Structure and phase behavior of fluids in porous media

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Structure and Phase Behavior of Fluids in Porous Media

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ABSTRACT

Fluids confined within pores, which are micro- to nanometer size in one dimension have been investigated in recent years due to unusual properties of these confined fluids as compared to those of the bulk. Their practical applications can be sought in the fields of capillary condensation, gas adsorption, and transport phenomena in porous materials. In such areas, the common geometries of confinement can be simplified as the slit, cylindrical and spherical shapes representing complex porous media. The experimental restriction due to small size stimulates molecular modeling approach to be an apt choice for characterizing atomistic behaviors in pores. Many studies have been conducted to understand phase behavior, thermodynamic properties, and packing of fluid molecules in the pore, yet there are little known about the dependence of phase behavior and structure in terms of different pore sizes and pore structure, in which our aim for this work lies. We first construct the simple cylindrical and spherical pores, which exert either repulsive or attractive forces on fluid particles, which exhibit simple model potentials; hard sphere and square-well. We investigate the thermo-physical properties by determining the equation of states using classical molecular dynamics method. Density profiles, axial distribution function, structure factor and bond order parameters are emphasized to reveal structural properties of fluid-like and solid-like ones. Next, we extend the simple confinement geometries to structural walls of realistic porous media such as single-walled carbon nanotubes (SWCNTs). The influences of the surface chirality of the SWCNTs to the confined fluid are investigated in terms of solidification.

Chapter 1

Introduction

Artificial manipulations at the molecular level have increased in recent years to understand and control macroscopic properties. The rapid development of the science and technology of nanomaterials requires insightful understanding of the atomistic scale behavior of molecules involving molecular size pores and nanotubes[1, 2]. Fluids in confined geometries are presently an area of intense experimental and theoretical research. Fluids confined in those pores with pore widths of a few diameters of molecular diameter, can exhibit significant physical properties that differ from the properties of the bulk fluids. The introduction of the interaction of fluid molecules with the confined wall, and the competition between the fluid-wall and fluid-fluid interaction, can lead to many interesting phase behavior driven by the wall surface such as layering transition, which cannot be found in bulk system. Some properties such as freezing is similar to the bulk but with large shift in the temperature and coexistence densities. To understand these unique properties in confined systems and the change compared to bulk system is of great fundamental and practical importance.

To understand the shift of phase transition in the confined fluids, one can look into the finite-size effect and the surface forces introduced by the wall. When the pore widths are small enough and of the order of the intermolecular interaction, a larger fraction of the fluid molecules under confinement will have reduction in the number of the nearest neighbor molecules and it is expected

that the shift of the phase coexistence curve might be caused by such effect[3]. The fraction of the molecules under direct interaction with the confined wall increases significantly when the pore widths reduce, and it also depends on the geometries of the pores. The phase behaviors of the confined fluids are found to be very sensitive to these two factors. For a slit-like pore, the reduction of pore widths will change the behavior of the confined fluids from nearly three-dimensional (close to bulk behavior) to two-dimensional; for a cylindrical pore, the reduction of pore diameter may cause the confined fluids to have one-dimensional behavior. A fundamental question is whether there is a threshold of pore widths that leads to such change and how the behaviors of the confined fluids change with variation of the pore variables such as pore size, geometries, surface structure, etc.

There are few experimental reports about the aforementioned properties due to the difficulties in pin-pointing accuracy on insertion of molecules into a nanoscale channel as well as the difficulties of observing the physical properties of the confined fluids. In experiments, the distribution of the pore sizes and the shape of the porous materials are poorly known, and the interaction of the confined fluids with the surface of the pores in the porous material is also little known. The fluids confined in the nano-scale pores are more likely trapped in the metastable state compared to the bulk system. The thermodynamic equilibrium in this system is difficult to be determined, and even worse, in some cases such as freezing of fluids to amorphous materials, the equilibrium cannot be attained in a reasonable time. The theoretical study of fluids confined in real porous materials is also a difficult challenge. The greatest problem is the poor knowledge of the morphology of the porous materials and the limited

understanding of the exact fluid-fluid and fluid-wall molecular interactions. Attempting to build a model, which resembles as close as possible the real system, is a highly difficult task. For complex systems, it is common to use approximations but there remains an intellectual gap between the exact behavior of the real fluids and the result provided by the theories. In this case, computer simulation approach is a suitable choice to bridge the theories and the experimental outcomes. Simulation methodologies can provide properties of the system given any kind of interactions and geometries of confinement, which can mimic the realistic systems of fluids confined in porous media or in a system that do not necessarily correspond to reality. Simulations offer the possibility of systematic investigations that is often not possible in the experimental studies in some cases. In this regards, simulations act as a guide to the theoretical development.

