Ordering of soft regular polygons in two-dimensions

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Submitted by

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CERTIFICATE

This is to certify that the thesis entitled **"Ordering of Soft Regular Polygons in Two-Dimensions"** submitted by Ms. Rupali Sharma is in partial fulfillment for the degree of Master of Science in Physics in this Institute. This work has been done under my supervision. She has not submitted this material for the credit towards any degree at Thapar Institute, Patiala or any other Institute.

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DECLARATION

I declare that the thesis entitled **"Ordering of Soft Regular Polygons in Two-Dimensions"** is an authentic record of my work carried out under the supervision of Dr. Debabrata Deb, Assistant Professor, SPMS Thapar Institute, Patiala. I have not submitted this work anywhere else for the award of any degree.

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ABSTRACT

Studies of phase transitions in two-dimensional (2D) system is a fundamental, long-standing problem in statistical mechanics and have an interesting melting phenomenon. It was observed that the 2D solid melted through three scenarios, depending upon both particle shape and symmetry. We investigate the phase behavior of regular soft polygons with the N number of the subatomic particle ($2 \leq N \leq 5$) in 2D. By studying these types of molecules, we show that the phase behavior depends upon both enthalpic and configuration entropy. For this, we study the phase behavior of a soft regular polygon under two types of interaction, Lennard-Jone potential (attractive) and Yukawa potential (repulsive), with different values of N. Our results show that the enthalpic entropy has a more significant effect on phase transition than configurational entropy. We present the results from the LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) simulation of a rigid body system under the influence of enthalpic and configurational entropy varied one by one. As a result, phase transitions are studied as a function of temperature and the number density of the system. We have used various investigating techniques such as tracking particle positions, radial distribution function, and statistical structure factor to identify the phases. We show the effect of enthalpic and configurational entropy on the phases of the system. Hence, we obtained a phase diagram of soft-regular-polygonal material under different conditions.

Contents

Chapter 1

Introduction and Literature Review

1.1 Introduction

During the phase transitions, the arrangement in the system changes due to which an ordered system gets disordered, or the disordered system gets ordered. The order or disorder designates the absence or presence of symmetry or correlation between particles. To create a good sample or sample with new modified properties, what we must know about the matter is the phase transition. It is an important phenomenon as it tells about the parameter values at which the transition occurs in phases of the sample. The values of thermodynamic parameters like temperature, density, pressure, volume, etc., become very important since the phase of the system changes at some fixed values of these parameters. At these values, the phase boundary (may) vanish, and the coexistence of the phase may exist depending upon the type of the phase transition. For example, the liquid-vapor critical point, the endpoint of the pressure-temperature curve that designates conditions under which a liquid and its vapor can coexist. At higher temperatures, the gas cannot be liquefied by pressure alone. We also know that glassy material is obtained by quenching the liquid. Quenching is the state which occurs when the disordered system is not equilibrated. Thus, if we want to create a sample of glass, then we must know the parameter values at which the disordered system occurs. As a result, it gets essential to know about the phase transition of that sample. So, in material processing, the sample goes through different phases. If we are interested in one particular phase, that can be achieved by a good knowledge of phase transition. That is the whole core of material processing. Entropy comes into the picture when we are talking about the order-

ing of a system. Entropy is the randomness measurement or the amount of order present or absent in a system. Entropy is a scientific concept and a measurable physical property most commonly associated with a state of disorder, randomness, or uncertainty. Entropy is of two types, enthalpic and configurational entropy. Enthalpic entropy occurs in the system due to the interaction present between the particle. Configurational entropy is due to the shape of particles. In any given system, both enthalpic and configurational entropy contribute to the system's entropy. Entropy becomes important as the melting transition of 2D solid depends on the shape and symmetry of the constituents. So far, it has been found that the melting of 2D solid proceeds from solid to liquid with an intermediate "x-atic" ordered phase.

Our work is to investigate the phase transition in materials consisting of regular soft polygons. Also, we present that from both types of entropies, which one has more effect on the total entropy of the system. For that, we are fixing one entropy and changing the other. For example, we fix repulsive interaction and then change molecules' shape, or we fix the shape of molecules and then vary the pair-interaction in the system. We use various investigating techniques such as tracking particle positions, radial distribution function, and statistical structure factor to identify the phases. For the time being, we are identifying the phases of the system and characterizing the phase diagram of the system. This work can be continued by characterizing that phase transition in more detail for a big system, where the locations of the phase boundaries may be identified precisely, and also the nature of the phase transitions can be investigated.

1.2 Literature review

The KTNHY theory, developed in the 1970s by John Michael Kosterlizt, David J.Thouless, Berytand Halperin, and David R.Nelsons, describes the melting scenario in two dimension(2D) solid. This theory was developed on topological defects which states that the 2D solid goes through phase transitions from solid to liquid by hexatic phase, which means that solid

converted to hexatic phase by second-order phase transition and after that hexatic to liquid by second-order phase transition. Previous studies[1-18] that study 2D solid melting scenarios find the three scenarios.

- Continuous fluid-x-atic-solid transitions.
- Fluid-to-solid by first-order isotropic transitions
- Fluid-to-x-atic by first-order and subsequent continuous x-atic-to-solid transitions.

So far, two of three scenarios have been observed. The simulation of point particles with hard core repulsion interaction follows the third scenario, and soft potentials lead to continuous melting [18]. Sharon C. Glotzer, Joshua A. Anderson, James Antonaglia, Jaime A. Millan, and Michael Engel's work report all three melting scenarios in a single family of hard, regular polgons[19]. By varying the number of polygon edges, they show that the melting transition scenario for a system of any given polygon is determined by the anisotropy of emergent entropic interactions and the symmetry of the particles relative to that of the solid phase. So far, people have worked on two types of systems. The atomic system, in which the particle's internal structure is ignored. That is, the particle is treated as spherical in nature. Like, colloidal, superparamagnetic, and coarse-grained. Luis A Padilla and Abelardo Ramirez-Hernandez's work used the coarse-grained representation of colloidal nanocrystals confined at a flat interface [20]. Where work done by Antonio M. Puertas, Matthias Fuchs, and Michael E. Cates, they identify the mechanisms causing aggregation and structural arrest of colloidal suspensions interacting with a short-ranged attraction at moderate and high densities by using computer simulations [21]. C. Reichhardt and C. J. Olson, in 2002, considered the particle as a colloid; they simulated the colloidal particles interacting via a Yukawa potential in a 2D system with the random disorder by Langevin simulation [22]. They find that the colloids form an ordered triangular array for weak substrates that depins elastically without generating defects. There is a sharp crossover to a disordered phase for increased substrate strength where the colloids depin elastically into river-like structures. Molecular systems, in

S.no.	Shape	Paper	Refs.
1.	Hard dimers	Monte Carlo simulations of a two-dimensional hard dimer system	K.W. Wojciechowski, A.C. Branka, and D. Frenkel, Physica A 196, 519 (1993).
2.	Rounded triangles	A simple mechanism for emergent chirality in achiral hard particle assembly	J. Chem. Phys. 139, 164705 (2013)
3.	Rounded hard-squares	Phase behavior of rounded hard-squares	C. Avendano and F. A. Escobedo, Soft Matter, 2012, 8, 4675–468
4.	Hard pentagons	Monte Carlo study of hard pentagons	T. Schilling, S. Pronk, B. Mulder, and D. Frenkel, Phys. Rev. E 71, 036138 (2005).
5.	Hard Triangular Bipyramids	Degenerate Quasicrystal of Hard Triangular Bipyramids	A. Haji-Akbari, M. Engel, and S. C. Glotzer, Phys. Rev. Lett. 107, 215702 (2011).

Table 1.1: Literature review

which the internal shape of particles is not ignored. The particles are no longer treated as single entities. For example, liquid crystal, prolate ellipsoid, oblate ellipsoid, and disc. We listed some papers in table 1 in which they consider the different shapes of particles. The first paper considers a molecule as a dimer, i.e., two spheres connected to each other. They use the Monte Carlo simulation to study the two-dimensional system of hard homonuclear dimers[23]. The term hard is for no-interaction between the molecules and determines the different properties of the system, like the equation of state, structural, and orientational properties. They reported the differences in Gibbs free energy between the various solid structures, not to exceed $0.1k_bT$ per particle.

The second paper showed why achiral particles assemble into chiral ma-

terials by using the simulation of hard regular polygons with rounded corners[24]. The third paper reports Monte Carlo simulation results of rounded hard squares of varying degrees of roundness, hence interpolating between disks and perfect squares [25]. In the fourth paper, they study the system of hard pentagons using Monte Carlo simulation in isobaric and isotensic ensembles and present the phase behavior of hard pentagons [26]. So far, the maximum work is done for the hard system. In some work, the molecules are considered in the soft system. Like, Zeyu Yeang's work, they simulate the system of dimer-shaped particles interacting with each other in combined LJ and YK potential. The equation of combined potential is in the form of,

$$V_{LJ}(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] + \frac{A}{r}e^{-kr} \tag{1.1}$$

They found that the monomeric spheres can produce most of the quasicrystalline patterns found in the dumbbell system [27].

Chapter 2

Model

As discussed earlier, two types of entropy contribute to systems behavior, i.e., enthalpic and configurational entropy. The enthalpic entropy is due to the interaction present between the molecules. The configurational entropy is due to the shape of molecules. Thus, we get a different phase behavior as we change the entropy. To see the effect of entropy's we fix the one entropy and change varied the another. By doing so, we are trying to check which type of entropy affects the phase behavior. So there is two interaction that we are considering. One is the attractive Lennard-jones potential (LJ-potential), and another is the repulsive Yukawa potential (YK-potential). Also, for configurational entropy, we consider the family of a regular polygon with N number of sub-atom.

2.1 Enthalpic entropy

We are considering the two type of interaction. One is the attractive Lennard-jones(LJ) potential , and another is the repulsive Yukawa(YK) potential.

2.1.1 LJ potential

Sir John Edward Lennard-Jones proposed a specific model called Lennard-Jones (LJ) potential. The LJ potential describes the potential energy of interaction between two non-bonding atoms or molecules based on their separation distance. The LJ potential equation accounts for the difference between repulsive and attractive forces (dipole-induced, dipole-dipole, and London interactions). The following equation gives the LJ potential:

$$V(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \tag{2.1}$$

where r is the distance between two interacting particles. ϵ is the depth of the potential well and σ is the distance at which the particle-particle potential energy. V is the intermolecular potential between the two atoms or molecules. The first term in the equation (2.1) represents the repulsive term that describes Pauli's repulsion at short ranges due to overlapping electron orbitals. The second term is the attractive long-range term, which describes attraction at long ranges. Differentiating the LJ potential to r expresses the net inter-molecular force between two molecules. This inter-molecular force may be repulsive or attractive, depending on the value of r.

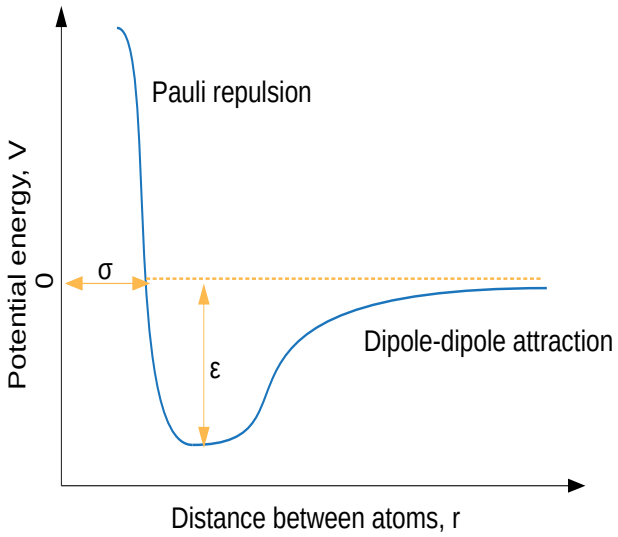


Figure 2.1: Lennard-Jones potential as a function of the particle distance r

The repulsive term is presumed to decay more rapidly (twelfth inverse power), and the attractive term is presumed to decay with distance as the inverse sixth power (dipole-dipole interactions). The attractive term dominates at long distances, and the repulsive term dominates at short distances. The forces due to the repulsive and attractive forces are balanced at the bottom of the potential well so that this is the interatomic distance at

Zero K. Technically, LJ potential is used to describe the properties of gases and overlap interactions in molecular models. However, they are equally reliable for modeling the solid-state of noble gases.

2.1.2 Yukawa potential

In particle, atomic and condensed matter physics, a Yukawa potential(YK), also called a screened Coulomb potential is a potential named after the Japanese physicist Hideki Yukawa. But in soft matter physics, yukawa potential is when colloids are in salty medium and that time the interaction between colloids are in the form of

$$V_{YK}(r) = \epsilon \frac{e^{-kr}}{r} \tag{2.2}$$

where ϵ is the strength of the potential, r is the radial distance to the particle. The form of yukawa potential in both case is same but the origin is different, or we can say the form of potential in colloids is similar to the form of high energy yukawa potential.

