for tetratic phase and solid phase. The data we gathered from the indicators of phase transitions, indicates the there were transitions at $\phi \approx 0.6$ and $\phi \approx 0.9$ and all of the information shown the phase transitions were at these packing fractions.

The most commonly known phases of matter are solid, liquid and gaseous state. But through computer simulation, other phases like tetratic phase (long-range orientational ordering along two perpendicular axes, but only short-range translational ordering) and plastic crystal (no-range orientational ordering along two perpendicular axes, but long-range translational order) are also some phases observed by computer simulation. Due to change of some macroscopic properties like pressure and temperature, there would be conversion between these states which is called phase transition. A crystal can melt by increasing the temperature beyond the melting temperature T_m at constant pressure or by decreasing pressure (or increasing packing fraction) at constant temperature. These two are well known methods to observe phase transitions.

Molec.	Bond	Transl.	Phase
—	—	—	isotropic liquid
X	—	—	molecular orient
—	X	—	bond-orient
X	X	—	tetratic
—	X	X	plastic (rotator) crystal
X	X	X	square crystal

Phase of the system of particles is determined by the average molecular order, the bond order and the translational order of the constituent particles of the system. Depending up on these properties, the phase of the system would be known [26].

Since we are considering NPT system, we have kept the system at constant temperature and varied the volume to study the phase transition. The other important thing is the search for continuous transitions between the disordered liquid and the ordered solid phase. In a previous work by Wojciechowski et al [27] on a system hard rectangular particles, they observed phase transition from isotropic to tetratic at $\phi \approx 0.7$. Our observations for the hard triangular system are relatively consistent with a continuous

phase transition from an isotropic to a tetratic liquid with quasi long-range tetratic order around packing fraction $\phi \approx 0.6$.

This thesis is organized as follows. In Chapter 2, the model we used to simulate the system in consideration would briefly be presented and the simulation technique we used in this work to get our results would be discussed in Chapter 3. Then, in Chapter 4, we present the results and discuss their physical meanings. By using the results presented in Chapter 4 as an input, we conclude the results Chapter 5.

Chapter 2

The Hard Particle Model

In simulating particles the interaction between the particles is the crucial information about the system. If the constituting particles of the system exert force on each other when they are not in contact, one of the soft particle model can be used depending up on the nature of the force between the particles. For example, if we are interested to simulate nucleons (protons and neutrons), we have to consider the nuclear force (some times called strong force) between the nucleons. On the other hand, if we are interested to study the macroscopic properties of system of charged particles, we have to use a model which consider the Coulomb force between the particles. Similarly, if we are interested to study the properties of objects of large mass (for example if we want to simulate the solar system), we have to consider the gravitational force within the system. In all such systems, the model chosen should take the interaction between the constituents in to consideration.

When we deal with hard particles, there is no interaction between the particles until they collide. As a result the model used for hard particles is different from the model used for soft particles and hard particle model is used for such particles. For hard particles, different models were introduced depending upon the nature and characteristics of the particle to be simulated. One of the most known model for hard particles is the hard sphere model which is used to simulate and study the macroscopic properties of a system composed of hard spheres. In this model the interaction potential is infinity if the distance from center to center between the particles is less than the radius of the spheres . Mathematically:

$$V = \infty, \text{ if } d < r$$

and

$$V = 0, \text{ if } d > r$$

where d is the distance between the spheres, r is the radius and V is the interaction potential.

The concept of hard sphere model was extended to hard cube [17], hard rods [11, 21], hard ellipse [6, 16]. Using this model, hard particles of different shapes were simulated and their properties were studied. One of these property is the phase transition from isotropic fluid to tetratic and from tetratic to solid phase is most known but not only the phase transitions also the behaviors of different phases were studied using the model [8]. By taking the ideas of previous works on hard particles of different shapes, we are

interested to use this model and study phase transition for a system composed of hard equilateral triangles.

By extending the concept of the hard sphere model, we understand that the state of overlap between the particles is the most important thing to know the interaction potential between the hard particles under consideration. For arbitrary particles, (let us call them i^{th} and j^{th} particles) the interaction potential is infinity, if the two particles overlap else there is no interaction between them [12]. Generally for particle of any shape, including hard triangles, the idea used in the hard sphere can be given by :

$$V = \infty, \text{ if there is overlap}$$

and

$$V = 0, \text{ if there is no overlap}$$

By using the above facts as reference, we can generalize their interaction. For any hard particles of any shape:

1. The force between two hard particles will be zero if the two particles doesn't overlap.
2. The force between them will be infinite if hard particles overlaps.

We have used this model to measure some properties which we want to obtain the phase of the system. The orientational order is one of the information used to know the phase of the system. We have used some techniques and equations to measure this quantity which included under section 2.2. The radial distribution and the packing fraction were also presented in section 2.3 and 2.4 respectively.

2.1 Pressure

Everything we use in our daily life is composed of microscopic particles. In order to use any thing existing in nature or man made, we have to know their macroscopic properties [18]. And one of the macroscopic property is pressure. Pressure is the ratio of the applied force to the area on which the force is applied. These force responsible for pressure might have different sources. Example of forces causing pressure in microscopic level are: interaction between the particles (molecules), the momentum transfer due to the existence thermal energy, the applied(external) force etc. To study the pressure and other macroscopic properties, we may use numerical method (computer simulation). Pressure have different equations by which we calculate it depending up on the microscopic constituents of the system of particles. It can be calculated analytically as well as numerically by computer simulation. Analytically, for ideal gases the pressure of the system will be obtained by using an equation, P = NKT/V while it has a form of $P = \rho gh$ at a depth h in a liquid of density ρ. For hard particles the pressure of the system is obtained by computer simulation. Similarly, it has a general equation $P/NKT = 1 + \frac{\phi\alpha}{2}$ [25]. Where, ϕ is the packing fraction and α is the rate at which the particles overlaps.

2.2 Orientational Order

The order metric of a given state of order parameter m is given by [20]:

$$Sm =< cos(m(\theta - \theta_0^{(m)})) >$$

Where $\theta_0^{(m)}$ is the orientational angle of the chosen particle, θ is the orientational angle of the particle with which orientational order is going to be calculated and m is the order parameter. For tetratic phase, m = 4 while m = 2 for nematic phase. The tetratic order metric measures how much the particles of the system are aligned with respect to the bi-director. For this phase, the bi-director is in the direction on which the particles of the system reaches close packing fraction.

Tetratic orientational order shows how much the particles of the system are aligned with respect to the bi-director. This property of the system helps us to understand the state (phase) of the system. For example if we consider isotropic phase, there is no long range orientational order but if we consider nematic, tetratic and solid phases there is long range orientational order. Thus, this property helps us to know the state of the system at any density (packing fraction) whether it is isotropic phase or not. By using other properties like tetratic order metric and the radial distribution functions. We can be able to decide the exact phase of the system at any density. This property is used as an input when we decide the phase of the system of particle by using numerical method(computer simulation). For example, in the case of tetratic phase, plastic crystal and the square crystal, these phase have bond oriented particles.

2.3 Radial Distribution Function

Radial distribution function is a measure of average density as a function of distance from some arbitrary origin [22] and it can provide information about dynamical change of structure, but not about transport properties (how fast atoms move). This function describe how (on average) atoms in a system are radially packed around each other. Particularly, effective way of describing the structure of disordered molecular systems (liquids)[5]. It is the probability of finding another molecule at a distance r from a given molecule [4].