There is much to understand regarding how the fluids behave under confinement in porous media. Therefore, the primary objective of this work is to understand the behavior of fluids under different confinements via simplistic models using molecular simulations. In the course of the work, our focus is to investigate properties including fluid-solid phase coexistence, equation of states, structures at different phases, and ordering at phase transition. In particular we would like to understand the effect of pore size and geometries, and the strength and range of interactions among the particles and the walls. Cylindrical and spherical pores of different size are chosen for this study due to their similarity and generality to the real pores. We then extend these simple pores to structured walls such as single-walled carbon nanotubes (SWCNT).

The rest of this thesis is arranged as follows. In the next section of this chapter, we give a brief review of the simulation methods and the current state of knowledge of the freezing/melting behavior of the confined fluids. Chapter 2 describes the models we used in details and the implementation of collision-based molecular dynamic method, as well as the methods to calculate the properties including the equation of state (EOS) and the structural properties. The application of the methods introduced in Chapter 2 is described in Chapter 3, which includes the discussions of the bulk hard-sphere fluids in initial face centered cubic (FCC), hexagonal close-packed (HCP) and body centered cubic (BCC) structures. In Chapter 4 we investigate the EOS and structure of hard-sphere fluids confined in cylindrical hard pores at the vicinity of fluid-solid transition. The pore diameters are chosen to be from 1.1σ to 15σ , where σ is the diameter of the confined particles, and the pore size dependence on freezing/melting densities, coexistence pressure and the pressure on the fluid phase, are emphasized. In Chapter 5 we use the quenched molecular dynamics simulation together with isobaric-isothermal ensemble Monte Carlo simulation to determine the fluid-solid transition and coexistence of square-well fluids confined in narrow cylindrical pore of diameter 2.2σ and 2.5σ . The effect of potential range and temperature is emphasized. In particular, we find a partially ordered phase prior to freezing. In Chapter 6 we change the cylindrical wall to the spherical shape for studies of higher degree of the confinement. Chapter 7 presents a study of hard-sphere fluids confined in modeled SWCNTs with various chiral indices. The fluid-fluid and fluid-wall interactions are considered as pure hard-sphere potential, thus the effect of surface chirality is only investigated. Chapter 8 summarizes our conclusions.

1.1 Simulation Methods

Molecular simulation is a generic term encompassing the molecular modeling philosophy. Generally, one can find two famous methods, which are Monte Carlo (MC) and molecular dynamics (MD). The primary motivation for those methods is to provide theoretically predicted results for any types of the systems, which can be interpreted with statistical mechanics principles. Sometimes empirical nature is embedded into the simulation to add more similarity with real systems. In any cases, comparison of simulation results with experimental data is an unambiguous test of the accuracy of the simulation model. The history of molecular simulation parallels with the one of the technology of the development of the computer. The first molecular simulation on a liquid was performed by Metropolis[4] in the MANIAC computer at Los Alamos National Laboratory, where he introduced the MC algorithm, which incorporates the Boltzmann's factor. During the MC simulation, different trial configurations are generated in random fashion. The intermolecular interaction energy in each configuration is evaluated and Boltzmann probability is used to either accept or reject the new configuration. Later, Alder and Wainwright[5, 6] introduced the MD method. In their simulation, the equations of motion of molecules are integrated with a specified time interval. The molecular coordinates and momenta are evaluated according to the intermolecular forces experienced among molecules. As the name implies, MD enables us to obtain the dynamics properties of the system. Unlike MC simulations, MD is deterministic. Another important distinction between two methods is that MD uses

intermolecular forces to evolve the system whereas MC simulation primarily involves the calculation of changes in intermolecular potential energy. To this date, both simulation techniques including modified ones are widely used by researchers in many disciplines, and the choice between the two alternatives depends often on the type and property of system being investigated. For example, a MD strategy is required to obtain time-dependant dynamics properties of the system whereas MC can be used in a situation where the system has no intrinsic dynamics.

There are a variety of simulation schemes to study the phase behavior and structure of the confined systems. The principal methods are the isobaric-isothermal MC, grand canonical MC, and Gibbs ensemble MC Simulation. Other methods that have been recently developed are the histogram-reweighting method, transition matrix Monte Carlo (TMMC), Gibbs-Duhem integration (GDI), and quench MD. Besides of the simulations, the theoretical studies of the confined systems are widely performed. The most widely used theoretical method is the classic density functional theory (DFT)[7]. Another method, the integral equation theories, is useful for investigating the structure of the confined fluids[8-10] in various geometries. A brief review of these simulation and theoretical methods is given below.

1.1.1 Isobaric-Isothermal Ensemble Monte Carlo

The isobaric-isothermal ensemble (i.e. constant-NPT) ensemble Monte Carlo (NPT MC) simulates a system specified by fixed number of particles N , pressure P and temperature T . The NPT MC method is widely used as most real

experiments are carried out under the condition that pressure and temperature are controlled. NPT MC was first introduced by Wood[11] for two-dimensional hard disks and later extended by McDonald[12] to a system with continuous intermolecular forces. The NPT MC is based on the use of a Markov chain[13] to generate a series of configurations of molecule with correct distribution of energy and density. In this method, the probability associated with a particular configuration of the N atoms (as specified by $\mathbf{s}^N$) at a given volume V is given by

$$P(V, \mathbf{s}^N) \propto \exp\left\{-\beta\left[U(\mathbf{s}^N, V) + PV - N\beta^{-1} \ln V\right]\right\} \quad (1.1)$$

where $U(\mathbf{s}^N, V)$ is the total intermolecular potential in the system, P is the pressure, $\beta = 1/k_B T$ is the inverse temperature.