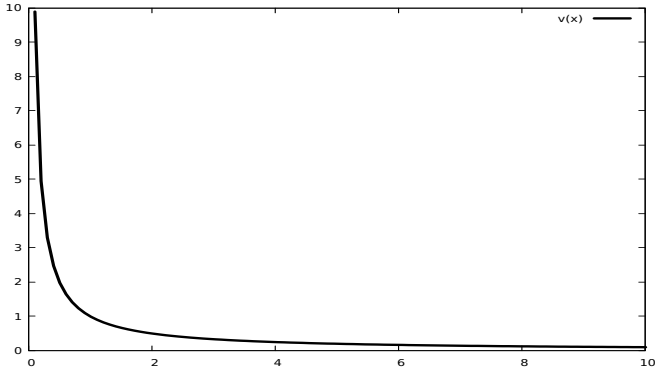


Figure 2.2: Yukawa potential

2.2 Configurational entropy

Configurational entropy is due to shape of molecules. To study the effect of this entropy we consider the family of regular polygon. The different

shape of regular polygon is shown in table 2.1. In a molecular system, sets of two or more atoms treat as independent rigid bodies. This means that the total energy on each rigid body is computed as the sum of the energy of its constituent particles. The coordinates, velocities, and orientations of the atoms in each body are then updated so that the body moves and rotates as a single entity. This is implemented by creating internal data structures for each rigid body and performing time integration on these data structures. The constituent particles' positions, velocities, and orientations are regenerated from the rigid body data structures in every step. This restricts which operations and fixes can be applied to rigid bodies. So we are considering the six different shapes for molecules in the system, like dimer, trimer, quadmer and pentamer.

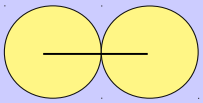
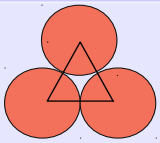
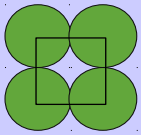
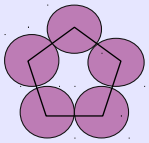
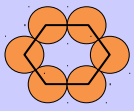
S.no.	Name	Shape of molecule
1.	Dimar	
2.	Trimar	
3.	Quadmar	
4.	Pentamar	
5.	Hexamer	

Table 2.1: Shape of molecule

By fixing the one type of interaction and changing the shape, we are getting a different configuration and phase behaviour. In a dimer shape, the two spherical particles are connected, which will move together. The distance between center of the particles is one sigma (σ=1). Energy is calculated by considering both of them as one entity. In trimar system, three sphere are connected to each other and the distance between the particle is one sigma (σ=1) and same as with other shapes.

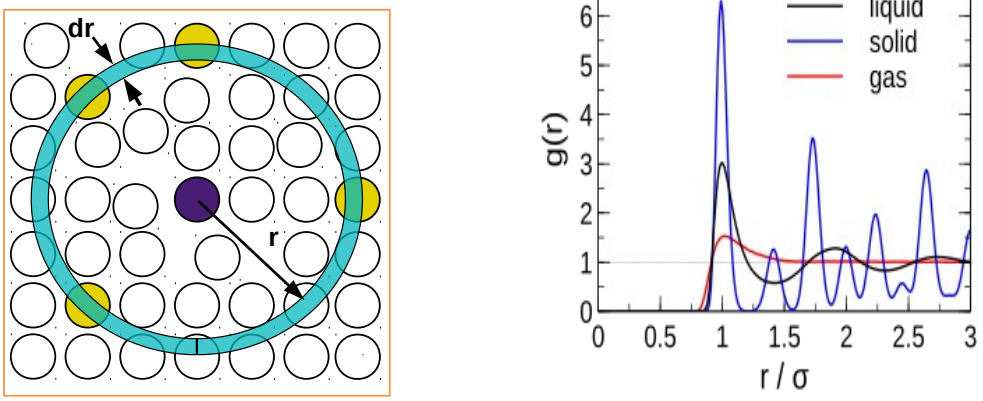
Chapter 3

Methods

At present, many methods for simulation techniques exist that can be used for the simulation of hard or soft matter systems. Some popular are molecular dynamics, Monte Carlo simulation, Langevin dynamics, etc. we are using Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) to simulate our system.
LAMMPS is a classical molecular dynamics code with a focus on materials modeling. It's a simulator with a Molecular Dynamics code that can model an ensemble of particles in any phase. We use the fix-rigid command to investigate the system of N=400 identical polygons with a different number of edges that interact. The circumcircle diameter of the polygons is denoted as σ. To determine the ordering of molecules in the system, we calculate the radial distribution function and statistical structure factor.

3.1 Radial distribution function (RDF)

The radial distribution function or correlation function describes how density varies as a function of distance from a reference particle. This function $g(r)$ gives us the probability of finding a particle at some distance r from a given reference particle. In MD simulation, the RDF is calculated by counting the number of atom pairs between given separation ranges. The results can be transferred to the average density of atoms as a distance function. The RDF is strongly dependent on the type of matter so that it will vary greatly for solids, gases, and liquids. The average density at any point in a liquid is the bulk density, ρ. This density is always the same for a given liquid. The density of the liquid at a given distance of r from another molecule is referred to as the local density, $\rho(r)$.



(a) Physical meaning of radial distribution function(RDF)

(b) RDF for a solid, liquid and gas

Figure 3.1

The radial distribution function can be evaluated as: it is simply the ratio between the average number density at a distance r from any given atom and the density at a distance r from an atom in an ideal gas at the same overall density. $g(r)$ is 1 for an ideal gas. Any deviation of $g(r)$ from unity reflects a correlation between the particles due to the intermolecular interactions. The nature of the RDF curve gives us an idea about the state of our system.We show here the RDF for a gaseous, liquid and solid phase. The RDF value is zero up to a certain distance as this is the particle, effectively the size of particles in the system as they cant overlap each other. The blue curve is for the crystalline solid phase. We observe the series of the peak where the distance between the peak is periodical of the crystal. This is due to the periodic nature of particles, i.e., the particle appears at a regular distance from each other in every direction. The black curve is for the liquid phase. The curve gives an initially sharp peak due to the shell of the particle closest to the reference particle. Then the curve fall rapidly and became uniform around the one. This issue to the isotropy nature of liquid as the probability of finding the particle at all distances is the same. The red one is for the gaseous phase. In the gaseous phase, no peak is observed as the particles are far from each other with no order.

3.2 Statistical structure factor (SSF)

According to liquid-state theory, a static structure factor can be used to address short-range order and the glass transition in amorphous/liquid samples and, more generally, in nano-structured or other structurally disordered systems. There are two methods of calculating it—one by Fourier transformation of the radial distribution function and Direct calculation with Fourier density correlation. We are using this relation to calculate the static structure factor.

$$S(\mathbf{k}) = \frac{1}{N}\Big\langle \sum_{i,j} e^{-i\mathbf{k}(\mathbf{r}_i - \mathbf{r}_j)} \Big\rangle \tag{3.1}$$

$$= \frac{1}{N}\Big\langle \Big| \sum_{i,j} \cos\Big(\mathbf{k}(\mathbf{r}_i - \mathbf{r}_j)\Big)\Big|^2 + \Big| \sum_{i,j} \sin\Big(\mathbf{k}(\mathbf{r}_i - \mathbf{r}_j)\Big)\Big|^2 \Big\rangle \tag{3.2}$$

Chapter 4

Computational Simulation Details

4.1 Brief discussion of LAMMPS package

Large-scale Atomic/Molecular Massively Parallel Simulator is the acronym for LAMMPS. It's a simulator with a Molecular Dynamics code that can model an ensemble of particles in any phase. It lets you model a range of systems (both solid-state and soft matter) with various force fields and other parameters. The LAMMPS can simulate systems with arbitrary numbers of particles (from just a few up to millions or billions). LAMMPS, developed by Sandia National Laboratories in the United States, has a wide range of features that the user can customize. Although the current version of LAMMPS is developed in C++, previous versions were written in Fortran 77 and Fortran go. LAMMPS can be executed on a single processor as well as in parallel. LAMMPS integrates Newton's equations of motion for massive collections of atoms/molecules or macroscopic particles interacting via short or long-range forces with various beginning and boundary conditions because it is an MD code. LAMMPS ensures efficiency by keeping track of adjacent particles using neighbor lists. All instructions to the LAMMPS package are delivered to the user in the form of an input script. LAMMPS includes an interpreter built-in that goes over the input script line by line. The input script must contain commands that the LAMMPS can understand. LAMMPS has a large number of commands that provide a lot of capability that any researcher can use. It appears that understanding how to write an input script is the most important part of learning LAMMPS. As a result, we go over how to construct an input script that meets your needs in great depth. LAMMPS performs calculations one line at a time by reading commands from an input script (text file).

LAMMPS terminates after the input script is finished. This is in contrast to programs that read and process all of the input before beginning a calculation. Each command causes LAMMPS to take immediate action, regardless of whether or not any further commands are processed. Set an internal variable, read a file, or conduct a simulation with commands. The input script treats each non-blank line as a command. LAMMPS commands are case-sensitive. Both the command name and the command arguments are in lower case. In file names and user-defined ID strings, upper case letters are permitted. A LAMMPS input script typically has 4 parts:

1. Initialization
2. System definition
3. Simulation settings
4. Run a simulation

The last two sections can be done as many times as needed. For example, run a simulation, alter some settings, run some more, and so on. Each of the four parts has now been detailed in greater depth. Remember that almost all commands should only be used if a non-default value is desired.

4.1.1 Initialization

The first section of the lammps input script is initialization. Macroscopic and microscopic properties are both simulated. The system of units to be employed, the lattice, the shape and size of the simulation box, and so on are all macroscopic features. The shape and properties of atoms/molecules and their interactions are all defined by microscopic features. The macroscopic ties will be mentioned first, followed by the microscopic ties. Set parameters that need to be defined before atoms are created or read in from a file. The relevant commands are units, dimension, newton, processors, boundary, atom_style, atom_modify. The system of units utilized in the simulation is the first thing that must be announced at the start of each simulation. All quantities in the input script, as well as those received as output in log or dump files, are set to this unit. This is done by using the command units the syntax of which is given as

`unit style`

where style = lj or real or metal or si or cgs or electron or micro or nano. This command determines the style of units employed in a simulation. All quantities indicated in the input script and data file and quantities output to the screen, log file, and dump files units are determined. This command is usually used at the start of a script. The units you choose only affect LAMMPS' internal conversion factors. This means that any simulation you run with one set of units can be replicated with any other unit configuration supported by LAMMPS. "Duplicate" means that the particles will have identical trajectories and that the simulation's output will be identical. Because the conversion factors for two separate unit systems are not equivalent to infinite precision, this will be the case for a certain number of timesteps until round-off effects accumulate.

To run the same simulation with a different set of units, you must update all unit-based input parameters in your input script and additional input files (data files, potential files, and so on) to the new units. And it would help if you correctly converted all output from the new units to the old units compared to the original results. All quantities in style LJ are unitless. LAMMPS sets the fundamental quantities mass, σ, ϵ, and the Boltzmann constant $k_b = 1$ without losing generality. The masses, distances, and energies you specify are multiples of these fundamental values. Some formulas relate the reduced or unitless quantity to the same quantity with units. As a result, you can utilize the mass, σ, and ϵ values for a particular material to transform the results of a unitless LJ simulation into physical quantities. Set the dimensionality of the simulation. By default, LAMMPS runs 3d simulations. To run a 2D simulation, this command should be used before setting up a simulation box via the create_box or read_data commands.

`dimension N`

where N = 2 or 3. Restart files also store this setting. This command must be used before the simulation box is defined by a read_data or create_box command.