Of the three states of matter, gases are the easiest to model because the constituent particles are so far apart on average that we can ignore inter-molecular interactions apart from during their brief collisions. While solids are arranged in a regular order, and for this reason we usually start a discussion of the solid state from the properties of regular solids. On the other hand, liquids show neither complete order nor complete disorder as a result it is much harder to model and study experimentally than gases and solids. The basis of this remark concerns a property called the radial distribution function $g(r)$ [9].

To obtain the radial distribution function of a given system we can choose some particle/molecule/atom randomly and we can draw two circles of radius r and $r + dr$ and count particles whose centers lies in the area covered by the circles.

Mathematically, it can be given by:

$$g(r)dr = \sum g_i(r)dr \tag{2.1}$$

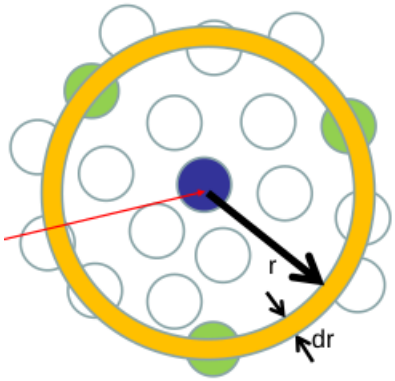


Figure 2.1: Radial distribution function[5]

It can also be defined as the ratio of the density of the atoms in the range r and $r + dr$ (local density) to the total density of the system(overall density). Mathematically

$$g(r)dr = \sum \frac{\rho(r)}{\rho}$$

The two equations have the same physical meaning as a result by using both equations we can obtain identical result. This process then has to be repeated for many complete shells over the range of values of r thought to be significant.

2.4 Packing Fraction

Packing fraction is the ratio of the original volume of the particles to the volume occupied. To clarify more, let us consider a system composed of N particles. Let the volume of a single particle be υ. The total volume occupied by these particles will be the number of particles times the volume of a single particle. Mathematically:

$$V_0 = N \times \upsilon$$

After some series of compression or expansion if the volume of the system is V, the packing fraction (ϕ) will be given by:

$$\phi = \frac{V_0}{V} \tag{2.2}$$

The maximum packing fraction of a system is known as close packing ϕ_c. For most of systems the close packing is less than 1 but in general the maximum value of ϕ_c is equal 1. For example for rectangles $\phi_c \approx 0.9934$ [8], $\phi_c \approx 0.82$ for sphere [2] while it is 0.907 for disks [13]. From this we can understand that the close packing fraction depends up on the shape of the particles constituting the system. In some cases the close packing fraction can even depend up on the system size and increase with the size of the system.

Chapter 3

Simulation Technique

In this chapter, the method used in this work is going to be discussed. Due to the temperature of the system, all of the microscopic particles constituting the system exhibit motion. The motion might be translational, rotational or vibrational(for lattice). By considering the above fact, in this work the random motion of the particles were done. A particle which is not attached to lattice can exhibit translational and rotational motion. The motion is led by thermal energy (E = kT, where k is Boltzmann's constant [k = 1.38×10^{-23}] and T is the temperature of the system). But this energy was occupied by the particle in the form of kinetic energy. The velocity of the particles due to thermal energy is random in direction which means the energy doesn't enforce the particles to move in some direction. Because of this, the probability of the particles to move in any direction will be equal. In addition to this, the probability of the motion to be translational and rotational motion is equal and we have taken this concept in to consideration.

We have implemented Monte Carlo method on (NPT) system with varying density by means of varying volume. Particles were represented by their centers (x,y), their vertices points named $(x_a(i), y_a(i))$, $(x_b(i), y_b)$ and $(x_c(i), y_c)$ and their orientational angle θ. During the Monte Carlo run, one particle was chosen randomly. Then, the selected particle was rotated or translated at random direction with equal probability to be rotational or translational. The maximum amplitudes of the x- and y-components of the translational displacements were equal to the maximal amplitude of the change of particle orientation (measured in radians). After each Monte Carlo (MC) step, check for overlap with the neighbors were taken place. To increase computational speed, identifying the near-neighbors of a given particle is the most important [7]. Thus, check for overlap was taken place for neighbors located within a radius of 1.2 times the length of the side of triangle (i.e for $r < 1.2 * l$). If there is overlap the trial move will be rejected else the position and orientation would be accepted and, the required macroscopic properties data were collected by numerical methods.

Since we were considering a system with variable volume, the change of volume were done through expansion and compression of the system. At the beginning, the particles were placed inside a two dimensional (2D) rectangle with a maximum packing fraction possible for equilateral triangles. Then, the system started to expand quasi-statically with change of the packing fraction $\triangle\ \phi$. To obtain the corresponding change of volume,

we can start from the definition of packing fraction given in equation [2.2].

$$\phi = \frac{V_0}{V} \tag{3.1}$$

Since V_0 is the total volume of all particles, it is constant. Thus, the change of packing fraction will obtained by change of volume of the system (V).

$$\phi + \triangle\ \phi = \frac{V_0}{V + \triangle\ V} \tag{3.2}$$

Let, $C = \frac{V+\triangle V}{V}$. Which means

$$V + \triangle\ V = C \times V$$

Thus,

$$\phi + \triangle\ \phi = \frac{1}{C}\frac{V_0}{V} \tag{3.3}$$

By using equation (3.1) in to equation (3.3) we get:

$$\phi + \triangle\ \phi = \frac{\phi}{C} \tag{3.4}$$

By rearranging equation (3.4) we get,

$$C = \frac{\phi}{\phi + \triangle\ \phi} \tag{3.5}$$

Let, l_x and l_y be the width and the height of the system. Thus, the volume will be: $V = l_x \times l_y$.

$$V + \triangle\ V = C \times l_x \times l_y \tag{3.6}$$

When the system is resized, l_x and l_y will be resized with equal proportion. Which means, when the system volume is changed by C, the length and the width of the system will be resized by $\sqrt{C}$ and the particles position can also be resized by $\sqrt{C}$. Which means the rate at which the volume resized is

$$C \times V = \sqrt{C}l_x \times \sqrt{C}l_y = \Lambda l_x \times \Lambda l_y$$

Λ is the rate at which the particle's position is changed. Which implies,

$$C \times V = \Lambda^2 l_x \times l_y = \Lambda^2 V \tag{3.7}$$

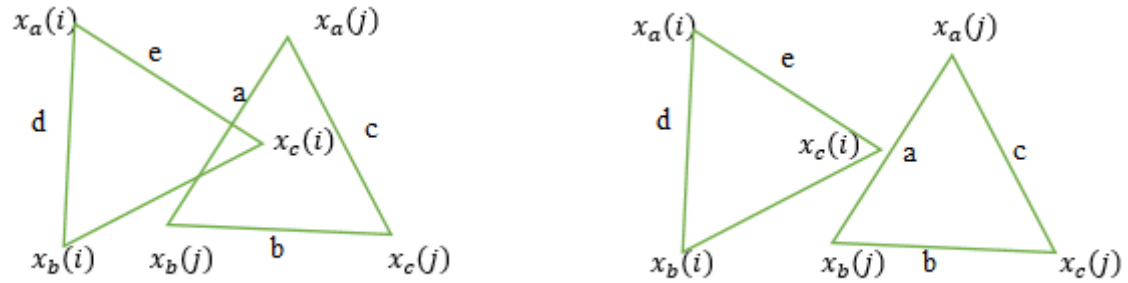
By using equation (3.5) and equation (3.7), we can relate the rate of change of position of particles in terms of the change of the packing fraction.

$$\Lambda = \sqrt{\frac{\phi}{\phi + \triangle\ \phi}} \tag{3.8}$$

When ϕ is change by $\triangle\ \phi$ particles position is resized by $\sqrt{\frac{\phi}{\phi+\triangle\phi}}$. The successful expansion of the system were followed by 15 Monte Carlo (MC) step per particles with check of overlap after each steps. Completing all MC steps, the required macroscopic quantities were calculated and the system was expanded again. This process is repeated until the packing fraction becomes less than or equal to ϕ_{min} (ϕ_{min} is packing fraction in the isotropic phase so that there is no phase transition below this packing fraction). As the expansion is completed, the final position and orientational angle were written in some file to be read at the beginning of the compression process.