Two trial moves are performed to modify the current configuration: 1) displacing a randomly-chosen atom by a random vector; 2) change the volume of the system randomly. The trial moves are accepted or rejected according to criteria given below.

1. *Displacement of particles*: a randomly selected particle is given a new position. The move is accepted with the probability

$$acc(s \rightarrow s') = \min\left(1, \exp\left\{-\beta\left[U(\mathbf{s}'^N) - U(\mathbf{s}^N)\right]\right\}\right) \quad (1.2)$$

2. *Changing volume*: the volume of the system is changed from V to $V' = V + \Delta V$, where ΔV is a random number uniformly distributed in the interval $[-\Delta V_{max}, +\Delta V_{min}]$. The move is accepted with the probability

$$acc(V \rightarrow V') = \min(1, \exp\{-\beta[U(\mathbf{s}^N, V') - U(\mathbf{s}^N, V) + P(V' - V) - N\beta^{-1} \ln(V' / V)]\}) \quad (1.3)$$

The virial pressure P_v of an N particle system with the volume V is defined as follows,

$$P_v(V) = -\left(\frac{\partial F}{\partial V}\right)_{NT} \quad (1.4)$$

where F is the Helmholtz free energy. This quantity equals to the pressure P in the NPT MC simulation.

NPT MC simulations are widely used to determine the EOS, where the density is determined by applied pressure and temperature. Furthermore, the EOS data can be fitted to an analytical EOS, and the phase coexistence curve can be determined from Maxwell's equal area construction or calculating the free energies. Although this method requires many simulations to obtain precise EOS data, and more convenient routes have been developed to determine the phase coexistence from a single simulation, the method well serves for obtaining a rough estimate of the coexistence curve.

1.1.2 Grand Canonical Ensemble Monte Carlo

The grand canonical ensemble Monte Carlo (GCMC) simulates an open system, where the temperature T , volume V , and chemical potential μ are fixed. It is generally applied to an adsorbed fluid in equilibrium with the bulk fluid reservoir resembling the experimental adsorption studies. At equilibrium, the temperature and chemical potential of the confined fluids inside and outside the

adsorbent must be equal. The equilibrium concentration inside the adsorbent is then determined by the temperature and chemical potential and the number of particles is allowed to fluctuate during the simulation. It is known that the thermodynamic potentials are not measured directly by the Metropolis scheme. Such potentials include the Helmholtz free energy F , the Gibbs free energy G , and the entropy S . Nevertheless, the difference of the free energy can be measured between two possible states of an N -particle system exploited by the GCMC. It is first implemented by Norman and Filinov[14], and later extended and improved by other groups[15-22], and now widely used to study adsorbed systems[23, 24].

In the GCMC method, the probability associated with a particular configuration of N atoms is given by

$$P_{\mu VT}(\mathbf{s}^N, N) \propto \frac{\exp(\beta\mu N)V^N}{\Lambda^{3N}N!} \exp[-\beta U(\mathbf{s}^N)] \quad (1.5)$$

where Λ is the de Broglie wavelength. The trial moves in GCMC and the acceptance criteria are:

1. *Displacement of particles*: this move is same as shown in NPT MC (see Eq. (1.2)).

2. *Insertion and removal of particles*. A particle is inserted to the system at the random position with the probability

$$acc(N \rightarrow N+1) = \min \left(1, \frac{V}{\Lambda^3(N+1)} \exp \left\{ \beta [\mu - U(N+1) + U(N)] \right\} \right) \quad (1.6)$$

or a particle randomly selected in the system is removed with the probability

$$acc(N \rightarrow N-1) = \min\left(1, \frac{\Lambda^3 N}{V} \exp\left\{-\beta[\mu + U(N-1) - U(N)]\right\}\right) \quad (1.7)$$

The GCMC method measures the number of particles by imposing the temperature and chemical potential. Other thermodynamic properties, such as pressure P , density ρ can also be calculated. The Helmholtz free energy F , or the entropy S can be derived from the chemical potential μ , but the absolute free energy cannot be calculated from the GCMC method.

1.1.3 Gibbs Ensemble Monte Carlo

Direct simulation of first-order phase coexistence in one simulation box (i.e. resembling the experiments of the initially homogeneous system separates into two distinct phases divided by an interface) is computational expensive since the finite size of number of particles studied make large interface that dominates the system and prevents the two phase reach true equilibrium. To overcome this, Panagiotopoulos[25, 26] developed the Gibbs ensemble Monte Carlo (GEMC) method to calculate the phase coexistence directly in one simulation by simulating the two phases in different simulation cells, with both mass and volume exchange between two phases and spontaneously reach equilibrium.