Reduced units		
Property	Symbol	Reduced form
Length	r*	$\frac{r}{\sigma}$
Time	t*	t $\sqrt{\frac{\epsilon}{m\sigma^2}}$
Temperature	T*	$\frac{k_B T}{\epsilon}$
Force	F*	$\frac{F\sigma}{\epsilon}$
Energy	U*	$\frac{U}{\epsilon}$
Pressure	P*	$\frac{p\sigma^3}{\epsilon}$
Density	$\rho*$	$\rho\sigma^3$
Surface tension	$\gamma*$	$\frac{\gamma\sigma^2}{\epsilon}$

Now to define what style of atoms to use in a simulation, the command used is atom_style. The syntax of this command is

```
atom_style style args
```

Where style can be angle or atomic or body or bond or charge or dipole or electron or ellipsoid or full or line or molecular or oxdna or peri or smd or sph or sphere or bpm/sphere or spin or tdpd or tri or template or hybrid. This defines which atoms are paired with which properties. This command must be used before any read data, read restart, or create box commands to build up a simulation. Because a style cannot be modified once it has been given, choose one that is broad enough to include all properties. Angular terms, for example, cannot be utilised or added afterward to the model while using style bonds. It is OK to employ a more generic style than necessary, even if it is slightly inefficient. What quantities are stored by each atom, what quantities are transmitted between processors to enable forces to be computed, and what values are listed in the data file read by the read data command depend on the chosen style.

```
atom_style atomic
```

Where atomic is only the default value which is used for coarse-grain liquids, solids, and metals. Now to set the formulas to compute the pairwise

interaction, the command used is pair_style. the syntax of the command is

```
pair_style style args
```

where style can be one of the styles discussed earlier, and args are arguments used by a particular style. Set the formula(s) LAMMPS uses to compute pairwise interactions. In LAMMPS, pair potentials are defined between pairs of atoms within a cutoff distance, and the set of active interactions typically changes over time. See the bond_style command to define potentials between pairs of bonded atoms, which typically remain in place for the duration of a simulation. In LAMMPS, pairwise force fields encompass a variety of interactions, some of which include many-body effects, e.g., EAM, Stillinger-Weber, Tersoff, and REBO potentials. They are still classified as "pairwise" potentials because the set of interacting atoms changes with time (unlike molecular bonds). Thus, a neighbor list is used to find nearby interacting atoms. For example, hybrid models where specified pairs of atom types interact via different pair potentials can be set up using the hybrid pair style.This command must be used before any coefficients are set by the pair_coeff, read_data, or read_restart commands. Some pair styles are part of specific packages. They are only enabled if LAMMPS was built with that package. The doc pages for individual pair potentials tell if it is part of a package. Coefficients associated with pair style are typically set for each pair of atom types and are specified by the pair_coeff command or read from a file by the read_data or read_restart commands. Specify the pairwise force field coefficients for one or more pairs of atom types. The number and meaning of the coefficients depend on the pair style. Pair coefficients can also be set in the data file read by the read_data command or in a restart file. Syntax is

```
pair_coeff I J args
```

where, I,J = atom types

args = coefficients for one or more pairs of atom types

In our input script, we use lj and yk system with there relevant coefficient.

Example,

```
pair_style lj/cut 6.0
pair_coeff * * 1.00 1.0
```

4.1.2 System definition

In LAMMPS, there are three approaches to create the simulation cell, reserve space for force field information, and populate it with atoms. Read them in from

(1) A data file

(2) A restart file

via the `read_data` or `read_restart` commands, respectively.

(3) Or, create a simulation cell and fill it with atoms on a lattice using these commands: `lattice, region, create_box, create_atoms or read_dump.` The entire set of atoms can be duplicated to make a larger simulation using the replicate command. We are using the read_data command to run the simulation.

```
read_data data.nsa.$nsa.nbp.$nbp
```

Read in a data file containing information LAMMPS needs to run a simulation. The file can be ASCII text or a gzipped text file. This is one of 3 ways to specify initial atom coordinates. This command can be used multiple times to add new atoms and their properties to an existing system by using the add, offset, and shift keywords.

4.1.3 Simulation settings

After the atoms and molecular structure have been defined, a variety of choices such as force field coefficients, simulation parameters, output options, and more can be provided. Pair coeff, bond coeff, angle coeff, dihedral coeff, improper coeff, kspace style, dielectric, and special bonds are instructions for setting force field coefficients (they can also be specified in the read-in files).The following commands change several simulation

parameters: neighbor, neigh modify, group, timestep, reset timestep, run style, min style, and min modify.

The neighbor command affects the construction of pairwise neighbor lists by setting parameters. The list stores all atom pairs within a neighbor cutoff distance equal to their force cutoff and skin distance. The larger the skin distance, the fewer neighbor lists are needed, but more pairings must be examined for possible force interactions at each timestep. The Syntax of his command is,

```
neighbor skin style
```

- skin = extra distance beyond force cutoff (distance units)
- style = bin or nsq or multi or multi/old

The algorithm used to generate the list is determined by the style value. The list is created using the bin style, which is a linear operation that scales with N/P, the number of atoms per processor, where N is the total number of atoms and P is the number of processors. It scales as $(N/P)2$ and is almost always quicker than the nsq style. The nsq choice can be faster for unsolvated tiny molecules in a non-periodic box. Either method should get the same results.

If the check parameter of the neigh modify command is set to yes, the skin distance is also utilized to determine how often atoms migrate to new processors. At the same timestep, as neighbor lists are re-built, atoms are migrated (communicated) to new processors. The simulation's unit selection determines the default value for skin.

Default

1. 0.3 bin for units = lj, skin = 0.3 sigma
2. 2.0 bin for units = real or metal, skin = 2.0 Angstroms
3. 0.001 bin for units = si, skin = 0.001 meters = 1.0 mm
4. 0.1 bin for units = cgs, skin = 0.1 cm = 1.0 mm

The neigh_modify command has additional options that control how often neighbor lists are built and which pairs are stored in the list. The Syntax

of this command is

```
neigh_modify keyword values
```

- one or more keyword/value pairs may be listed

This command controls the construction and usage of pairwise neighbor lists. Depending on the pair interactions and other instructions set, a simulation may require one or more neighbor lists. The parameters every, delay, check, and once influence how frequently lists are created as the simulation runs. The delay setting indicates that no new lists are built until at least N steps have passed since the previous construction. Every setting denotes the creation of lists every M step (after the delay has passed). If the check setting is no, the lists are created on the first step that meets the delay and all other requirements. If the check setting is set to yes, the every and delay settings decide when a build is possible, but only if some atom has moved more than half the skin distance (given in the neighbor command) since the previous build.

Once the setting is yes, the neighbor list is only built once at the start of each run, and it is never rebuilt, except on steps where a restart file is written or steps where a fix necessitates a rebuild. e.g. fixes that create or delete atoms, such as fix deposit or fix evaporate. This setting should only be used if you are confident that atoms will not migrate far enough to require the neighbor list to be regenerated, such as when simulating a cold crystal. This command has a restriction: if the "delay" setting is non-zero, it must be a multiple of the "every" setting. Only atom styles that define molecule IDs can use the molecule/intra and molecule/inter exclude options. The page setting's value must be at least ten times that of the one setting. This ensures that neighboring pages aren't mostly empty space.

The compute command is used to compute the values of observables of interest in real-time. A Compute can hold both the current and prior time step's information. Both the global and per-atom attributes can be calculated using a compute. Compute has the following syntax.

```
Compute Compute_ID group_ID style args
```

The group_ID is the group of atoms on which the compute must be performed. compute_ID is the user-assigned name for the compute. Style and arguments govern the nature of computation performed. In our work, we used the statements

```
compute ketran all ke/rigid 1
compute kerot all erotate/rigid 1
compute temp all temp
```

for computing the temperature of a group of atoms, the translational kinetic energy of a collection of rigid bodies, and the rotational kinetic energy of a collection of rigid bodies. The "fix" is any operation that is applied to the system during timestepping or minimization. Examples include updating of atom positions and velocities due to time integration, controlling temperature, applying constraint forces to atoms, enforcing boundary conditions, computing diagnostics, etc. Set a fix that will be applied to a group of atoms. The Syntax of command is,

```
fix ID group-ID style args
```

- ID = user-assigned name for the fix
- group-ID = ID of the group of atoms to apply the fix to
- style = one of a long list of possible style names
- args = arguments used by a particular style

There are hundreds of fixes defined in LAMMPS, and new ones can be added. Fixes perform their operations at different stages of the timestep. If two or more fixes operate at the same stage of the timestep, they are invoked in the order specified in the input script. The ID of a fix can only contain alphanumeric characters and underscores. Fixes can be deleted with the unfix command. There are many options for style and arguments depending upon the nature of the fix to be applied. For example, the ensemble can be fixed by using a style such as npt/asphere, nvt/sphere, etc. After fixing the option for style and arguments, we may need to collect important information at certain timesteps of the simulation. These can be

particle position or particle orientation etc. This can be done by using the dump command. The syntax of this command is

```
dump ID group_ID style N file args
```

- ID = user-assigned name for the dump
- group_ID = ID of the group of atoms to be dumped
- N = dump every this many timesteps
- file = name of file to write dump info to
- args = list of arguments for a particular style

4.1.4 Run a simulation

The run command is used to run a molecular dynamics simulation. The syntax of the command is

```
run N
```

Where N = number of timesteps. The minimize command is used to accomplish energy minimization (molecular statics). The temper command can be used to execute a parallel tempering (replica-exchange) simulation. For a set amount of timesteps, run or continue dynamics. N refers to outer loop (biggest) timesteps when the run style is RESPA. A value of N = 0 is allowed; simply, the system's thermodynamics are computed and displayed, and no timestep is taken. The up to keyword indicates that a run should begin at the current timestep and end at the specified time step. For example, if the current timestep is 10,000 and the command "run 100000 up to" is used, an extra 90,000 timesteps will be executed. This is excellent for extended runs on a computer that allocates time chunks and terminates your job when the time limit is reached. You can keep restarting your script if you need to restart it numerous times (reading in the last restart file). You can keep restarting your script with the same run command until the simulation finally completes.

4.1.5 Simulation detail

We have used the LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) using a rigid package to simulate our system. We begin each of our simulations by distributing N = 400 particles in a square box of area A = $L_x * L_y$. We start the simulation by NVT ensemble first for 10,0000 timesteps. Next, we switched the simulation ensemble to NPT and waited for $2 * 10^6$ MD steps for the system to get equilibrated. The reason for performing NVT first is that, as we reach high density for some value of (P, T) the particles have less chance to move in the ensemble. Like in glass formation, the particles get cooled rapidly by applying high pressure to lower the temperature. Similarly, the particle gets compressed very fastly at high pressure in our case. Thus NVT gives the particular time to move in the system. After that, they are simulated in the NPT ensemble. After this, every 100 timesteps, the data is collected, such as temperature, energy per pair, the total energy of particle, pressure, volume, and density. We repeated this procedure by assigning a different value of a number of sub-atom,i.e., nsa 2-6, pressure 2-20 at an increment of 2, and different temperatures from 0.6 to 2.0 at an increment of 0.2. The use of Radial distribution function and Statistical structure factor helped in determining the phase of the system at each of these point so as to form a phase diagram,which raveled the effect of external potential on the phase transition of our system.

4.2 Analysis of input script

In this section, we will analyze the LAMMPS script that we use to simulate our system. We divide our script into three parts -initialization, simulation settings, and data collection. we will discuses each one by one.

4.2.1 Part 1 of script

The first part is divided into two sections. In the first part, the variables are defined, and in the second part, we initialize the microscopic and macro-

scopic properties for simulation.

```
variable nsa equal 2 # number of sub-atoms
variable nbp equal 400 # number of atoms
variable T equal 1.0
variable P equal 18
variable Tstart equal $T
variable Tstop equal $T
variable Tdamp equal 1
variable Pstart equal $P
variable Pstop equal $P
variable Pdamp equal 10
log log.YK.nsa.$nsa.nbp.$nbp.T.$T.P.$P
# 2D polygonal rigid body system
variable tfreq equal 100 # thermo frequency
variable dfreq equal 100 # dump frequency
variable stime equal 100000
variable rtime equal 100000
```

This part defines the variables and commands used for assigning one or more strings to a variable name for evaluation later in the input script or during a simulation. For example, we define nsa(number of sub-atoms), nbp(number of particles), Temperature, Pressure, etc. The command log is used to close the current LAMMPS log file, open a new file with the specified name, and begin logging information to it. If the specified filename is none, no new log file is opened. We use this command to save information in file log.YK.nsa.$nsa.nbp.$nbp.T.$T.P.$P.

```
units lj
dimension 2
atom_style full
read_data data.nsa.$nsa.nbp.$nbp
velocity all create 0.1 87287 loop geom
pair_style lj/cut 6.0
pair_coeff * * 1.00 1.0
#pair_style yukawa 2.0 6.0
#pair_coeff * * 100.0 6.0
bond_style harmonic
bond_coeff 1 999.9 1.16 # fake number
#angle_style harmonic
#angle_coeff 1 999.9 180.0 # fake number
neighbor 0.5 bin
neigh_modify every 10 delay 20 check yes
```

In this part, we initialize the macroscopic properties like unit, dimension, and atom style and give the position of the initial configuration of a particle in the simulation box. We used the LJ units and began each of our simulations by distributing N = 400 particles in a rectangular box of area A = $L_x * L_y$. After this, we defined the pair style and pair coefficient. Here the bond style and bond coefficient are just fake numbers since they were not used during the simulation.