During the compression process, the packing fraction were slightly changed by $\triangle\ \phi = -1 \times 10^{-4}$ and the particle's new position were obtained in the manner discussed above. And the new position were taken as temporary position and overlap were checked. If there is no overlap, the position would be taken, else the temporary position were rejected and new position were generated by dividing the previous $\triangle\ \phi$ by 2. Then 15 MC step per particle were taken place and the compression of the system continued until ϕ reach the close packing fraction. This process takes more computation time than expansion process because of there was no overlap on the expansion but in compression. Specially, as ϕ increases $\triangle\ \phi$ should be decreased this is why compression takes more computation time near the close packing.

As stated above, after each MC step overlap test takes place. Assume the i^{th} particle is either displaced or rotated. Instead of checking overlap of this triangle with the rest N-1 particles, we can check only for triangles within radius of $1.2 \times l$ from this i^{th} particle. Let us choose the j^{th} from the N-1 particles whether the particle overlaps with the i^{th} or not. In this test, the vertices of the particles used to generate three (3) equation of lines; which pass through the vertices. Thus, while the check for overlap between two triangles, we can have three lines for one triangle and three for the neighbor particle. Which means we can have nine (9) combinations to be checked during the overlap test. Assume we are going to check the test for a side ($x_a(i)$,$y_a(i)$) and ($x_b(i)$,$y_b(i)$) with one of the side of the neighbor triangle.



(a) (b)

Figure 3.1: The state of overlap of two equilateral triangles. (a) As clearly seen, the two triangles overlaps. (b) There is no overlap between the two triangles even if they are close to each other.

To check for overlap between the two triangles, we can take each sides and check whether it overlaps with each sides of the neighbor triangle. Let us check if the side 'e' of the i^{th} particle overlaps with side 'b' of the j^{th} particle. We can take $((x_a(i) + x_c(i))/2, (y_a(i) + y_c(i))/2)$ as reference point and $((x_a(j) + x_b(j))/2, (y_a(j) + y_b(j))/2)$ from the chosen neighbor. To check for overlap we use an equation :

$$\epsilon = \sqrt{(x_a(i) + x_c(i))/2 - x_{int})^2 + [(y_a(i) + y_c(i))/2 - y_{int}]^2}$$

$$f = \sqrt{(x_a(j) + x_b(j))/2 - x_{int})^2 + [(y_a(j) + y_b(j))/2 - y_{int}]^2}$$

where
ϵ is the distance of point of overlap of the chosen sides of the overlap from the midpoint

of chosen side of the i^{th} triangle, f is the distance of point of overlap of the chosen sides of the overlap from the midpoint of chosen side of the j^{th} triangle ,

$$x_{int} = \frac{y_a(j) - y_a(i) - m_{n1}x_a(j) + m_1 x_a(i)}{m_1 - m_{n1}}$$

and

$$y_{int} = m_1(x_{int} - x_a(i))$$

The expression of m_1 and m_{n1} is given in Chapter 6.
We can do the same thing for all chosen side of the j^{th} particle. If the calculated value of $\epsilon < l/2$ and $f < l/2$ the two particles overlaps. But if $\epsilon > l/2$ and $f < l/2$ for the other, there is no overlap. Similarly, to find the point of intersection for all possible combinations of the lines and evaluate f and ϵ to check for overlaps. Generally, if the point at which the lines intersect from $((x_i + x_j)/2, (y_i + y_j)/2)$ (Here, i and j specify the vertices) from both triangles, is less than $l/2$ the two triangles overlap else there is no overlap.

Chapter 4

Result and Discussion

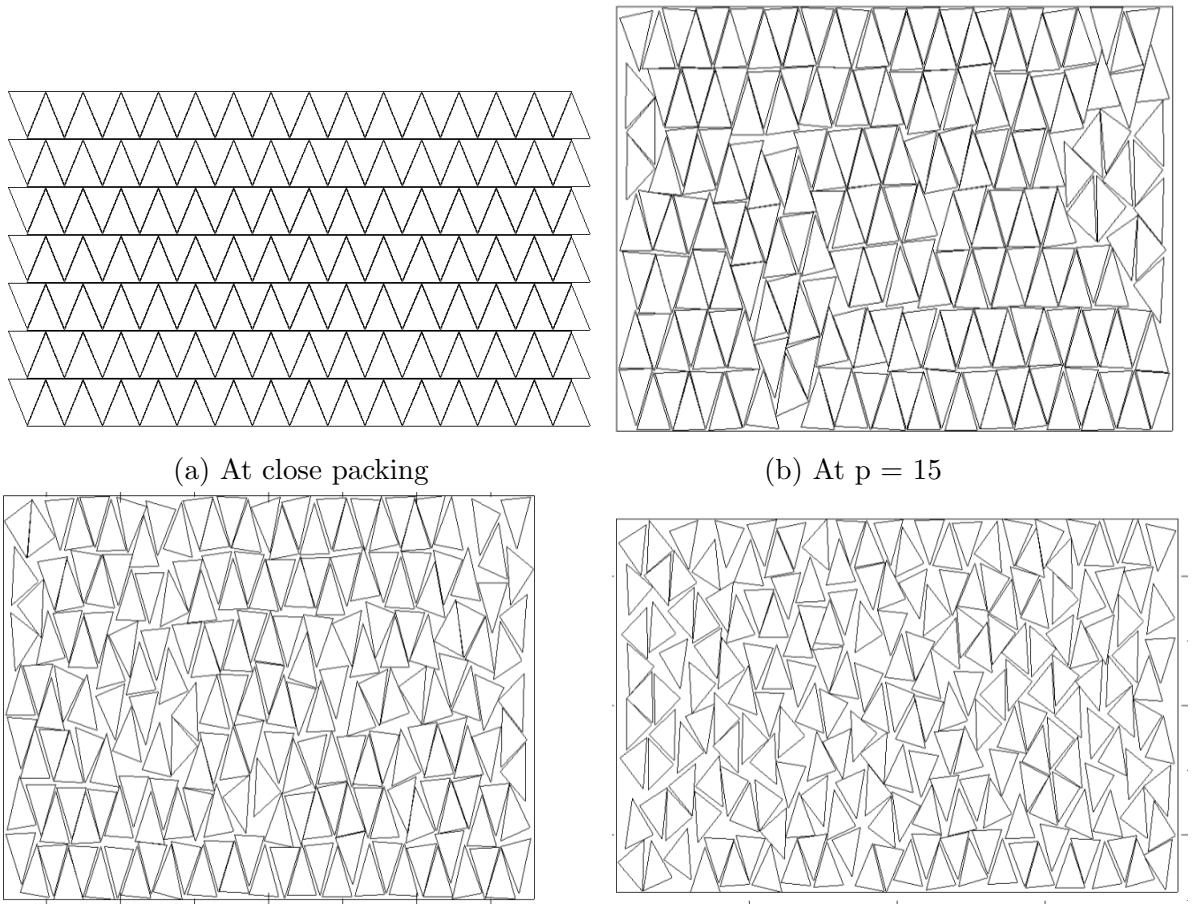
In this section we are going to discuss the result of simulation done on the system composed of hard triangles. The simulation has done for a system composed of different number of particles. We have used a system composed of N = 200, N = 700, N = 2500 and N = 6000 triangular particles to check whether the macroscopic properties and/or the phase transitions depend on the system size or not.Through computer simulation, different results were obtained. In this section we are going to present them and discuss their physical meanings. In this work, some unusual results were obtained so we have tried to explain their physical meaning as much as we can.