The conditions for the phase coexistence are that the pressure P , the temperature T and the chemical potential μ in different phases are equal. The GEMC method automatically equates these three variables in both phases, and

the total volume and particles of two phases are kept unchanged. The difference of chemical potential $\Delta\mu$ in both phases is fixed at 0. Let us consider that two phases have the volume V_1 and V_2 and the total volume $V = V_1 + V_2$, and the number of particles in the two phases are N_1 and N_2 , and total number of particles $N = N_1 + N_2$. The probability associated with the configuration with N_1 particle in phase 1 with volume V_1 and the positions $\mathbf{s}_1^{N_1}$ and $\mathbf{s}_2^{N_2}$ is given by

$$P(N_1, V_1, \mathbf{s}_1^{N_1}, \mathbf{s}_2^{N_2}) \propto \frac{V_1^{N_1} (V - V_1)^{N - N_1}}{N_1! (N - N_1)!} \exp \left\{ -\beta \left[U(\mathbf{s}_1^{N_1}) + U(\mathbf{s}_2^{N_2}) \right] \right\} \quad (1.8)$$

The GEMC method is based on the Markov chain generation, thus the different trial moves are: 1) displacement of molecules in each box representing each phase; 2) transfer of a randomly selected particle from one box to a random position in another box; 3) change of the volume of both boxes in a way that the total volume is kept constant. The acceptance criteria of the three trail moves are given below:

1. *Particle displacement*: displacement of a randomly selected particle in one box by a random vector in the same simulation box. If we assume the selected particle is from box 1 with the old state o , the probability of accepting the move to the new state n is

$$acc(o \rightarrow n) = \min \left(1, \exp \left\{ -\beta \left[U(s_n^{N_1}) - U(s_o^{N_1}) \right] \right\} \right) \quad (1.9)$$

which is an identical criterion in the NVT ensemble.

2. *Transfer of particle*: we assume that a particle is removed from box 1 and

inserted to box 2. The probability of this move from the old state o to the new state n is

$$acc(o \rightarrow n) = \min \left\{ 1, \frac{N_1(V - V_1)}{(N - N_1 + 1)V_1} \exp \left(-\beta [U(\mathbf{s}_n^N) - U(\mathbf{s}_o^N)] \right) \right\} \quad (1.10)$$

3. *Volume Change*: change of the volume of box 1 is by an amount of ΔV so that $V_1^n = V_1^o + \Delta V$, $V_2^n = V_2^o - \Delta V$, and the total volume V remains unchanged.

The move is accepted with the probability

$$acc(o \rightarrow n) = \min \left\{ 1, \frac{(V_1^n)^{N_1} (V_2^n)^{N_2}}{(V_1^o)^{N_1} (V_2^o)^{N_2}} \exp \left(-\beta [U(\mathbf{s}_n^N) - U(\mathbf{s}_o^N)] \right) \right\} \quad (1.11)$$

The GEMC method is an excellent technique to study vapor-liquid and liquid-liquid equilibria of bulk phase[27, 28] and can be extended to mixtures[26]. It can also be used to obtain the capillary condensation phase diagram in the confined systems[29]. However as the GEMC relies on a reasonable number of successful of the particle exchange, which makes the method insufficient for studying equilibria involving very dense phase. Some improvement has been made recently by applying the aggregation volume bias algorithm (AVB)[30, 31] to make GEMC simulation of phase coexistence involving solid phase possible[32].

1.1.4 Gibbs-Duhem Integration

Once a point on the coexistence curve is know, the rest can be calculated by solving the first-order Clausius-Clapeyron equation given by[33]

$$\left(\frac{dP}{d\beta}\right)_\sigma = -\frac{\Delta h}{\beta\Delta v} \quad (1.12)$$

where P is the pressure, $\beta = 1/k_B T$ is the inverse temperature, Δh and Δv are the difference of molar enthalpy and molar volume between two phases, respectively. The subscript σ represents the path along coexistence. Kofke[34, 35] has shown that the equation can be integrated for the direct evaluation of phase coexistence and the method is called Gibbs-Duhem integration (GDI). A predictor-corrector method is used for performing the integration.

Like the GEMC method, the GDI method also utilizes two simulation boxes, but it does not rely on particle exchange, of which idea makes it useful for all kinds of system even with solid phases. To perform GDI simulations, two coupled NPT simulations are performed in parallel with a given point of coexistence curve (e.g. from GEMC). The state of the next point on the coexistence is evaluated from the current state by solving Eq.(1.12) using the predictor-corrector method, thus the rest points on the coexistence line are obtained subsequently. The major limitation of the GDI method is getting an initial point of coexistence in order to start the integration procedure. Also, even small error in the integration may cause large deviations of the computed coexistence points from the true ones, Thus, the stability of the integration must be concerned[36]. Nevertheless, the application of the GDI method is quite broad. It can be used in conjunction with GEMC and also a popular choice for system containing solid phase where GEMC and insertion based methods fail. The method has been employed for calculating the fluid-solid coexistence of various molecular models[37, 38] and multi-component systems[39].