4.2.2 Part 2 of Script

In this second part, we divided this section into two parts. In the first part, we are fixing the conditions for simulation. The second part computes the different properties like particle motion after simulation, system temperature, density, and volume.

```
reset_timestep 0
fix 1 all rigid/nvt/small molecule temp $Tstart $Tstop $Tdamp
fix 2 all enforce2d
thermo $tfreq
run $stime
unfix 1
unfix 2
#fix 1 all rigid/nve molecule
#fix 1 all rigid/nve/small molecule
#fix 1 all rigid/nvt/small molecule temp $Tstart $Tstop $Tdamp
#fix 1 all rigid/small molecule langevin $Tstart $Tstop $Tdamp 4363426
fix 1 all rigid/npt/small molecule temp $Tstart $Tstop $Tdamp iso
$Pstart $Pstop $Pdamp

fix 2 all enforce2d
```

In this part, we reset the timestep to zero. Then fix the NVT ensemble for the first 10^5 time steps. The reason for doing so is the particle doesn't get enough time and space to move in the system at high pressure and temperature. They come close to each other very fast at the high temperature and pressure, as the density gets very high. After this time step, we fix the NPT ensemble for the system.

```
compute 1 all rigid/local 1 id mol x y z
#dump 1 all atom $dfreq dump.LJ.nsa.$nsa.nbp.$nbp.T.$T.P.$P.atom
dump 1 all custom $dfreq
dump.LJ.nsa.$nsa.nbp.$nbp.T.$T.P.$P.custom id mol x y z ix iy iz xu
yu zu
#dump 1 all local $dfreq
dump.LJ.nsa.$nsa.nbp.$nbp.T.$T.P.$P.local c_1[1] c_1[2] c_1[3] c_1[4]
#dump 2 all image $dfreq
jpg/image.LJ.nsa.$nsa.nbp.$nbp.T.$T.P.$P.t.*.jpg type type &
# zoom 1.75 adiam 1.0 size 1000 1000
#dump_modify 2 pad 5
compute ketran all ke/rigid 1
compute kerot all erotate/rigid 1
compute temp all temp
#thermo_style custom step c_ketran c_kerot temp c_temp pe ebond ean-
gle
thermo_style custom step temp epair etotal press vol density
```

In this part, we performe simulation settings. Then we use comupte command, which simply stores rigid body attributes for rigid bodies defined by the fix rigid/small command or one of its NVE, NVT, NPT, NPH variants and then store that that in dump file. After that we calculate the translational kinetic energy of a collection of rigid bodies, and the rotational

kinetic energy of a collection of rigid bodies, as defined by one of the fix rigid command variants. We used the thermo_style command to print the timestep, tempreature, pair energy, total energy, pressure volume, and density in the log file.

4.2.3 Part 3 of Script

In the last part, we use the restart command to make the restart file. In case we want to restart the simulation from the point where the simulation ends. After that, we run the simulation for the next 10^5 time step. As the system gets equilibrated, we took the output for the next 10^5 time step in the log file.

```
restart $dfreq restart.LJ.nsa.$nsa.nbp.$nbp.T.$T.P.$P.1
restart.LJ.nsa.$nsa.nbp.$nbp.T.$T.P.$P.2
write_data data.LJ.nsa.$nsa.nbp.$nbp.T.$T.P.$P nocoeff nofix
write_data data.LJ.nsa.$nsa.nbp.$nbp.T.$T.P.$P nocoeff nofix
thermo $tfreq
run $stime
log log.LJ.nsa.$nsa.nbp.$nbp.T.$T.P.$P.equ
thermo $tfreq

run $rtime
```

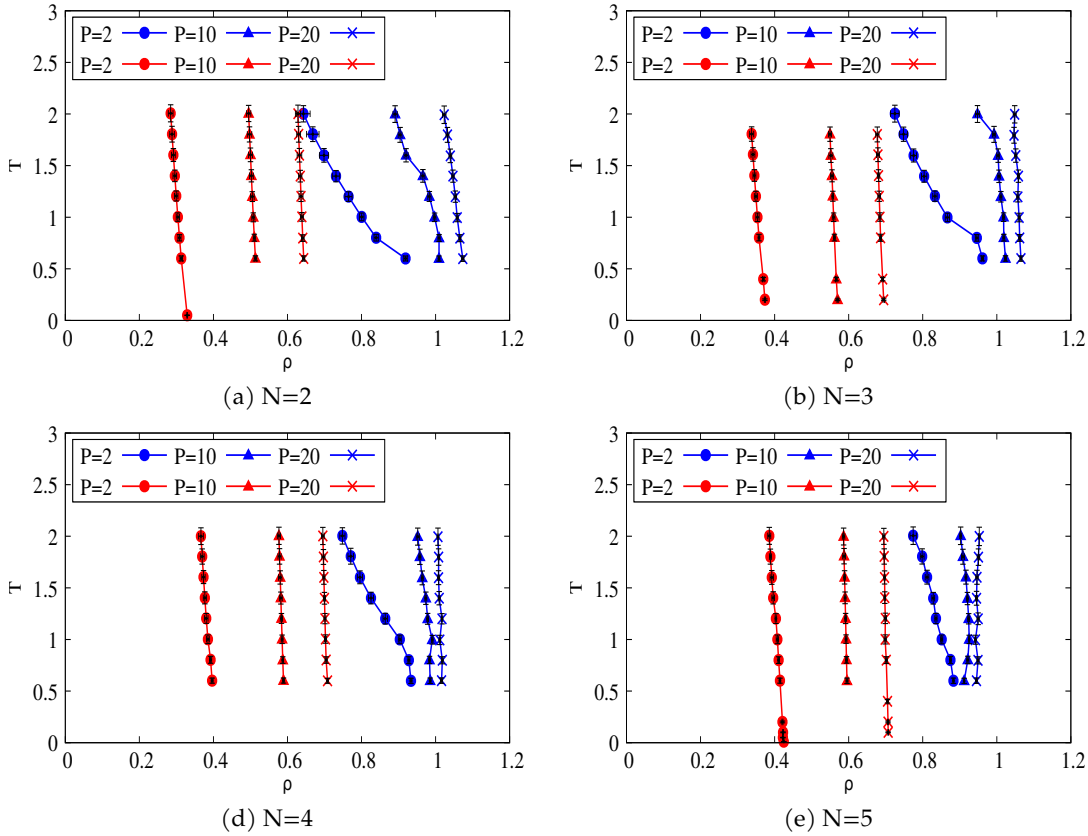
Chapter 5

Result and Discussion

In this chapter, we discussed the result of our simulation. We interpreted the data obtained using different techniques such as the graph between the temperature and density, RDF, and SSF. By using such techniques, we are trying to note the effect of changing the interaction between the molecule and the shape of the molecule and then we identify the phases of the system by observing the phase images.

5.1 Effect of enthalpic entropy

To observe the effect of enthalpic entropy, we plotted the graph between density vs. temperature for a different shape of molecules in both interactions at different value of pressure, shown in figure 5.1. In this figure, the curve with red color is for YK-potential and blue is for LJ-potential. From these curves, it was clear that temperature has less effect on density for YK potential. For YK potential as the temperature rises, the density changes very slowly. Also, as the pressure increases, the temperature's effect on density becomes less. For example in figure 5.1, for N=2 in YK potential (curves in red color) at P=2, the slope of the line is greater than the slope of the line P=20. Whereas for LJ-potential, temperature has a significant effect on density. The density of the system increase as the temperature decreases. Also the pressure on the system increases, the effect of temperature on density decreases. In figure 5.1, it was clear that when we change the interaction, behavior of curve is the same for one at lower pressure in YK-potential and another at higher pressure for LJ-potential. For example in figure 5.1, the curve for N=3 in YK-potential at P=2 is the same as for LJ-potential at P=20. The error bar of the curve points indicate the error



(a) N=2 (b) N=3

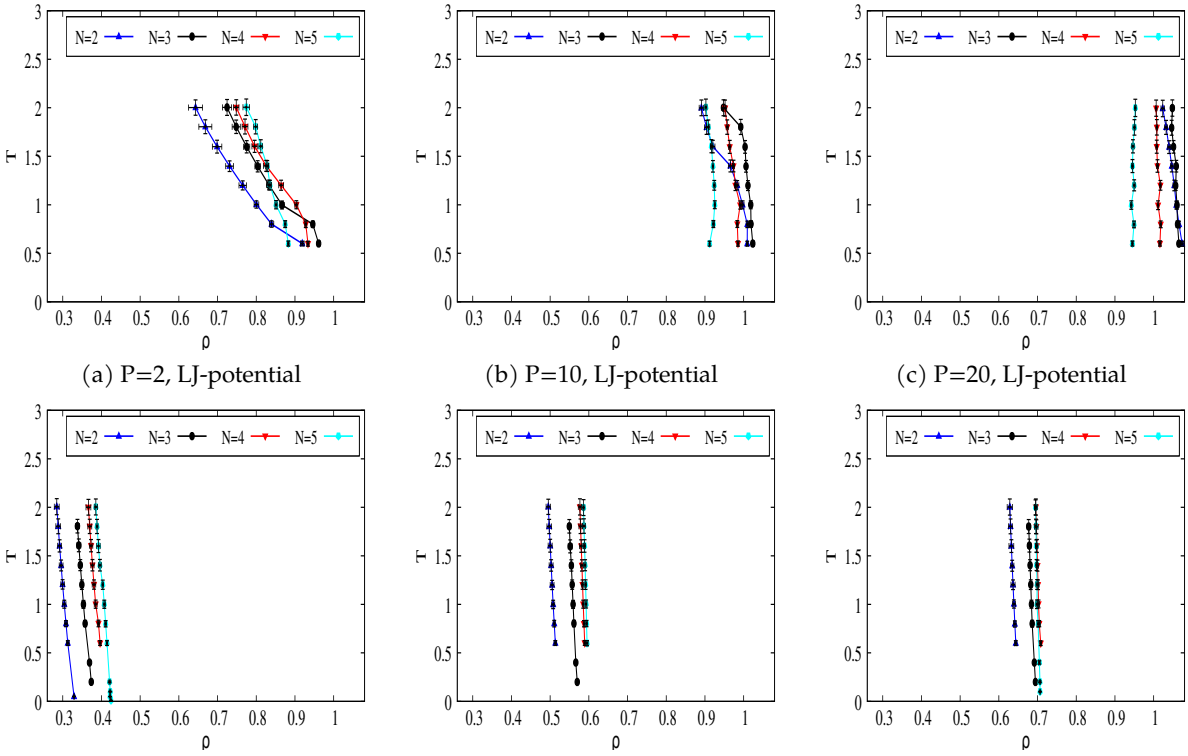
(d) N=4 (e) N=5

Figure 5.1: Effect of enthalpic entropy

or uncertainty in a reported measurement. As the system's temperature decreases, the error bars are also reducing. This is because the entropy of a system approaches a constant value when its temperature approaches absolute zero(third law of thermodynamics).

5.2 Effect of configurational entropy

In this section, we see the effect of configuration of molecule on the phase of system. For this, we plot the graph between density vs. temperature for different values of N. Density is directly proportional to pressure and indirectly proportional to temperature. As pressure increases, with constant temperature, density increases clearly shown in figure 5.2. Conversely, when temperature increases, with pressure constant, density decreases.



(a) P=2, LJ-potential (b) P=10, LJ-potential (c) P=20, LJ-potential

(d) P=2, YK-potential (e) P=10, YK-potential (f) P=20, YK-potential

Figure 5.2: Effect of configurational entropy

For example in figure 5.2(a), the curve for P=2 the density of the system decreases with the increase in temperature. But as the value of N increases, the effect of temperature on density decreases. The density value reduces from 0.912 to 0.643 ($\Delta = 0.269$) whereas for N=5, the density goes from 0.882 to 0.774 ($\Delta = 0.108$) which is very small change. Also, as the pressure gets high, the curve for a high value of N moves backward. For example, the curve for N=4 gets closer to the N=3 curve in figure5.2.

5.3 Phase Diagram

Now we present the phase diagram of our system, shown in figure **??** and figure 5.13. To determine the different phases of the system, we plotted the particle's final positions after equilibrium, their RDF, and SSF. To determine the phase, we check every point which we simulate.

5.3.1 Phase Diagram for LJ-system

For phase diagrams of LJ-system, we have plotted the points on density-temperature plane shown in figure **??**. This represent the phase diagram obtained for different values of N in LJ-potential.

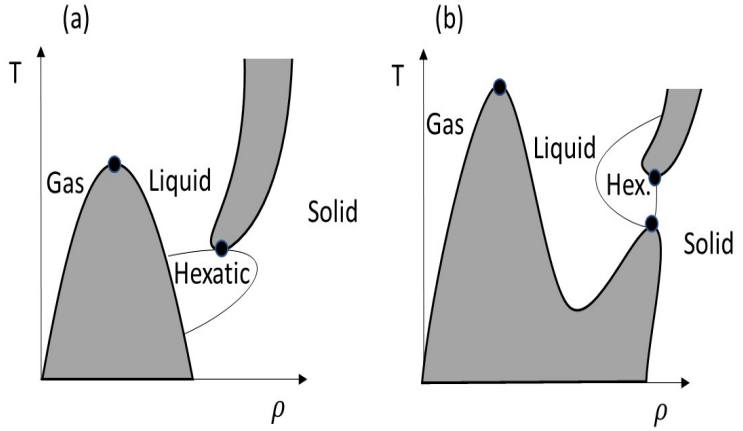


Figure 5.3: Speculated phase diagrams of the two-dimensional LJ systems, in T -ρ plane. The shadowed regions indicate phase coexistence [28].

Figure 5.3 represent the speculated phase diagrams of the two-dimensional LJ systems, in T-ρ plane[28]. The shadowed regions indicate phase coexistence. The phase diagram for N=2 is similar to the phase diagram of the LJ system fluid of the spherical shape particles, shown in figure 5.4. As the number of sub-atomic(N) particles increases, the liquid region shrinks, and the whole region solidifies at a higher value of N. The blue dots represent the liquid phase, and the red dot represent the solid phase. In the investigation of the system phase, we plotted the position of all particles of the system at equilibrium. This gave us the initial picture of the phase of the system. By looking at these plots, we can easily check whether the system is ordered in some symmetry which representing the solid phase of the system or liquid if it's disordered.