4.1 Pressure

Pressure is one of the most important macroscopic property in physics because of its applications in the real world. Due to its importance we are interested to deal the pressure of hard particle system we are considering. In studying this property we have considered system of particle with different number of particles; N = 200, N = 700, N = 2500 and N = 6000 and we are going to present observations in an organized manner and, discuss their physical meanings and evaluated the pressure of the system at different packing fractions by using $P/NKT = 1 + \frac{\phi\alpha}{2}$ [25]. Where, ϕ is the packing fraction and α is the rate at which the particles overlap.

It is obvious as pressure has effect on the orientation of particles. That is why we are interested to observe its effect on the system of particle we are considering. As the pressure varies the translational order also changes. As seen from the results, as the pressure increases the orientational correlation and the translational ordering of the particles increases and vice versa. This means the variation of pressure results in the phase change. Through the phase change(transition) we can get the tetratic phase which we are interested to deal with. The snapshots at different pressure for N = 200 particles is shown below.

As pressure decreases the volume of the system increases which results in the existence of additional space to be occupied by the particles. Due to this free space, the probability of the particle to be orientationally as well as translationally to be disordered would be increased. This result tells us something about the relation between the orientation of the particles and the corresponding pressure which completely agrees with the result obtained previously. To clarify our results, it is better if we see the relation between the pressure and packing fraction.



(a) At close packing

(b) At p = 15

(c) At p = 9

(d) At p = 6

Figure 4.1: The orientation of the system at different pressure. (a) The system was at close packing. As seen from the figure, all the particles are orientationally and translationally ordered which means the system is in solid phase at this packing fraction. (b) At this pressure, the particles are disordered. The translational ordering and the orientational ordering is less than the values at close packing. The particles are more disordered as the pressure decreased. Thus, the orientational ordering in (c) is less than for pressure p = 15 while the system shows the most disordering in (d).

As the volume of the system expands, packing fraction and the pressure of the system decreases and phase transition occurs. At the phase transitions the graph of reduced pressure versus the packing fraction shows cusp. For hard rectangles the cusp was observed at $\phi \approx 0.7$ but in our case (for hard equilateral triangle) the cusp was obtained at $\phi \approx 0.6$ which implies there is phase transition from tetratic phase (with long-range orientational ordering and short-range translational ordering) to isotropic liquid and the graph shows slight bending around $\phi = 0.9$ which shows another phase transition from tetratic to solid. In these transitions hysteresis was not observed which means the transitions were continuous.

Simply by observing the relation between the reduced pressure (P/NKT) and the packing fraction for different system size, we understood that the phase transitions both solid - tetratic and the tetratic-isotropic have the same behavior. Which means the packing fraction at which the phase transitions observed doesn't vary with the number of par-

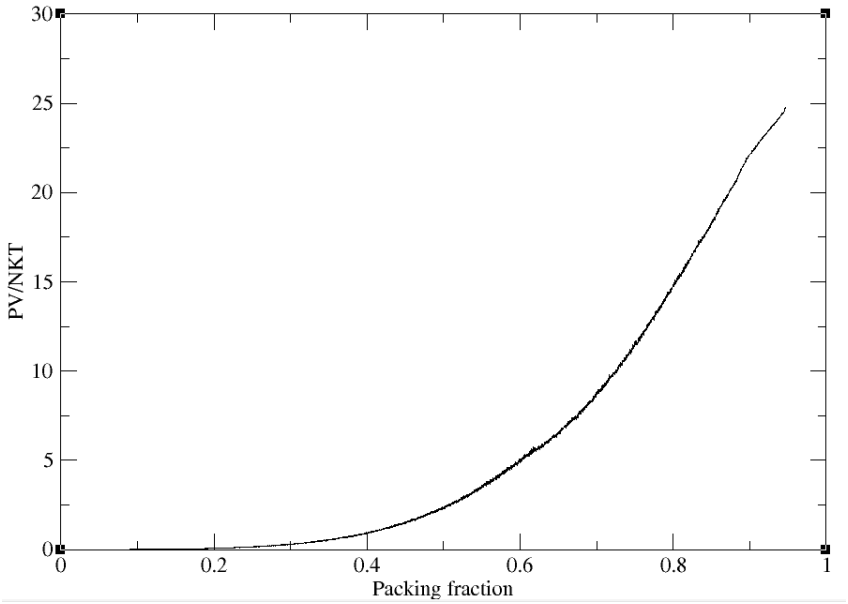


Figure 4.2: This shows the variation of pressure as a function of the packing fraction. As clearly seen, there is cusp near $\phi \approx 0.6$ which shows there is phase transition at this packing fraction and there is slight bending at $\phi \approx 0.9$.

ticles of the system. For N = 700, N = 2500 and N = 6000 the phase transitions were observed at the same packing fractions. Taking these facts as an input we were able to say something about the stability of the tetratic phase at the thermodynamic limit. The tetratic phase for system of hard triangles is stable.

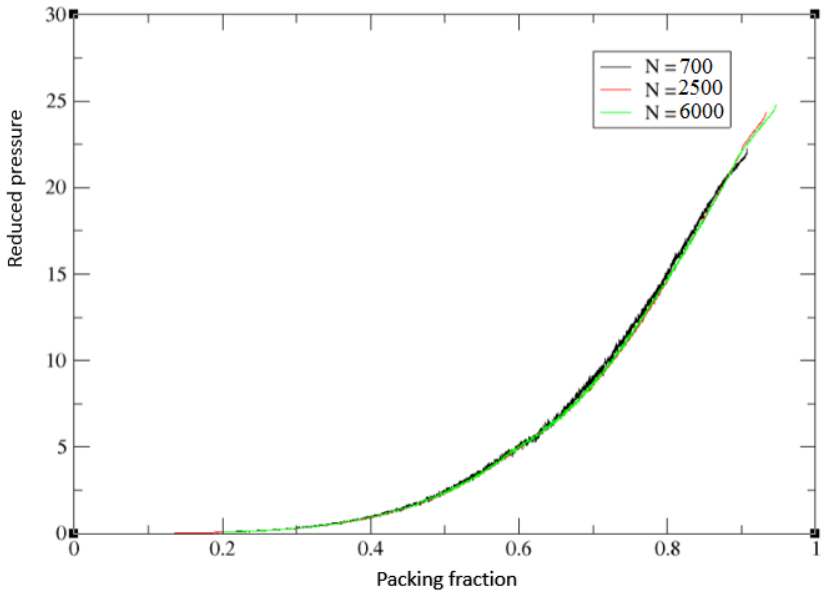


Figure 4.3: The graph of the reduced pressure versus packing fraction (ϕ for a system composed of 700(black color), 2500 (the red one) and 6000(the green line)). The graphs almost overlaps for any number of particles. This clearly shows the independence of the phase transition on the system size but for N = 700, the maximum packing fraction was 0.9 while it is greater for the larger system which shows the system size dependence of the close packing fraction.