1.1.5 Quenched Molecular Dynamics

Molecular dynamics (MD) is a form of molecular simulation methodologies wherein atoms and molecules are allowed to interact under the Newton's laws of motions. Thermodynamic properties can be obtained through the time average, and dynamical properties that cannot be obtained from MC simulations can also be obtained from this method. MD simulations are generally performed in constant energy (NVE) or constant temperature (NVT) ensembles [40-42].

To simulate phase separation using MD, the system is initially prepared at supercritical temperature, then quenched to the lower temperature at which two phases may coexist. The phase separation occurs dynamically and the different phases can be characterized by the respective energy of the system or structural quantities such as bond order parameters, density profiles, and pair-correlation functions. The system size must be very large to minimize the influence due to interfaces generated when the phase separation occurs. The method can be applied to the complex structural media[43] where volume-change-based scheme cannot be applied, and also in the simple pores such as slit-like [44] and cylindrical pores[45, 46].

1.2 Freezing and melting of confined fluids

In this section we review the simulation studies of freezing and melting behavior in porous media. Such studies are essential to the areas related to lubrication, fabrication of nano-fluidic devices and nanomaterials.

While the fluid-solid phase transition and coexistence in bulk systems has been well established for various models, such phase transition in the confined systems is less known and rather complex. Some studies argue that true phase transition in some of the confined systems is not possible or cannot be demonstrated. Thus the transition of the confined systems from fluid-like to solid-like behavior that is similar to the bulk fluid-solid phase transition is commonly referred to as freezing and the reverse process as melting. Freezing and melting can be driven by the change of the temperature or by the effect of geometrical packing.

A work of the freezing hard spheres confined between two parallel hard plates for different plate separations is given by Schmidt and Löwen[47], using MC simulation and free volume theory. They applied the Maxwell construction to the van der Waals loop found in the pressure versus density curves and obtained the coexistence conditions. The full phase diagram was obtained for wide ranges of densities and confining widths (i.e. between one to two diameter of the hard sphere). The system exhibits solid-solid transitions between buckled, layered and rhombic crystalline structures. They also found that with the finite system size, the fluid-solid transition is always first order, and both weak and strong solid-solid transitions can be found following the fluid-solid transition at higher densities.

Systematic studies were conducted by Miyahara and Gubbins[48], who studied the freezing and melting of Lennard-Jones (LJ) fluids confined in the slit-like pore with various pore sizes and fluid-wall potential functions by using GCMC simulations. The freezing temperature under confinement was

significantly lower than that in the bulk when the fluid-wall interactions were repulsive, while a large increase of freezing temperature was found for strongly attractive walls. Also, they found that the contact layers behaved differently than the rest of the fluids. For example, the freezing temperatures of the contact layers were found to be different than the rest of the fluid confined in the pore.

The early simulation studies of freezing and melting made use of various of structural functions such as pair correlation function, structure factor, and density profiles to monitor the freezing process. By monitoring only these functions, however the phase transition region cannot be precisely located. Freezing and melting generally display large hysteresis loops and the nature of freezing and melting was not clear due to the fact that the transition in small pores can be continuous rather than the first-order. To overcome this problem, one shall look into the free energy calculation of the phases involved in the phase transition. Dominguez *et al.* [49] used thermodynamic integration[50] to calculate the Gibbs free energy of fluid and solid phases for LJ fluids confined in slit pores with various wall-fluid potentials. They used an ensemble such that the pressure P_z normal to the wall was fixed. The method they used for calculating free energy was referred to Frenkel-Ladd method[50], which made use of numerical integration starting from a known reference phase to the state of interest. The path of the integration must be thermodynamically reversible, which must not involve any first-order phase transition. The reference state can be the ideal gas for the fluid phase or the Einstein crystal for the solid phase. Dominguez *et al.* found that the freezing line was shifted to lower temperatures for repulsive walls, while the shift to lower temperatures was much smaller in magnitude for weakly attractive walls. Their result also indicated that the

transition was of the first-order. For strongly attractive walls, the techniques they used could not be applied due to the occurrence of prior freezing of the contact layer. Radhakrishnan and Gubbins[51] overcame the problem by calculating Landau free energy based on a suitable order parameter. The Landau free energy Λ as the function of the bond order parameter Φ was defined as

$$\Lambda(\Phi) = -k_B T \ln(P[\Phi]) + \text{constant} \quad (1.13)$$

where $P[\Phi]$ is the probability of the system to have an order parameter between Φ and $\Phi + \delta\Phi$. The grand free energy Ω of each phase can then be obtained by the integration of the Landau free energy over the bond order parameter in the form of