Consider figure 5.5 in each of these figures, we plotted the positions of all the dimmers(N=2) after the equilibrium in the LJ-potential. In fig. 5.5(a), we notice that at pressure(P)=2 and temperature(T)=0.8, particles are not

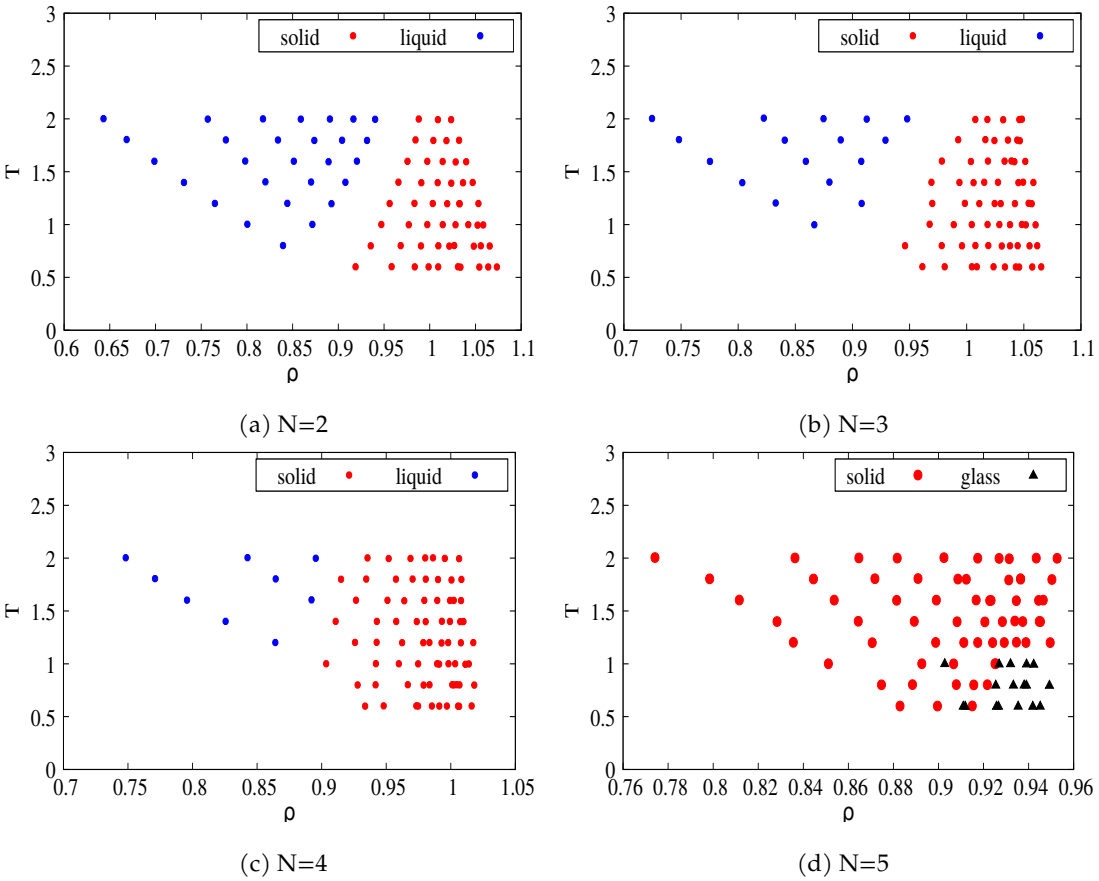
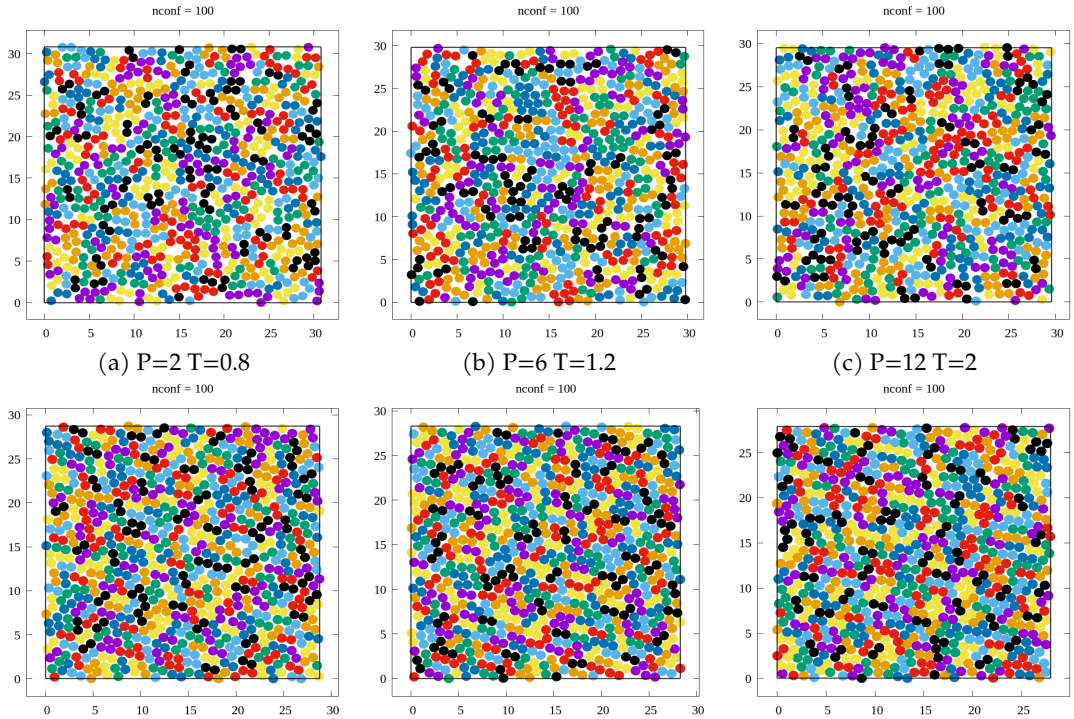


Figure 5.4: Phase diagram of the LJ system. The blue dots represent liquid phase, and red dots represent the solid phase. Figure 5.4(a) represent the phase diagram for system consisting of dimer molecules. Figure 5.4(b) represent the phase diagram for system consisting of trimer molecules. Figure 5.4(c) represent the phase diagram for system consisting of quadmer molecules. Figure 5.4(d) represent the phase diagram for system consisting of pentamer molecules.

arranged in any symmetry. This means that the particle is aligned in a random direction and does not contribute to any symmetry. If we draw a line along any axis, we don't observe any particle alignment. This means that the system is in liquid phase.

Similarly, in fig. 5.5(b), and 5.5(c) the particles are not aligned in any direction. Hence these also represent the liquid phase. Where in the figure 5.5(d), 5.5(e) and 5.5(f), it represent the solid phase of the system. We have checked the RDF and SSF for these states to analyze their phase. Figure 5.8 represent the behavior of RDF and SSF at a specific P and T. By



(a) P=2 T=0.8 (b) P=6 T=1.2 (c) P=12 T=2

(d) P=6 T=0.8 (e) P=10 T=1 (f) P=18 T=1.8

Figure 5.5: Snapshot of dimer, N = 2 of 400 particle. The system size is $L_x * L_y$. (a) Snapshot of system at pressure(P) = 2 and temperature(T) = 0.8, (b) P = 6 and T=1.2 , (c) P=12 and T=2, (d) P=6 and T=0.8 , (e) P=10 and T=1, (f) P=18 and T=1.8

observing the figure 5.6(a), 5.6(b), 5.6(c), the RDF curve clearly shows that these phases are liquid and SSF plots shows that phase is disordered.

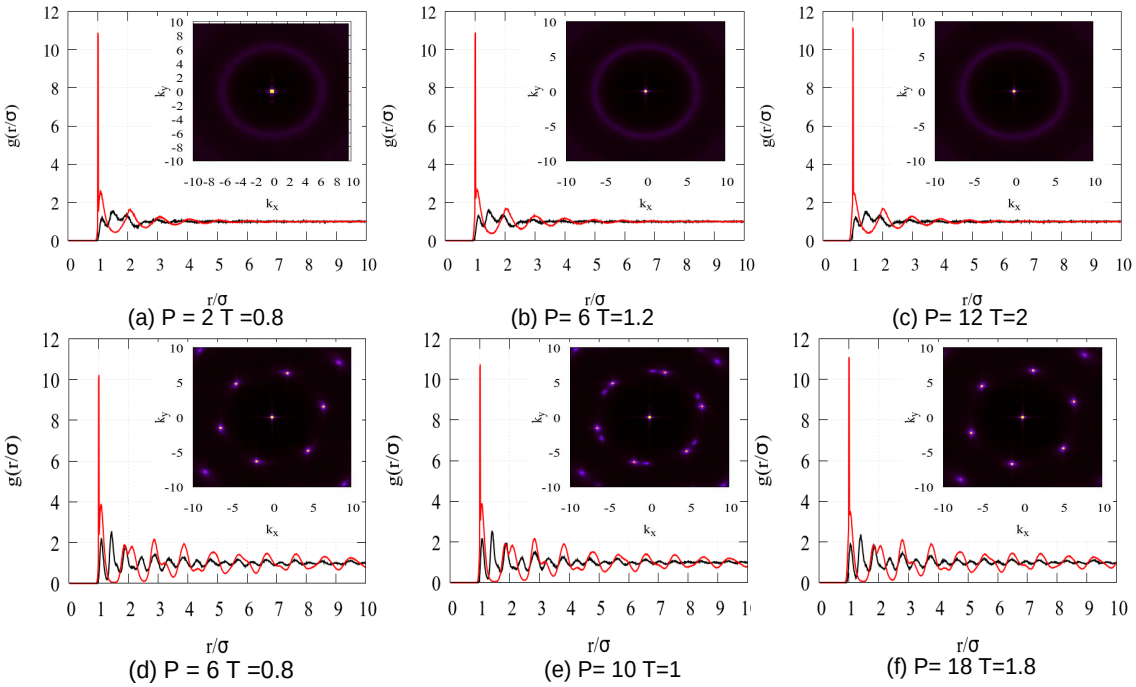
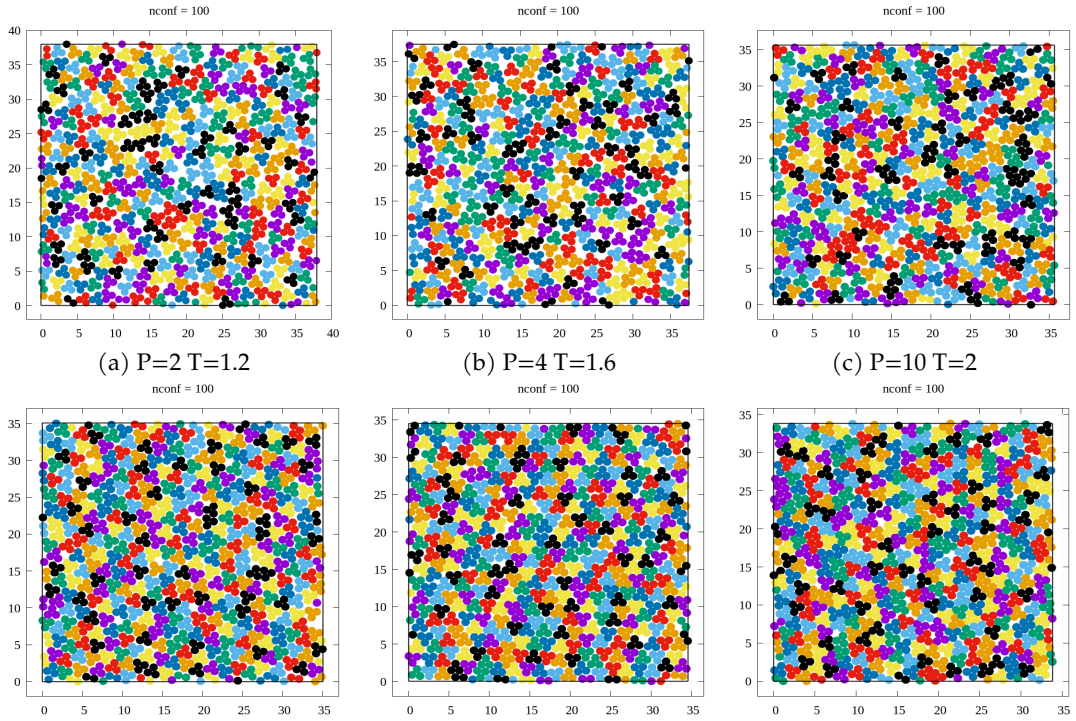


Figure 5.6: Radial distribution function with their associated structure factors.