4.2 Angular distribution

The angular distribution shows the probability of the particles to have a given angle θ. The angular distribution function can vary depending up on the packing fraction and pressure of the system. Here are some snapshot of the angular distribution of the system at different pressures.

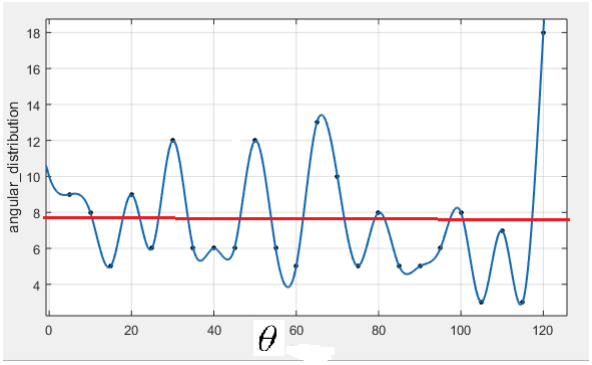


Figure 4.4: The angular distribution at p = 3. The blue line represents the data fitted non-linear data fitting method. While the red line represents the linear data fit of the result obtained. The black dots are the data points given by computer simulation.

The vertical axis represents the non-normalized angular distribution it shows the normalized function times the number of particles of the system. These results clearly shows

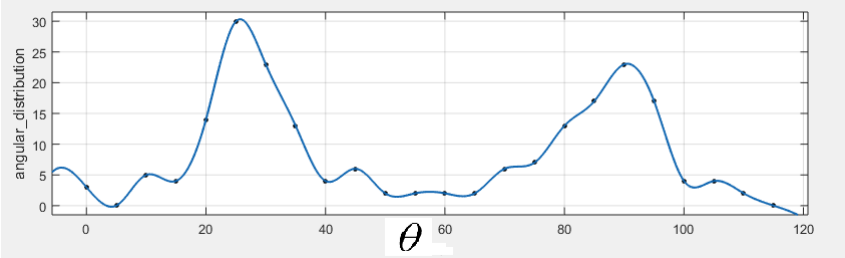


Figure 4.5: At p = 9

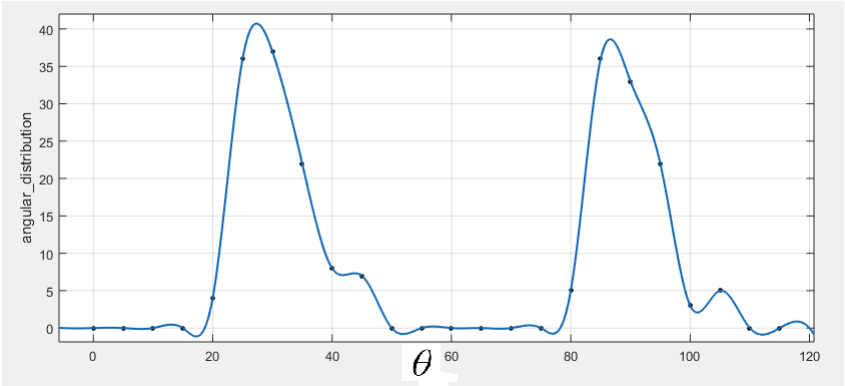


Figure 4.6: At p = 13

The angular distribution of the system shown in figure 4.4,4.5 and 4.6 at different pressure p = 3, p = 9 and p = 13 respectively. The dots represents the results of simulation while the lines are generated by using data fitting software. At p =3, the angular distribution was random. Which means the particles were free to be at any orientational angle which implies there is no translational ordering. But for higher pressures the angular distribution shows peaks at $\theta = 30^0$ and 90^0 which indicates there is orientational ordering.

the relation between pressure and packing fraction. Even if the system was a perfect 15×7 lattice at the close packing, it was no more lattice as the pressure decreased. At lower pressure (in our case p = 3) the particles were more disordered. Thus the probability of a given particle to be in any orientation is almost equal if the pressure of the system is low. This is because of there is no interaction between the particles except the collision between them. As there is enough space created between them, the particles can be free to be in any orientation. But as the system compresses, the probability of occurrence of collision increases which increases the pressure of the system. As the pressure increased the particles was more aligned which allows the system occupy the compressed volume easily. Thus, the angular distribution of the system starts to show peaks at an angles which allows the maximum packing fraction. In this work the results show that these angles are $\theta = 30^0$ and $\theta = 90^0$. The distribution at p = 9 shows that the particles orientation with peaks at the stated angles. The result of the distribution at p = 13 also agrees with p = 9 because the peaks were observed at same angles. When we consider the magnitude of the peaks, for p = 9 the peak was 30 while 39 for p = 13. This confirms the fact that the particles aligns as the pressure increases. By looking at figure [4.2] we can understand that, p = 3 lies in the isotropic phase while p = 9 lies in the tetratic phase. As shown in figure [4.6] there is no orientational ordering for p = 3 while the particles have orientationally ordered for p = 9 and the ordering increased for p = 13.

4.3 Orientational order of the particles

Orientational order is a property which distinguishes the system as isotropic, tetratic or square crystal phases. It is the measure of the deviation of the angle from $\theta_0^{(m)}$. For a system of equilateral triangle system, as shown by the angular distribution and figure [4.1a], $\theta_0^{(m)} = 90^0$ and 30^0. This because of the system reaches its close packing if almost half of the particles are at $\theta = 90^0$.

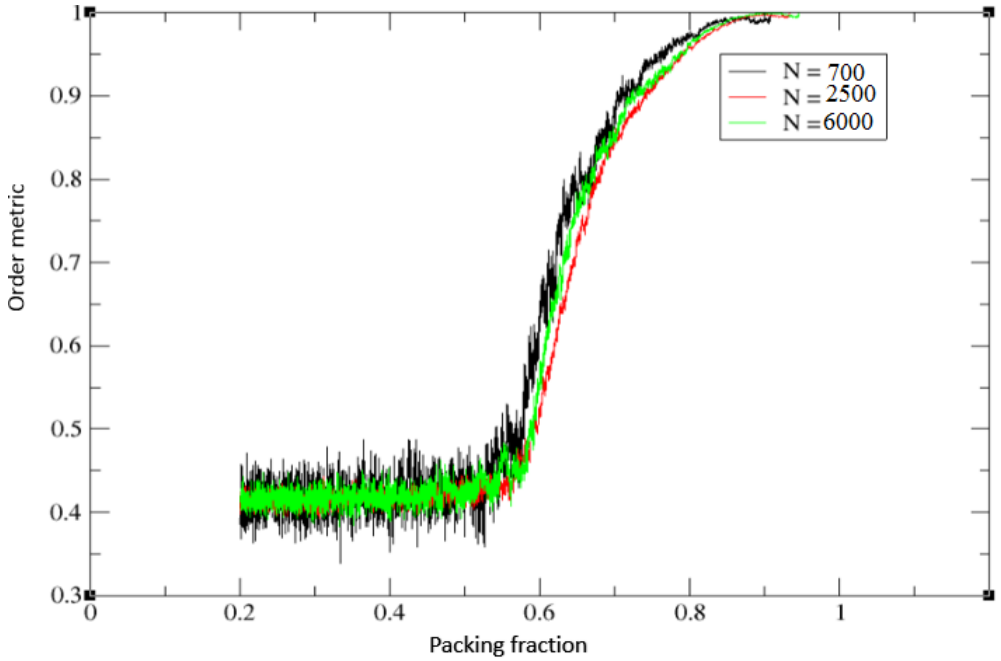


Figure 4.7: The graph of tetratic order versus the packing fraction. The order of the systems with different number of particles was shown for N = 700, N = 2500 and N = 6000. The graph doesn't show any significant variation for different number of particles.