$$\exp(-\beta\Omega) = \int d\Phi \exp(-\beta\Lambda[\Phi]) \quad (1.14)$$

This approach was based on the histogram-reweighting methods[52-54] and had been used to study fluid-solid phase transitions in bulk systems by other researchers[55, 56]. Radhakrishnan and Gubbins carried out simulations for hard and attractive walls modeled with carbon atoms. The fluid-solid transition was found to be the first order as indicated by the grand free energy. For strong attractive walls, they found that there were three phases corresponding to: a) all layers had liquid structure; b) the contact layer is frozen while the rest of the layers still had liquid structure; c) all layers were frozen. The study also showed a strong evidence for the liquid to exhibit a hexatic phase transition prior to freezing in the strongly attractive pore, which was also suggested in the simulation studies of CCl_4 confined in activated carbon fibers

(ACF)[57, 58]. For weakly or poorly repulsive walls there was no evidence of the hexatic phase.

For pores of cylindrical shape, Maddox and Gubbins[59] combined GCMC simulations with MD to study confined LJ methane. The MD method allows better relaxation of the particle displacement in the cylindrical pore. Maddox and Gubbins reached similar conclusions on the shift of the freezing point in slit-pores, but the big difference was that the freezing temperatures were found to be lower than those in slit-pores, due to additional degree of confinement by the cylindrical pores. Kanda *et al.* [60] studied the freezing of LJ methane confined in model carbon cylindrical pores of reduced pore diameters ranging from 4.5 to 9.5, using GCMC. They found that the frozen state had the arrangement of LJ particles forming hexagonal concentric layers. The dependence of the freezing point on the pore diameter was found to be nonmonotonic in strongly attractive carbon pores. They addressed this as a result of the competition of the "geometrical hindrance effect", which originates from excess energy of cylindrical frozen state relative to the FCC lattice state, and the fluid-wall interaction. The "geometrical hindrance effect" was found to become stronger for small pore sizes. Another study on the pore size dependence on freezing was done by Sliwinski-Bartkowiak *et al.* [61], who studied the freezing of nitrobenzen and CCl_4 in porous glasses and MCM-41 in both experiment and simulation. They found that the confined fluids were able to crystallize into single crystalline structure in the average pore size greater than 20σ , where σ is the diameter of fluid particles. For average pore size between 20σ and 15σ , part of the fluids froze into frustrated crystal with the rest forming amorphous solid. For reduced pore size smaller than 15, the whole

system became amorphous even with absence of the partial crystallization. Hung *et al.* [62] and Sliwinska-Bartkowiak *et al.* [63] studied nitrobenzene and CCl_4 confined in multi-walled carbon nanotubes (MWCNT) using parallel tempering grand canonical Monte Carlo simulation and conducting dielectric relaxation spectroscopy experiments. They found that the confined molecules were solidified into concentric layers, with structure of quasi-two-dimensional hexagonal crystals. The formation of common three-dimensional crystalline structures was not found in confinement and the results suggested the presence of inhomogeneous phases composing of crystalline and liquid regions. The freezing temperature of the outer layer was slightly larger than that of the bulk, whereas the inner layers had lower freezing point.

The aforementioned studies were mostly focused on models with both attractive and repulsive interactions, in which the properties were obtained from the competition of energetic and entropic influences that could not be separated easily. Gordillo *et al.* [64] considered hard spheres confined in narrow cylindrical hard pores, in which the energetic effects were suppressed, and the system was under pure confinement/entropic influences. They performed a series of NPT simulations to determine the equation of states with the structure monitored by structure factor and axial distribution function. They found that for pores of radii larger than 1.1σ the structure could change from fluid-like to solid-like, indicating of the onset of freezing. The frozen threshold of the pore size was $R \geq 1.08\sigma$, where R was the radius of the pore, in which the trimetric arrangement of particles can be formed. The structure of the frozen fluids in cylindrical pores could be rather complex. Pickett *et al.* [65] reported spontaneous chirality of hard spheres in narrow cylindrical pore of reduced

diameters ranging from 1.0 to 2.155. A variety of crystal phases were obtained with various pore diameters. The maximum volume fraction was found to have complex dependence with the pore diameter. Durán-Olivencia *et al.* [66] studied the ordering of hard spheres in cylindrical pores of radii 1.1σ to 2σ using NPT simulations. The hard spheres formed order structures from loosened arrangement when the pressure increased and the patterns at higher pressure were determined by the radii of the cylindrical pore. For $R < 1.5\sigma$ the ordering structure was determined by the number of coplanar spheres that can fit within the pores, and for wider pores the ordering structure was determined by the deformed two-dimensional triangular lattices rolled to fit inside the cylindrical pores considered.