Figure 5.6(d), 5.6(e), 5.6(f) represent the solid phase at these specific value. At P=6 and T=0.8, shown in figure 5.6(d), the RDF behavior shows that phase is solid with hexagonal symmetry. Whereas P=10 and T=1, the RDF shows the solid phase, but the SSF plot indicates that there is no symmetry. Thus, at this point, the phase is solid without any symmetry. Figures 5.6(f) is also solid phases with hexagonal symmetry. Thus, the plots for SSF in fig. 5.6(a), 5.5(b), and 5.5(c), we identify them as liquid phase and in Fig. 5.6(d), 5.6(e), 5.6(f) we identify them as solid phase.



(a) P=2 T=1.2 (b) P=4 T=1.6 (c) P=10 T=2

(d) P=4 T=0.8 (e) P=8 T=1.0 (f) P=20 T=1.8

Figure 5.7: Snapshot of trimer, N = 3 of 400 particle. The system size is $L_x * L_y$. (a) Snapshot of system at P=2 and T=1.2, (b) P=4 and T=1.6 , (c) P=10 and T=2.0, (d) P=4 and T=0.8, (e) P=8 and T=1.0, (f) P=20 and T=1.8.

Figure 5.7 shows the trimar molecule (N=3) position after the equilibrium is achieved at some specific value of P and T. They are arranged in random order. In fig. 5.7(b), they are also arranged in random order. Hence this is the liquid phase of system. Thus we represent the fig.(a) to fig(c) as liquid phases. To confirm the phase, we have to look at their RDF and SSF plots. Also, in fig. 5.7(d) to (f) are in the solid phase. At the values of P and T, the molecules are arranged in symmetry. In fig.5.7(f), if we draw the line diagonally, the molecules are trying to Aline diagonally. But as the value of T increases, the order of particles decreases. In fig 5.7(f), at P=20 and T=1.8, it is clear that the symmetry of the molecule is low. To observe the symmetry of molecule and phase, we must consider their RDF and SSF plots. In fig. 5.8, we show the RDF and SSF plot for these values of P and T.

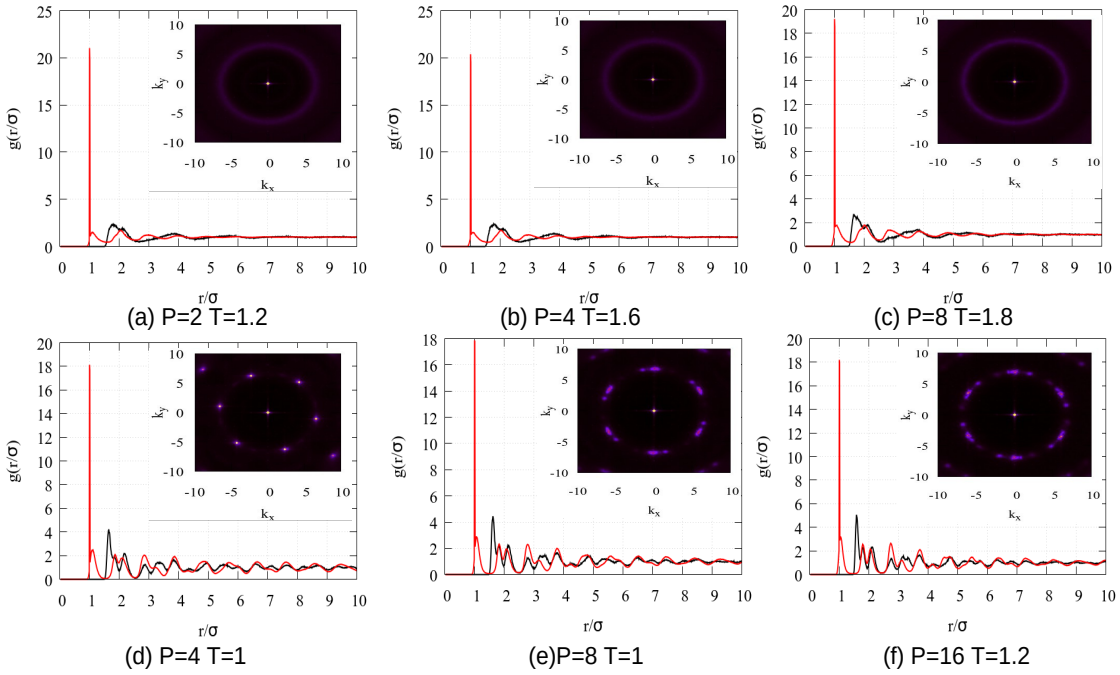


Figure 5.8: Radial distribution function with their associated structure factors.

From fig.5.8(a) to 5.8(c), it is clear that these values are disordered liquid phases. In fig. 5.8(d), the phase is solid. There is hexagonal symmetry in the system. Which means that the molecules are trying to arrange themselves in hexagonal symmetry. In fig 5.8(e),5.8(f) we identify them as solid phases. But according to the SSF plot, there is not any specific symmetry. They are trying to come in order but are in the solid phase.

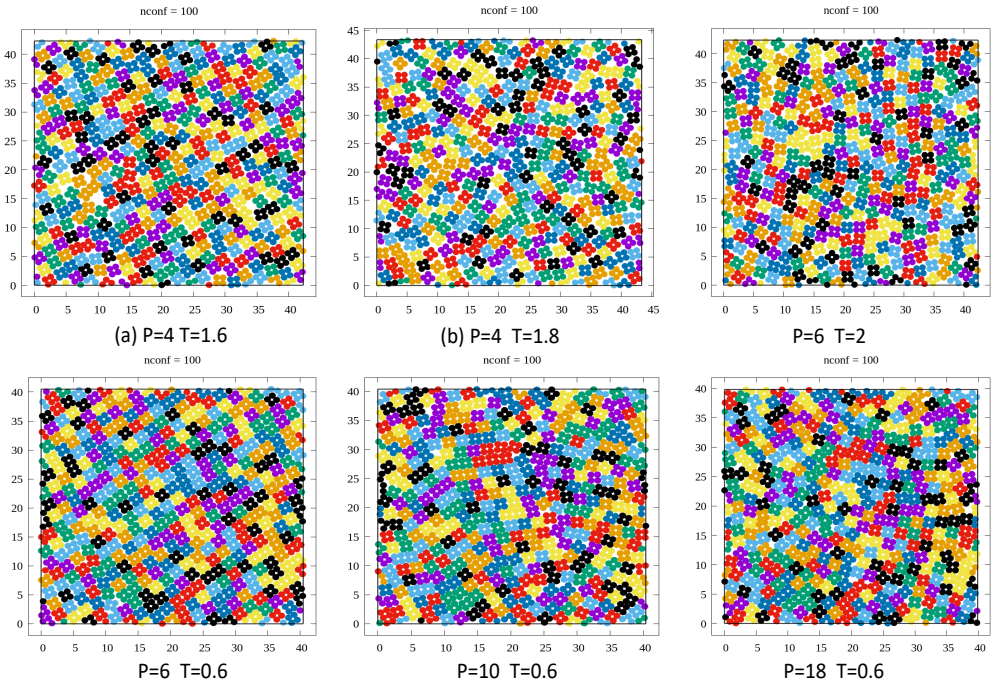


Figure 5.9: Snapshot of quadmer, N = 4 of 400 particle. The system size is $L_x * L_y$. (a) Snapshot of system at P=4 and T=1.6, (b) P=4 and T=1.8, (c) P=6 and T=2, (d) P=6 and T=0.6, (e) P=10 and T=0.6 & (f) P=18 and T=0.6

Now we will discuss the result for N=4. In fig.5.9, we represent the snapshots of the molecule's position after equilibrium. As there are four particles in one molecule hence we should expect that we get the rhomboid symmetry for the solid phase. In fig.5.9(a), the molecules are not arranged in any particular direction. Thus seems to be a liquid phase. Similarly, as the pressure and temperature increase, the randomness also increases. And the reason is that as the system's temperature increases, the molecule will move fast in the system. In fig.5.9(d), at P=6 and T=0.6 the molecules are well arranged. In fig. 5.9(d), if we draw the line the molecules are aligned along this line hence contribute to the symmetry of the system.

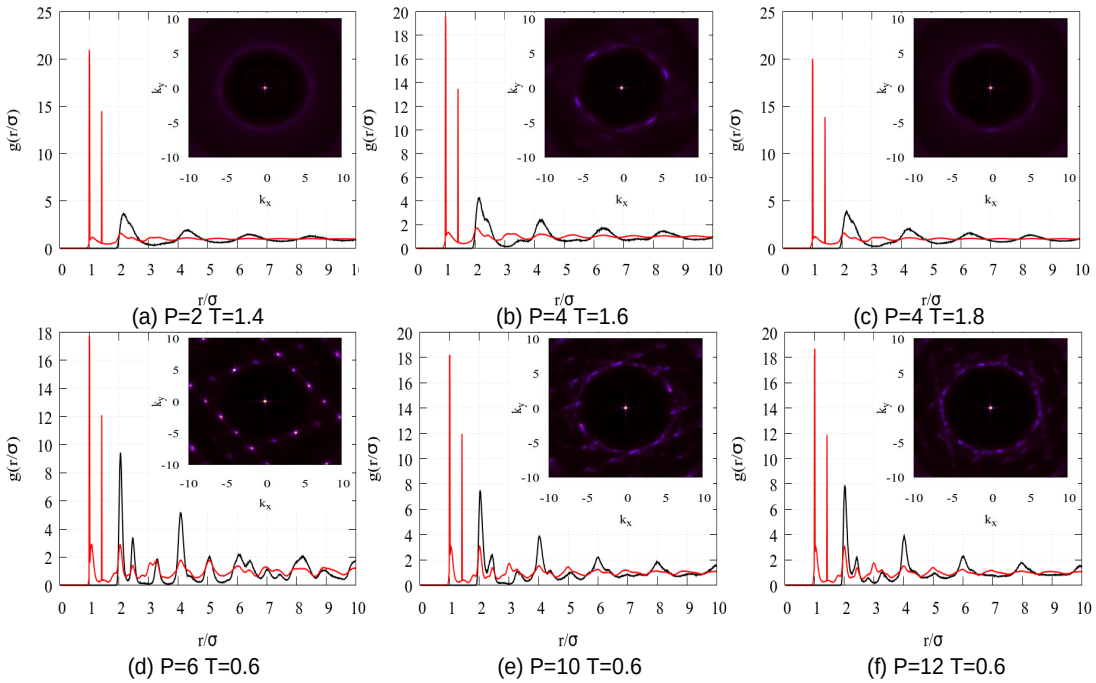
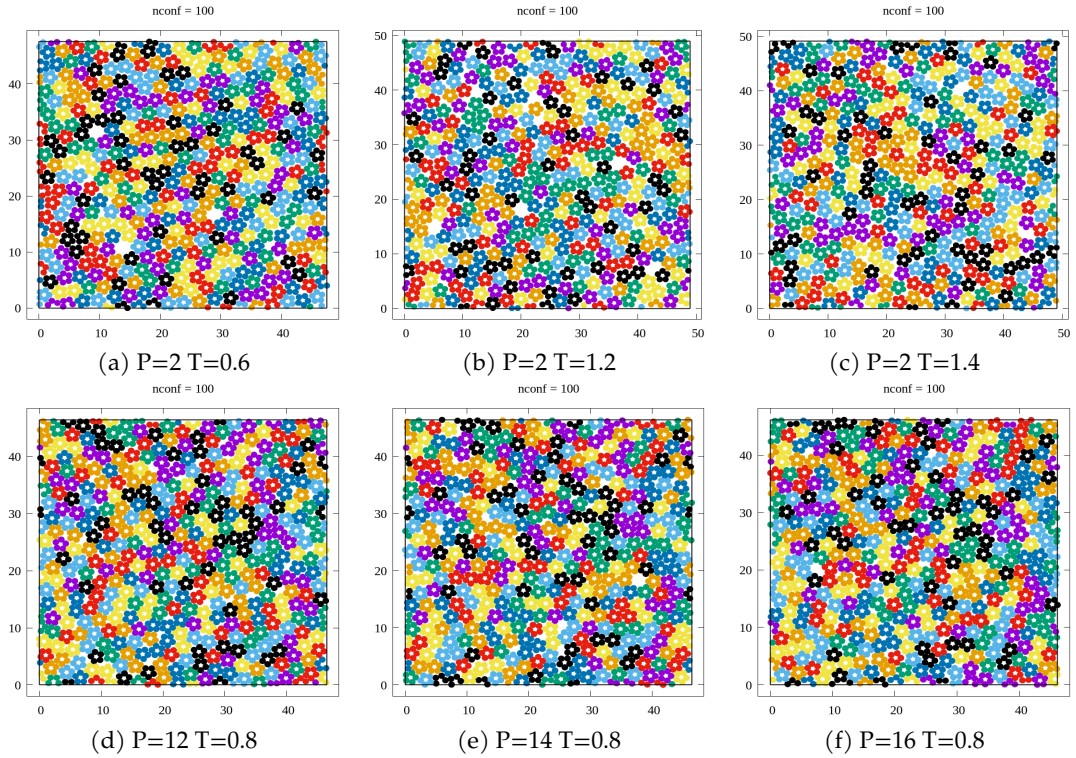