This result seems it contradicts with a result shown by Aleksandar Donev [8] because of the order metric they obtained for hard rectangles was almost zero for until the packing fraction reaches 0.6. But in our case, the graph shows in average the minimum value of the order metric was $S_4 \approx 0.41$. Thus our result agrees with the analytic value given in equation (4.2). This seems it doesn't agree with previous results obtained for hard rectangles. Thus, complete isotropic phase wasn't observed. This happened because of there are two reasons. The first one is, there are two are angles corresponding to $\theta_0^{(4)}$ ($\theta = 90^0$ and 30^0) and the second reason is the system we are considering. We are working with equilateral triangles so that the orientation repeats it self after 120^0. Thus we consider angle within the range of 0^0 to 120^0. By combining these two reasons we can understand that, the maximum deviation from $\theta_0^{(4)}$ is $\Delta\theta = \theta - \theta_0^{(m)} = 30^0$. Since we were dealing with tetratic phase, we had taken $4\Delta\theta$ which implies angle within the range of 0 to 120 was taken in to consideration. For uniform distribution, the probability of a particle to have an orientational angle within the angle range is equal. As a result for uniform distribution:

$$< cos(\theta) >= \frac{\int cos(\theta) d\theta}{\frac{2\pi}{3}} \tag{4.1}$$

Where the integral evaluated from 0 to 120^0 for angle θ between 0 and 120 degree,

the analytic value for the integral in equation (4.1) will be:

$$< cos(\theta) > \approx 0.41 \tag{4.2}$$

From the order metric we understood that there is isotropic phase for $\phi < 0.6$ because of $S_4 \approx 0.41$. At $\phi \approx 0.6$, the order metric shows an exponential growth until the packing fraction reach $\phi \approx 0.9$ which implies the tetratic phase was observed within this range of ϕ. From this result we conclude that: tetratic order cannot be zero for a system of hard equilateral triangle system and, the isotropic - tetratic phase transition and tetratic - solid phase transitions were at $\phi \approx 0.6$ and $\phi \approx 0.9$ respectively.

4.4 Root mean square displacement

For a system of 2500 hard equilateral triangular particles, the root mean square displacement is related the packing fraction and the relation is shown by the figure given below.

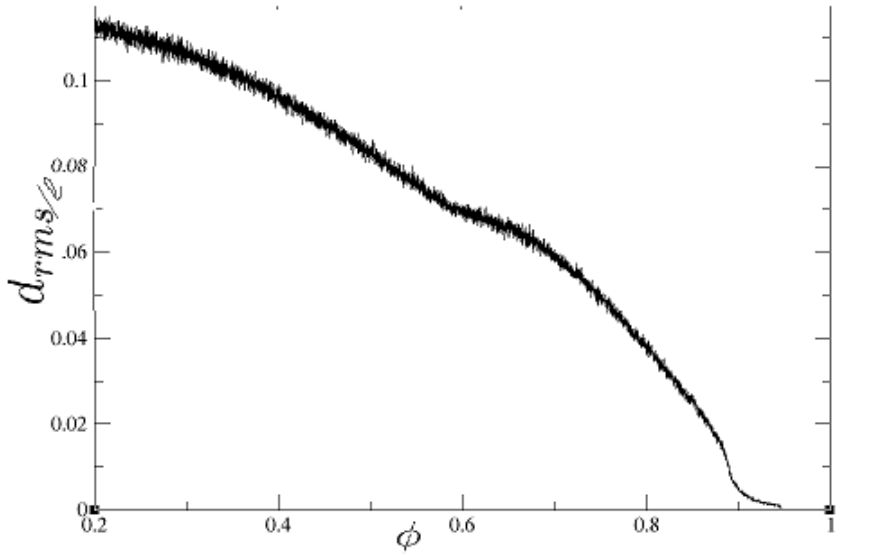
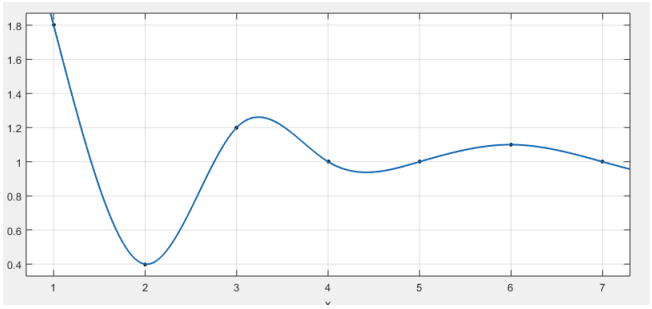


Figure 4.8: The root mean square displacement of particles at different packing fraction.

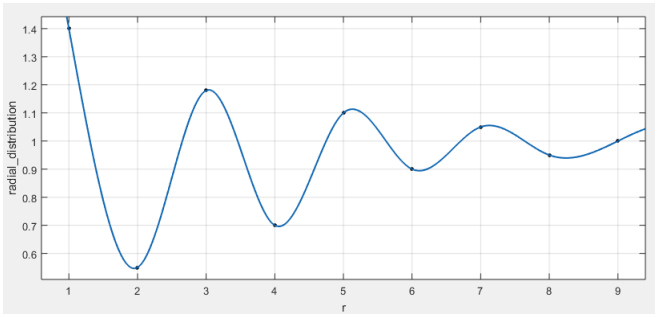
The root mean square displacement (d_{rms}) shows different characters at different phases of the systems. Except at the phase transitions, the graph shows the linear decrement of the function. But at $\phi \approx 0.6$ and $\phi \approx 0.88$ the d_{rms} shows slight deviations which confirms the phase transition at the specified packing fractions. But in general, the d_{rms} decreases as ϕ increases. Both in the tetratic phase and in the isotropic liquid, d_{rms} decreases almost with the same rate which means the slope of the graph is almost equal. At the boundary between these phases, the d_{rms} shown slight slope change (the slope of the graph near the transition decreased). In similar manner, near the solid-tetratic phase transition, the graph shows exponential decrement of the function.

4.5 Radial distribution

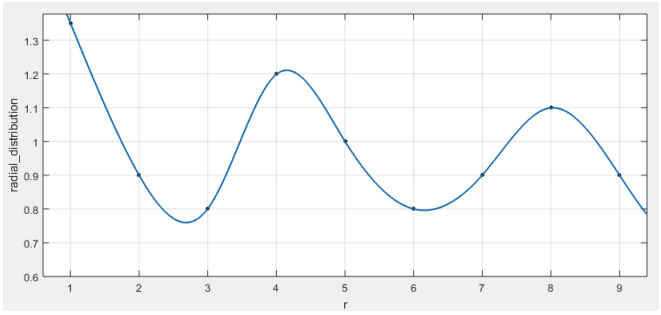
Figure [4.9] shows radial distribution of a system of particles with N = 700 particles at different pressures.