Chapter 2

General Methodology

2.1 Dimensionless Units

Typically, the system size is small in this work (i.e. hundreds or thousands of atoms are taken into consideration). Because the quantities are extremely small in magnitude when expressed in macroscopic units, dimensionless units are conveniently used. For example, here are some quantities for a simulation system in macroscopic units:

Table 2.1. Constants and variables in molecular simulation

Symbol	Definition	Value
1. Constants		
k	Boltzmann's constant	1.3806×10^{-23} J/(molec·K)
N_0	Avagadro's number	6.022×10^{23}
2. Simulation Variables		
N	Number of molecules	$\sim 10^3$
V	Simulation cell volume	$\sim 10^{-24} \text{ m}^3$
m	Mass	$\sim 10^{-25} \text{ kg/molec}$
ρ	Number density	$\sim 10^{27} \text{ molec/m}^3$
E	Energy	$\sim 10^{-20} \text{ J/molec}$
t	time	$\sim 10^{-12} \text{ s}$
3. Model Variables		
σ	Size variable	$\sim 5 \times 10^{-10} \text{ m}$

ε	Energy variable	$\sim 10^{-21}$ J/molec
r_b	Bond distance	$\sim 10^{-10}$ m

In order to magnify the quantities, one way is working with atomic-scale units such as *ps*, *amu*, *nm* or Å. The other is conveniently making dimensionless with characteristic values with respect to potential model; size σ , energy ε and mass m . We adopt the values of the units such that σ and ε are unity. All length scales are in unit of σ , thus the number density $\rho = N/V$ becomes $\rho^* = N\sigma^3/V$. Other dimensionless quantities used in this work are listed in Table 2.2:

Table 2.2. Definition of dimensionless units

Symbol	Meaning	Definition
r^*	Dimensionless distance	r/σ
E^*	Dimensionless energy	E/ε
T^*	Dimensionless temperature	kT/ε
U^*	Dimensionless internal energy	U/ε
t^*	Dimensionless time	$t/[\sigma(m/\varepsilon)^{0.5}]$
v^*	Dimensionless velocity	$v/(\varepsilon/m)^{0.5}$
F^*	Dimensionless force	$F\sigma/\varepsilon$
P^*	Dimensionless pressure	$P\sigma^3/\varepsilon$
D^*	Dimensionless self diffusion coefficient	$D/[\sigma(\varepsilon/m)^{0.5}]$

For hard-sphere potential, there is no nature unit of energy since the hard-sphere potential is either zero or infinite. The thermal energy kT is used as the energy unit. The reduced pressure becomes $P^* = \beta P\sigma^3$, and the reduced time

is $t^* = t/[\sigma(m/kT)^{0.5}]$.

2.2 Periodic Boundary Conditions

Most molecular simulations are applied to systems containing a few hundred to a few thousand particles. This small number of particles is far from the thermodynamic limit. With this number of particles, the systems are dominated by the interaction of atoms with the container's wall. In a three-dimensional N -particle system, the fraction of surface atoms is proportional to $N^{1/3}$. For example, in a simple cubic crystal of 1000 atoms, the fraction of surface atoms is about 50%, while for 10^6 atoms the fraction reduced to only 6%. But even the system as large as 10^6 atoms still cannot represent the bulk behavior and the surface effect cannot be ignored. In simulations that surface effects are not of interest, the walls are removed by employing periodic boundary conditions. Let us consider a simulation cell containing N particles and has volume V . To use periodic boundary conditions, we imagine that volume V is only a portion of the bulk material. The volume V is treated as the primary cell of an infinite periodic lattice of identical cells that surrounded the primary cell in all directions. These surrounded cells are exactly the same with the primary cell and called image cells. The atoms in the image cells are images of the atoms in the primitive cell. Any particle interacts with all particles in the primitive cell through periodic boundary condition.

During a D -dimensional simulation, we only need to store the positions of N atoms in the primary cell. The positions of image atoms can be calculated by adding a D -dimensional cell translation vector α , whose components are zero or

positive integers. For example, in three dimensions the primary cell has $\alpha = \{0,0,0\}$. Assume an atom in the cubic primary cell has the position $\mathbf{r}$, the position of any image of this atom can be calculated as

$$\mathbf{r}_{image} = \mathbf{r} + L\alpha \quad (2.1)$$

where L is the scalar length of the cubic cell. By employing periodic boundary conditions, any atom that leaves the primary cell is replaced by the image that simultaneously enters the primary cell. For example, an atom, which leaves the primary cell and enters the image cell of α , will be replaced by an image atom from the image cell of $-\alpha$. Thus the total number of atom in the primary cell remains unchanged.

2.3 Simulation Models

2.3.1 Hard-sphere Model

Hard-sphere model is widely used as model particles in molecular simulations of fluid and solid due to theoretical tractability. It is defined simply as impenetrable spheres that can not overlap in space. It can mimic the strong repulsion that atoms and spherical molecules experienced at contact distance. The particles of diameter σ have the following pair-wise interaction potential:

$$U(r_{ij}) = \begin{cases} 0 & r_{ij} > \sigma \\ \infty & r_{ij} \leq \sigma \end{cases} \quad (2.2)$$

where $U(r_{ij})$ is the potential energy between two particles at relative distance r_{ij} . The potential is infinite if two particles are overlap, otherwise zero. Thus the

hard spheres exert forces on one another only when they collide. Between collisions the hard spheres exhibit free flight. The collisions are considered as perfect rigid elastic, thus during collision both kinetic energy and momentum are conserved.