Figure 5.10: Radial distribution function with their associated structure factors

But as the pressure is increased, keeping the temperature constant, the ordered system gets disordered but remain in the solid phase. Figure 5.10 represents the RDF and SSF plots for these specific P and T values. In fig.5.10(a) to 5.10(c) shows the liquid phase of the system. The RDF curve doesn't give any peak, indicating that the system is in the liquid phase at these specific points. Also, the SSF plot does not show any order. Thus the system is a disordered liquid phase. Fig 5.10(d) to 5.10(f) represent the solid phase of the system. The RDF curve indicates the solid phase of the system. In fig. 5.10(d), the SSF plot shows the rhomboid symmetry. This means that in the system at P=6 and T=0.6, the molecules are arranged in a square symmetry. But if we kept the temperature constant and increased the pressure, as shown in fig.5.10(d) to fig.5.10(f), it is clear that the ordered system gets disordered. This means that the pressure affects the ordering or symmetry of the system. Fig.5.11 represent the snapshots of system for N=5, at some specific value of P and T. For this system the glass phase is observed. The glass phase is deemed to be a special form of



(a) P=2 T=0.6 (b) P=2 T=1.2 (c) P=2 T=1.4

(d) P=12 T=0.8 (e) P=14 T=0.8 (f) P=16 T=0.8

Figure 5.11: Snapshot of pentamer, N = 5 of 400 particle. The system size is $L_x * L_y$. (a) Snapshot of system at P=2 and T=0.6, (b) P=2 and T=1.2, (c) P=2 and T=1.4, (d) P=12 and T=0.8, (e) P=14 and T=0.8, (f) P=16 and T=0.8.

a solid. While the material feels hard, it lacks a regular crystalline structure. Glass formation usually takes place by rapid cooling of the molten mass past the crystallisation temperature and the solidification starts at the glass transition temperature. Similarly, when we apply the high pressure the molecules not get enough time to move and they get close to each other making system density rapidly high. For this system we are observing maximum solid point in phase diagram, but for some value of low temperature and high density, glass phase is observed. Thus to confirm the phase of system, we have to investigate the RDF and SSF plots.

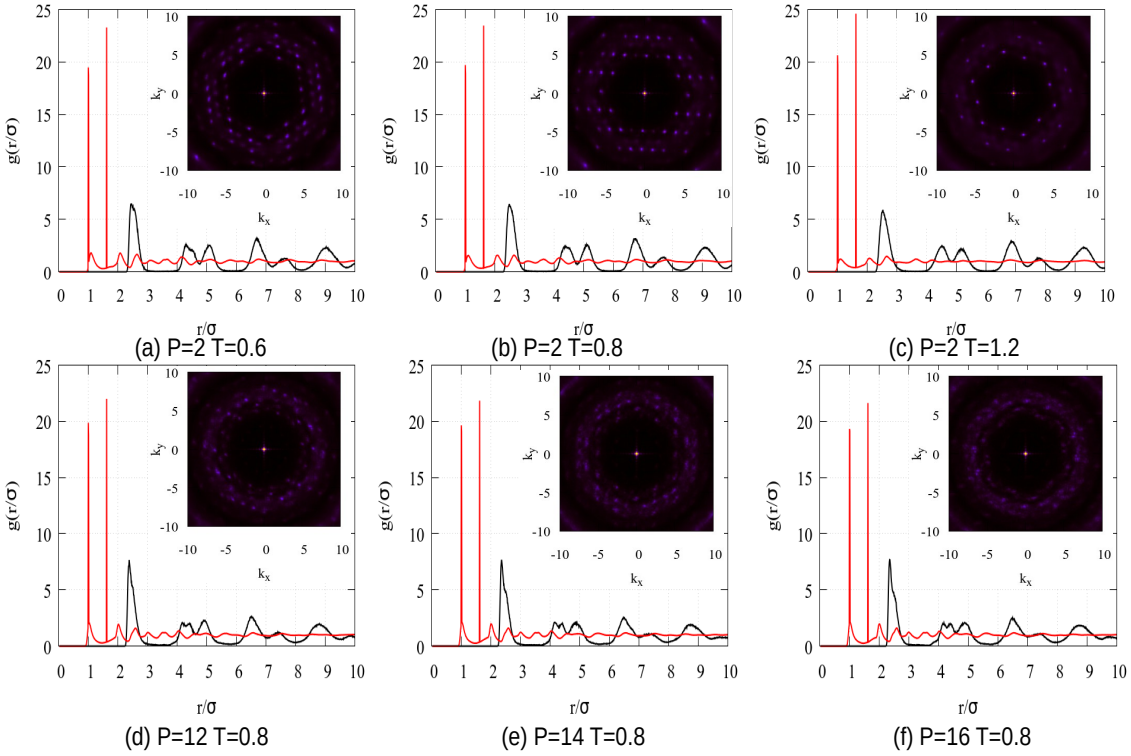


Figure 5.12: Radial distribution function with their associated structure factors.

According to the fig.5.12(a) to fig.5.12(c), these phases are solid. At P=2 and T=0.6, this system is solid, but the order is not clear of the system. Similarly, in fig.5.12.(b) the system is not showing any symmetry. Fig.5.12(c) show the hexagonal symmetry in the system.

5.3.2 Phase Diagram for YK-system

For the YK-system, we have investigated each point that we simulate and found the phase and symmetry of that system. To determine the phase and symmetry of the system, we observe the positions of the molecules, pair correlation function, and statistical structure factor.

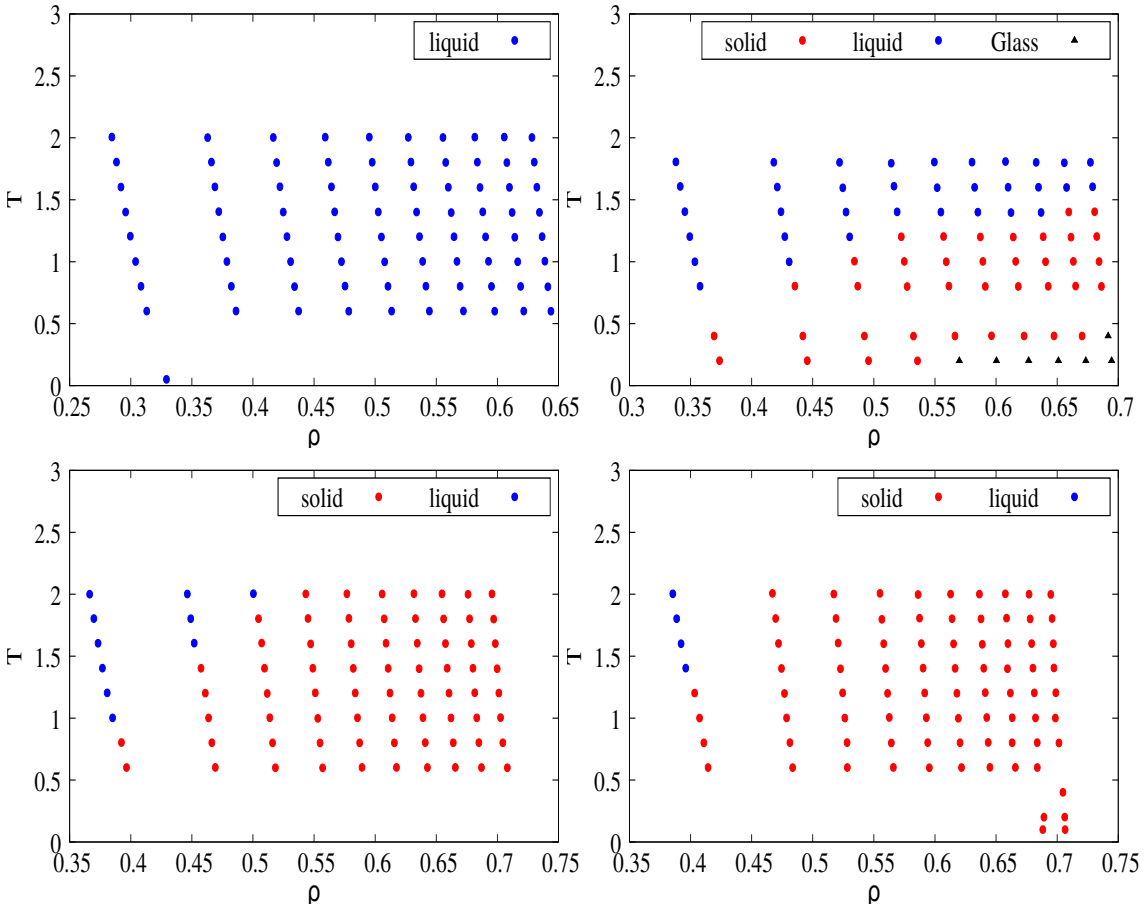


Figure 5.13: Phase diagram for YK-potential for different values of N. The blue dots represent the liquid phase, reds represent the solid phase, and black represent the glass phase.

Figure 5.13 represent the phase diagram for different value of N in YK-potential. Fig.5.13(a) represents the phase diagram for the dimer in a range of pressure of 2-20 in the density-temperature plane. We get the liquid phase over all the plane for dimer in YK-potential. The system is in the solid phase for trimer molecules at high density and low temperature.

And at high temperatures and low density, the system is in a liquid state. Also, the glass phase is identified at T =0.2 and high density.

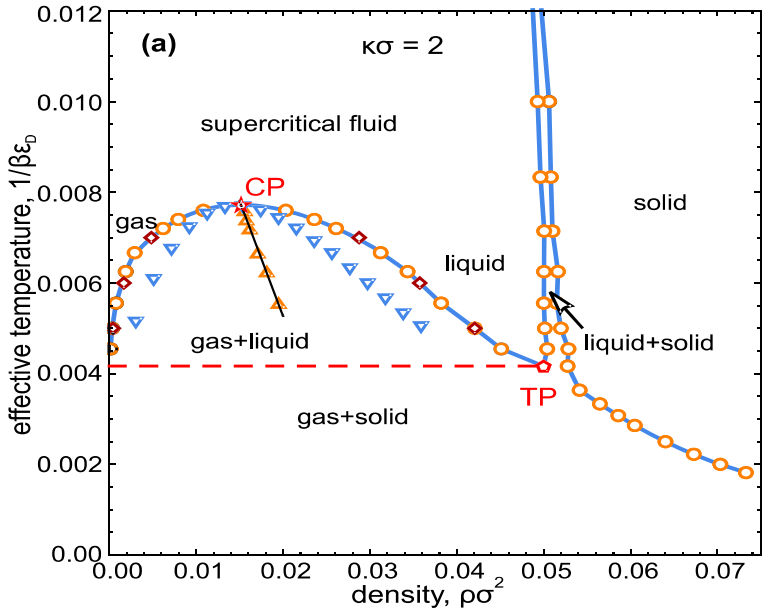


Figure 5.14: Phase diagram for YK-potential calculated at $\kappa\sigma = 2$. [29]

But as the number of subatomic particles(N) increases, the liquid phase shrinks. Like quadmer molecules, almost the region is in the solid phase. The reason for that is as the molecule's subatomic particle increased; the repulsion potential decreased because interatomic interaction is not considered for total potential. Fig. 5.14 represents the phase diagram of a two-dimensional (2D) system of colloidal particles, interacting via an isotropic potential with a short-ranged Yukawa repulsion and a long-ranged dipolar attraction [29].

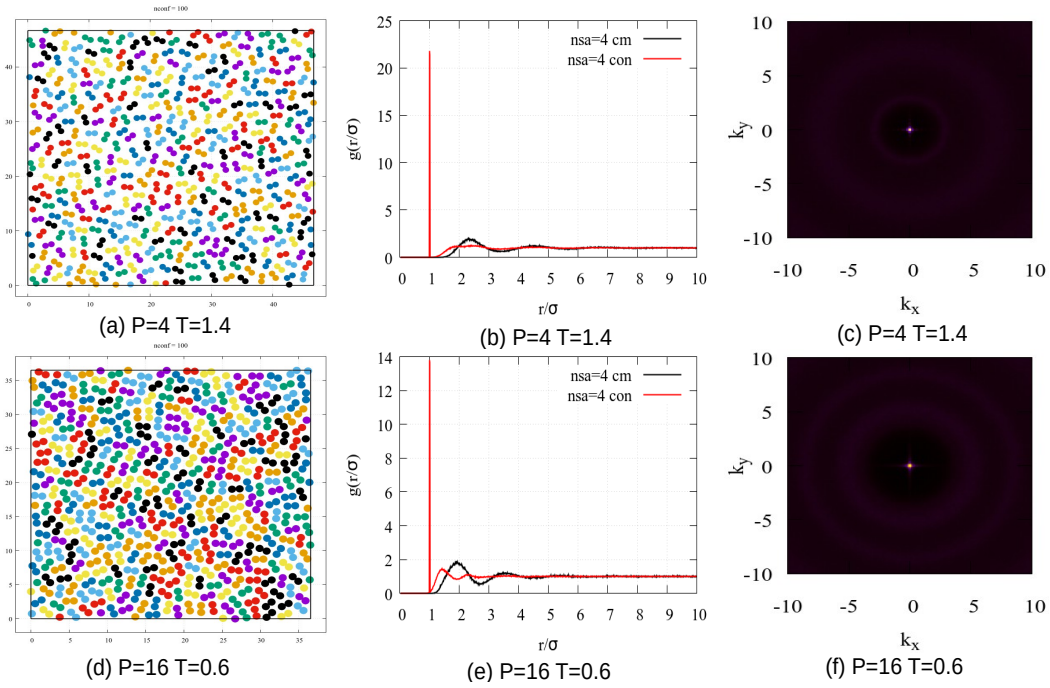


Figure 5.15: Snapshot of particles position in YK-potential after equilibrium. The system size is $L_x * L_y$. (a) Snapshot of system at P=4 and T=1.4, (b) RDF plot for P=4 and T=1.4, (c) SSF plot for P=4 and T=1.8, (d) Snapshot of system at P=16 and T=0.6, (e) RDF plot for P=16 and T=0.6, (f) SSF plot for P=16 and T=0.6.