(a) At p = 3



(b) At p = 5



(c) At p = 9

Figure 4.9: This graph shows the radial distribution of the system at pressures p = 3, p = 5, and, p = 9 respectively

At low pressure the graph shows that the functions decays exponentially. But at higher pressure, since the particles were highly structured the function were not accurate. At p = 9, the function decayed slowly when compared with the lower pressures. While for the intermediate pressures, the function decayed faster than the lower pressure. Similarly, for p = 3 it decayed fast. Which implies the particles were more transitionally ordered.

4.6 The phases of the system

The NPT system we were considering was in different phases at different pressure and packing fraction. The phases observed in the system of consideration are isotropic liquid,

the tetratic phase and the square crystal. For a packing fraction $\phi <\approx 0.6$, the order metric shows an average value of 0.41 which means the system has no orientational ordering, for the radial distribution of the particles shows that the system has no translational ordering. Since the system has no orientational ordering, translational ordering the phase within this range is isotropic liquid. When we consider the graph of reduced pressure versus the packing fraction, we observe the cusp around $\phi \approx 0.6$ which shows there is phase transition around there. Similarly, the tetratic order metric also started to increase exponentially within the range of $0.6 < \phi < 0.9$. In addition to this, the radial distribution also shows as the translational ordering which shows there another phase called tetratic phase. For a packing fraction greater than 0.9 the tetratic order didn't shown any increment it becomes almost constant. While there were translational ordering. This implies that the system is square crystal for the specified packing fraction.

As discussed above, the phases observed in our work on hard equilateral triangle system are the isotropic phase, the tetratic phase and the square crystal. Which means the bond orientation phase and the plastic crystal phases were not observed for a system under consideration.

Some of the results we obtained are unexpected. For example the minimum value of the tetratic order metric s_4 is ≈ 0.41 which is different from the result obtained for hard rectangles and the same true for the nematic order for our system. As expected, there is a cusp in the graph of reduced pressure versus the packing fraction near the tetratic-isotropic phase transition and the tetratic order was exponentially increasing near the transition. We have seen the variation of pressure with packing fraction at constant temperature and number of particles and, we obtained phase transitions due to the decrement of pressure even if the temperature of the system is kept constant. The angular distribution, orientational order of particles and the radial distribution function were also considered in our work and, their physical meaning helped us to come in to conclusion about the phases and their stability.

Generally, the phase transitions doesn't vary with the system size but the packing fraction of our system depends on the number of particles of the system. As system size increased the packing fraction increased from $\phi \approx 0.88$ for N = 200 to $\phi \approx 0.94$ for N = 6000. Which means as N increases the packing fraction also increases and close to unity. This occurred because of we are putting triangles in rectangle due to this some space will be left at the corners of the rectangle. Due to this space the packing fraction decreases. As the number of particles of the system increases, the ratio of the number of particles in contact with the wall of the container decreases which reduce the ratio of the unoccupied space. Which means as the number particles of the system increases the ratio of unoccupied space left to the total volume of the particles will be small which in other words means the packing fraction will be increased. Except the packing fraction, almost all of the results we found are independent of the system size.

Chapter 5

Conclusion

A simulation did on 2D liquid crystal system composed of hard triangles using Monte Carlo method on NPT system shown phase transition as the volume of the system expanded or compressed. By observing the macroscopic parameters we considered as an indicators of phase transition like pressure, orientational order and the root means square displacement of the particles of the system, phase transitions were observed at different packing fractions. And the transition from crystal to tetratic as well as from tetratic to isotropic phase as well as from crystal to tetratic phase for such particles no hysteresis were observed which implies the transition is continuous in expansion as well as compression of the system. For a system of hard triangle particles, the phase transition from isotropic to tetratic takes place around $\phi \approx 0.6$ and crystal to tetratic around packing fraction $\phi \approx 0.9$. The phases observed for these particles are isotropic phase (at low density), the tetratic phase (at intermediate density) and solid phase (at high density). The plastic crystal (short-range orientational ordering and long-range translational ordering) didn't observed for this system during the phase transition.

By simply observing the isotropic to tetratic phase transition at different number particles, one can understand that the tetratic region is independent of the system size. The other most interesting investigation is the non-existence of complete isotropic phase. In order to get complete isotropic phase the order metric S_4 should approximately be zero. In our case the minimum tetratic order for this system is $S_4 \approx 0.41$ which implies the system couldn't be in a complete isotropic phase.

It may be interesting to perform analogous studies for the hard triangle-mixtures. Some interesting results might be observed in the study. These results might include the packing fraction at which phase transitions observed that might be different from our observation of this work. Also plastic crystal may or may not not observed for the system.

Chapter 6

Appendix

Under this section we are going to present the most important points used in our work. These are the overlap test and the algorithm used in this work. When we deal with the overlap test, we remember one common property of matter in general. Since matter has its own volume, no two matter could occupy the same space. Thus no two or more particles could also occupy the same space. This is why we are carrying out the overlap test. The overlap test as well as the expansion and the compression are done by computer. As a result, there is some step followed during the simulation of the particles under consideration which we call algorithm. Thus, under this section we are going to present the overlap test and the algorithm we used in this work.

Overlap Test

Since a matter have its own volume, it can occupy some space. Any particles is a matter as a result it can have have a space that couldn't be occupied by others until it is deformed. As known, all objects are rigid to some extent and deformed if the applied force or torque exceed beyond the tolerance of the object. Since we are not interested in the behavior of the particles in their deformation, we cannot take it in to consideration.

By knowing the three vertices,in our case, $(x_a(i), y_a(i)), (x_b(i), y_b)$ and $(x_c(i), y_c)$, of each triangles, we can find the slope (m) of the line passing through each pair of the points on the vertex. The slope of line passing through $(x_a(i), y_a(i)), (x_b(i), y_b)$ is:

$$m_1(i) = \frac{y_b(i) - y_a(i)}{x_b(i) - x_a(i)} \tag{6.1}$$

Thus, the equation of line will be from the rearrangement of the above equation. Which can be given by:

$$m_1(i) = \frac{y - y_a(i)}{x - x_a(i)} \tag{6.2}$$

Thus,

$$y = y_a(i) + m_1(i)(x - x_a(i)) \tag{6.3}$$

Similarly, the equation for the rest two pairs of vertices will be:

$$y = y_b(i) + m_2(i)(x - x_b(i)) \tag{6.4}$$

$$y = y_c(i) + m_3(i)(x - x_c(i)) \tag{6.5}$$

where

$$m_2(i) = \frac{y_b(i) - y_c(i)}{x_b(i) - x_c(i)} \tag{6.6}$$

and

$$m_3(i) = \frac{y_c(i) - y_a(i)}{x_c((i) - x_a(i)} \tag{6.7}$$

Similarly, we can generate equation of line for the neighbor and we get:

$$y = y_a(j) + m_1(j)(x - x_a(j)) \tag{6.8}$$

$$y = y_b(j) + m_2(j)(x - x_b(j)) \tag{6.9}$$

$$y = y_c(j) + m_3(j)(x - x_c(j)) \tag{6.10}$$

Thus by using the above equations of line, we can obtain the point of intersection of the lines by using the following equation.

$$x_{int} = \frac{y_a(j) - y_a(i) - m_1(j)x_a(j) + m_1(i)x_a(i)}{m_1(i) - m_1(j)} \tag{6.11}$$

$$y_{int} = m_1(i)(x_{int} - x_a(i)) \tag{6.12}$$

Similarly, we can calculate the point of intersection of the rest eight combination of the lines. Finally, we can check for overlap by calculating the distance of the point of overlap from $((x_a(i) + x_b(i))/2, (y_a(i) + y_b)/2)$ and $((x_a(j) + x_b(j))/2, (y_a(j) + y_b(j))/2)$ and if the distances are greater than $l/2$, there is no overlap else the two triangles can overlap. As a result the trial move should be rejected.