Figure 5.15 represents the snapshots of the molecule's position after equilibrium. Fig.5.15(a) represents the dimer system at P=4 and T=1.4. The state of this system is liquid. It can be clearly seen that the system is not arranged in any particular direction, and no symmetry exists. In fig. 5.15(b), the RDF plot shows the liquid state, and the SSF plot in fig. 5.15(c), shows that the system is highly disordered. For the dimer system, we get all the states in the liquid phase, and the reason for that is the repulsive potential, due to which the particle cannot come closer to each other so that they can contribute to any symmetry.

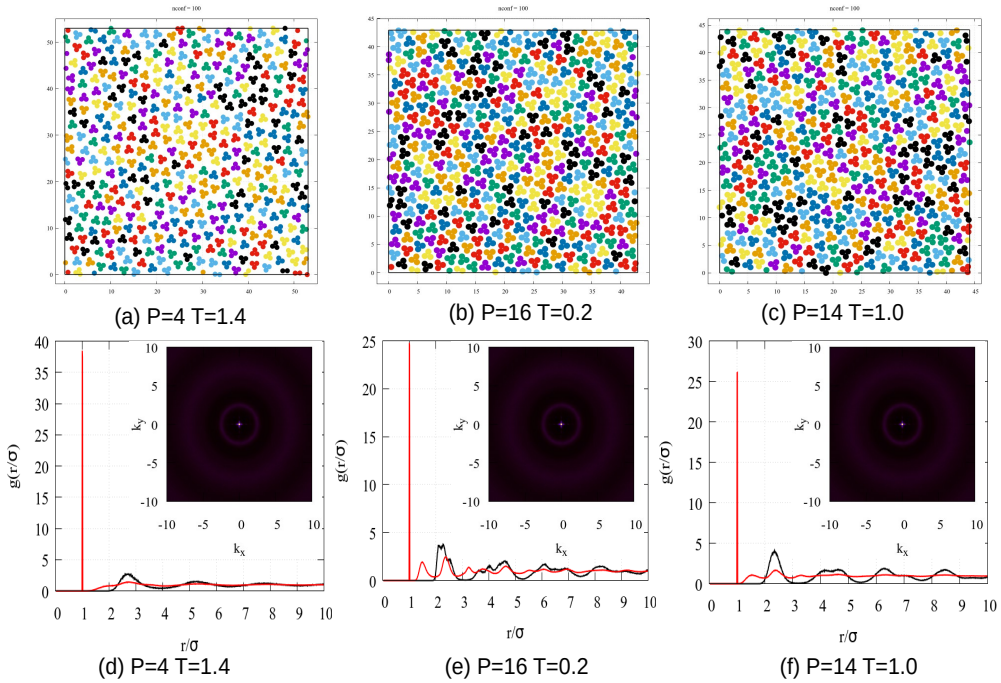


Figure 5.16: Snapshot of particles position in YK-potential after equilibrium. The system size is $L_x * L_y$. (a) Snapshot of system at P=4 and T=1.4, (b) Snapshot of system at P=16 and T=0.2, (c) Snapshot of system at P=14 and T=1.0, (d) RDF plot and their associated SSF plot for P=4 and T=1.4, (e) RDF plot and their associated SSF plot for P=16 and T=0.2, (f) RDF plot and their associated SSF plot for P=14 and T=1.0.

In fig. 5.16 represent the system of trimer molecule. Fig.5.16(a) represent the liquid phase of the system as the particle are not arranged well. According to RDF and SSF plot, Shown in fig. 5.16(d), indicate the liquid phase as the SSF plot not shown any type of symmetry. Fig. 5.16(c) represent the solid states for quadmer molecule. The fig.5.16(f) confirm that solid state for this values. For trimer molecule system at P=16 and T=0.2, shown in fig 5.16(b), the system is in glass phase, which is the crystalline solid without any symmetry. The RDF curve, in fig.5.16(e) shows the solid phase, but SSF has no symmetry. Thus we identify this phase as glass phase.

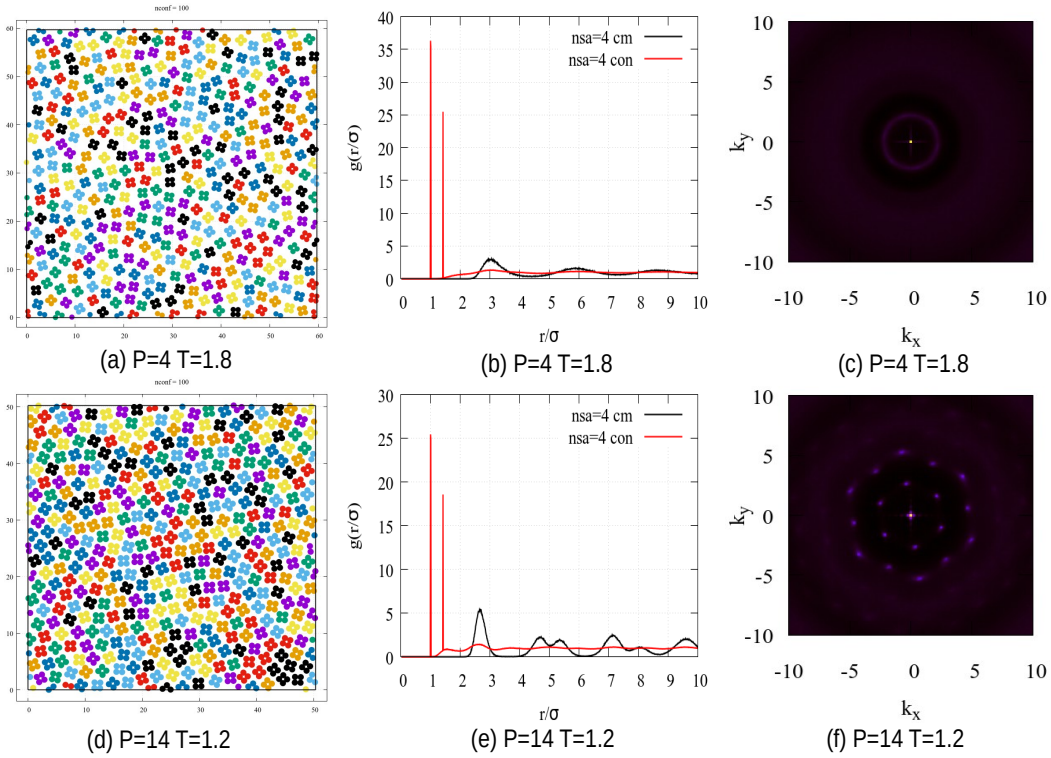


Figure 5.17: Snapshot of particles position in YK-potential after equilibrium. The system size is $L_x * L_y$. (a) Snapshot of system at P=4 and T=1.8, (b) RDF plot for P=4 and T=1.8, (c) SSF plot for P=4 and T=1.8, (d) Snapshot of system at P=14 and T=1.2, (e) RDF plot for P=16 and T=0.6, (f) SSF plot for P=16 and T=0.6

In fig. 5.17, this represent the quadmer molecule system. Fig 5.17(d) represent the liquid phase of the system. The RDF and SSF plot shows the liquid phase with hexagonal symmetry, shown in fig. 5.17(e) and 5.17(f) respectively.In fig 5.17(d) represent the solid phase of the system. The RDF and SSF plot shows the solid phase with hexagonal symmetry, shown in fig. 5.17(e) and 5.17(f).

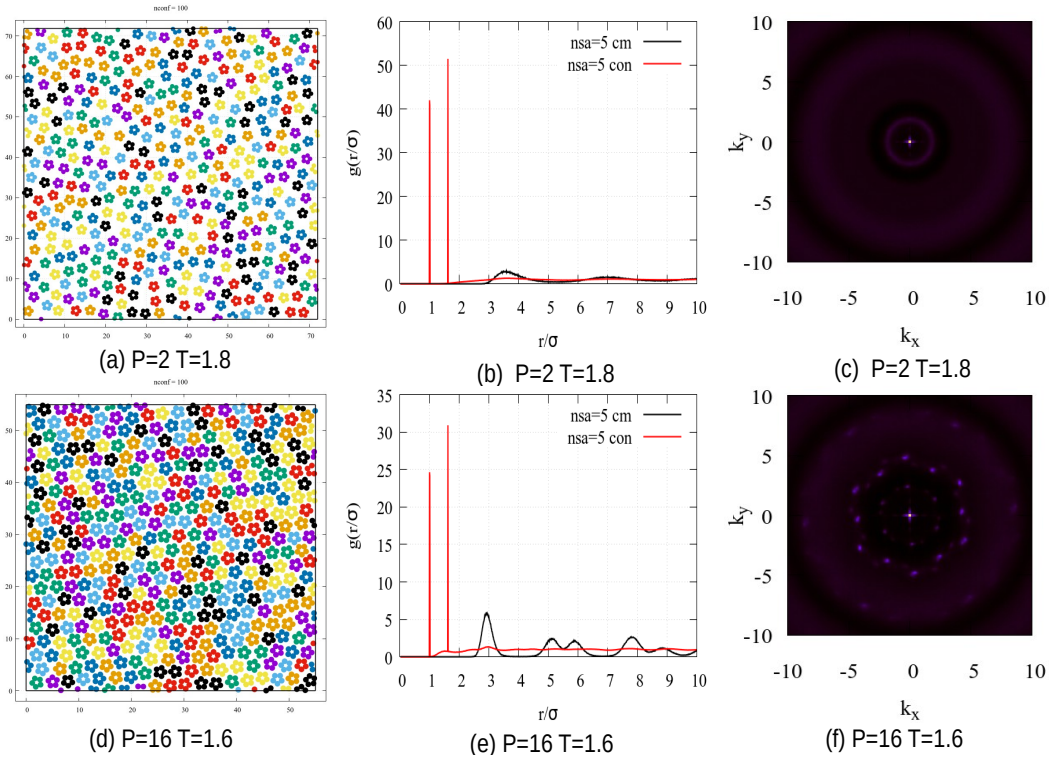


Figure 5.18: Snapshot of particles position in YK-potential after equilibrium. The system size is $L_x * L_y$. (a) Snapshot of system at P=4 and T=1.8, (b) RDF plot for P=4 and T=1.8, (c) SSF plot for P=4 and T=1.8, (d) Snapshot of system at P=14 and T=1.2, (e) RDF plot for P=16 and T=0.6, (f) SSF plot for P=16 and T=0.6.

Similarly, Fig. 5.18 represent the system for pentamer molecules. In fig. 5.18(a), the system is in the liquid phase. the RDF curve and the SSF plot showes the liquid phase which is disorder state. In fig.5.18(d) the system is solid phase ordering in hexagonal symmetry. The RDF curve and the SSF plot indicate that solid phase.

Chapter 6

Conclusion

In this work, we aimed to investigate the phase transitions and the effect of the type of entropy on total system entropy. Since the phase transition is an important property in material processing, thus the study of phase transition in a different kind of entropy becomes interesting. Also, to see the effect of different types of entropy, i.e., configurational and enthalpic entropy, on total system entropy. In order to achieve this task, we simulated a system of differently shaped molecules and observed the effect of interaction on different shape molecules. We considered a number of different systems with varying the shape of molecules and interactions between molecules so as to obtain a complete phase diagram. For each interaction, we simulated four types of different shapes of molecules system, like dimer, trimer, quadmer, and pentamer. To get better statistical averages from the simulations, we simulated each system initialized with different P and T. We investigated the phase of our system at each pair of pressure and temperature (P, T) using different techniques. From this study, we concluded that configurational entropy has a negligible effect, whereas enthalpic entropy has a considerable effect on system entropy. Also, the enthalpic entropy has well enough effect on the phase transition of the system, as the interaction change between the molecules, the phase behavior of the system also changes drastically. Thus we have successfully established the effect of entropy on system behavior. In the future, a more detailed phase diagram can be obtained for a big system, where the locations of the phase boundaries may be identified precisely, and also the nature of the phase transitions can be investigated. Moreover, one may also investigate the defects in those phases and determine whether the defects are the same in different conditions.

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