Algorithm

The algorithm we used has two parts. These are the algorithm used in the expansion and the algorithm used while the compression. We have listed all of them in the following manner.
For expansion of the system the algorithm we used is given below.

1. Place the particles in an almost square 2D box at close packing. To do this:
   (a) Fix the sizes of the box depending up on the number of particles.
   (b) Place the particles at close packing within the box.
2. Expand the system by decreasing the packing fraction by $\triangle\ \phi = -1 \times 10^{-4}$. If $\phi < 0.1$ end the expansion and write the position and orientation of all particles in some file else the position of all particles will be multiplied by $vstep = \sqrt{\frac{\phi}{\phi + \triangle\phi}}$.
3. Apply 15 Monte Carlo step per particle and check for overlap with the neighbors after each MC step.

4. Calculate the macroscopic parameters and got to step 2.

For compression of the system the algorithm we used is given below.

1. Get the position and orientation of all particles written at the end of the expansion.
2. Compress the system by increasing the packing fraction by $\triangle\ \phi = -1 \times 10^{-4}$.
3. Get the new position of all particles by multiplying their position by $\sqrt{\frac{\phi}{\phi+\triangle\phi}}$ and record this position as temporary position.
4. Check for overlap between the particles.
5. If there is overlap, reject the temporary position and divide the previous $\triangle\ \phi$ by 2 and go to step 3.
6. If there is no overlap, take the position.
7. Apply 15 Monte Carlo step per particle and check for overlap with the neighbors after each MC step.
8. Calculate the macroscopic parameters.
9. If $\phi > 0.9$ end compression else go to 2.

Bibliography

[1] B. J. Alder and T. E. Wainwright. Phase transition for a hard sphere system. *The Journal of chemical physics*, 27(5):1208–1209, 1957.

[2] J. G. Berryman. Random close packing of hard spheres and disks. *Physical Review A*, 27(2):1053, 1983.

[3] R. Blaak and J. A. Cuesta. Continuous phase transition in polydisperse hard-sphere mixture. *Journal of chemical physics*, 115, 2001.

[4] W. Brostow. Radial distribution function peaks and coordination numbers in liquids and in amorphous solids. *Chemical Physics Letters*, 49(2):285–288, 1977.

[5] M. J. Buehler. property calculation ii, 2011.

[6] J. Cuesta, C. Tejero, and M. Baus. Isotropic-nematic transition of hard ellipses. *Physical Review A*, 39(12):6498, 1989.

[7] A. Donev, S. Torquato, and F. H. Stillinger. Neighbor list collision-driven molecular dynamics simulation for nonspherical hard particles. i. algorithmic details. *Journal of computational physics*, 202(2):737–764, 2005.

[8] A. Donev, J. Burton, F. H. Stillinger, and S. Torquato. Tetratic order in the phase behavior of a hard-rectangle system. *Physical Review B*, 73(5):054109, 2006.

[9] A. Hinchliffe. *Molecular modelling for beginners*. John Wiley & Sons, 2005.

[10] A. Jaster. Orientational order of the two-dimensional hard-disk system. *EPL (Europhysics Letters)*, 42(3):277, 1998.

[11] S.-D. Lee. A numerical investigation of nematic ordering based on a simple hard-rod model. *The Journal of chemical physics*, 87(8):4972–4974, 1987.

[12] B. D. Lubachevsky. How to simulate billiards and similar systems. *Journal of Computational Physics*, 94(2):255–283, 1991.

[13] B. D. Lubachevsky and F. H. Stillinger. Epitaxial frustration in deposited packings of rigid disks and spheres. *Physical Review E*, 70(4):041604, 2004.

[14] Y. Martínez-Ratón, E. Velasco, and L. Mederos. Orientational ordering in hard rectangles: The role of three-body correlations. *The Journal of chemical physics*, 125(1):014501, 2006.

[15] A. M. A. Michael Nayhouse and G. Orkoulas. A monte carlo study of the freezing transition of hard spheres. *Journal of physics: condensed matter*, 2011.

[16] M. Moradi, S. Hashemi, and F. Taghizadeh. Monte carlo simulation of a confined hard ellipse fluid. *Physica A: Statistical Mechanics and its Applications*, 389(21): 4510–4519, 2010.

[17] W. L. Nichols and J. H. Weare. Homonuclear diatomic scattering from solid surfaces: A hard cube model. *The Journal of Chemical Physics*, 62(9):3754–3762, 1975.

[18] B. E. Poling, J. M. Prausnitz, J. P. O'connell, et al. *The properties of gases and liquids*, volume 5. Mcgraw-hill New York, 2001.

[19] V. Ryzhov and S. Stishov. A liquid-liquid phase transition in the "collapsing" hard sphere system. *Journal of Experimental and Theoretical Physics*, 95(4):710–713, 2002.

[20] R. Sánchez and L. A. Aguirre-Manzo. Concentric tetratic orientational order in a confined quasi-2d tubular system. *Physica Scripta*, 90(9):095002, 2015.

[21] P. Sheng. Hard rod model of the nematic-isotropic phase transition. In *Introduction to Liquid Crystals*, pages 59–70. Springer, 1975.

[22] D. Tabor and D. Tabor. *Gases, liquids and solids: and other states of matter*. Cambridge University Press, 1991.

[23] R. van Roij, M. Dijkstra, and R. Evans. Interfaces, wetting, and capillary nematization of a hard-rod fluid: Theory for the zwanzig model. *The Journal of Chemical Physics*, 113(17):7689–7701, 2000.

[24] R. van Roij, M. Dijkstra, and R. Evans. Orientational wetting and capillary nematization of hard-rod fluids. *EPL (Europhysics Letters)*, 49(3):350, 2000.

[25] J. Veerman and D. Frenkel. Phase behavior of disklike hard-core mesogens. *Physical Review A*, 45(8):5632, 1992.

[26] L. Walsh and N. Menon. Ordering and dynamics of vibrated hard squares. *Journal of Statistical Mechanics: Theory and Experiment*, 2016(8):083302, 2016.

[27] K. W. Wojciechowski and D. Frenkel. Tetratic phase in the planar hard square system. *Comput. Methods Sci. Technol*, 10(22):235–255, 2004.

Declaration

This thesis is my original work, has not been presented for a degree in any other University and that all the sources of material used for the thesis have been dully acknowledged.

Name: Eshetu Leka Burayu

Signature:– –

Place and time of submission: Addis Ababa University, January 2020

This thesis has been submitted for examination with my approval as University advisor.

Name: Dr. Tatek Yirgou

Signature:– – – – – – – – – ––