2.3.1.1 Hard-sphere Collision Dynamics

In MD simulation, we need to deal with collision dynamics by solving the equations of motion. Let us consider two particles, whose masses are m_1 and m_2 , respectively. At some time the two particles are separated and have initial momenta $\mathbf{p}_1$ and $\mathbf{p}_2$, respectively. No forces act on these two spheres, hence $\mathbf{p}_1$ and $\mathbf{p}_2$ are constant. When two particles collide, an infinite force is exerted over an infinitesimal time. Directions of forces are evaluated along with the line joining the centers of the two particles. After collision, both momentum and kinetic energy are conserved and shown as follows,

$$\mathbf{p}_1^{new} = \mathbf{p}_1^{old} + \Delta\mathbf{p} \quad (2.3)$$

$$\mathbf{p}_2^{new} = \mathbf{p}_2^{old} - \Delta\mathbf{p} \quad (2.4)$$

$$\frac{1}{m_1}|\mathbf{p}_1^{new}|^2 + \frac{1}{m_2}|\mathbf{p}_2^{new}|^2 = \frac{1}{m_1}|\mathbf{p}_1^{old}|^2 + \frac{1}{m_2}|\mathbf{p}_2^{old}|^2 \quad (2.5)$$

where $\Delta\mathbf{p}$ can be expressed in terms of $\mathbf{r}_{12}$

$$\Delta\mathbf{p} = a\mathbf{r}_{12} \quad (2.6)$$

where $\mathbf{r}_{12} \equiv \mathbf{r}_2 - \mathbf{r}_1$. Combining these equations yields

$$\frac{1}{m_1} \left| \mathbf{p}_1^{old} + a \mathbf{r}_{12} \right|^2 + \frac{1}{m_2} \left| \mathbf{p}_2^{old} - a \mathbf{r}_{12} \right|^2 = \frac{1}{m_1} \left| \mathbf{p}_1^{old} \right|^2 + \frac{1}{m_2} \left| \mathbf{p}_2^{old} \right|^2 \quad (2.7)$$

Solving we obtain

$$a = \frac{2m_1 m_2}{m_1 + m_2} \frac{\mathbf{v}_{12} \cdot \mathbf{r}_{12}}{\sigma^2} \quad (2.8)$$

and

$$\Delta \mathbf{p} = \frac{2m_1 m_2}{m_1 + m_2} \frac{\mathbf{v}_{12} \cdot \mathbf{r}_{12}}{\sigma^2} \mathbf{r}_{12} \quad (2.9)$$

where $\mathbf{v}_{12} \equiv \mathbf{v}_2 - \mathbf{v}_1$.

2.3.1.2 Collision Times

Before applying the momenta change during collision we must determine whether two particles will collide and when they will collide. With two particles at time t , each having diameter σ . Between collisions, the particles travel along a straight line with constant velocities, so the position of a particle after a period of time Δt is:

$$\mathbf{r}(t + \Delta t) = \mathbf{r}(t) + \mathbf{v}(t) \Delta t \quad (2.10)$$

The collision time for any pair are solved by finding Δt such that the centers of the pair of particles will be separated by distance σ

$$\left| \mathbf{r}_2(t + \Delta t) - \mathbf{r}_1(t + \Delta t) \right|^2 = \sigma^2 \quad (2.11)$$

which leads to a quadratic equation:

$$\mathbf{v}_{12}^2 \Delta t^2 + 2(\mathbf{v}_{12} \cdot \mathbf{r}_{12})(\Delta t) + (\mathbf{r}_{12}^2 - \sigma^2) = 0 \quad (2.12)$$

where $\mathbf{r}_{12} = \mathbf{r}_1 - \mathbf{r}_2$ and $\mathbf{v}_{12} = \mathbf{v}_1 - \mathbf{v}_2$.

Solving Eqn.(2.12) gives us

$$\Delta t = \frac{-\mathbf{v}_{12} \cdot \mathbf{r}_{12} \pm \sqrt{(\mathbf{v}_{12} \cdot \mathbf{r}_{12})^2 - \mathbf{v}_{12}^2 (\mathbf{r}_{12}^2 - \sigma^2)}}{\mathbf{v}_{12}^2} \quad (2.13)$$

Equation (2.13) allows us to distinguish three important situations shown in Figure 2.1.

Situation 1: $\mathbf{v}_{12} \cdot \mathbf{r}_{12} > 0$

If the product $\mathbf{v}_{12} \cdot \mathbf{r}_{12}$ is positive, the two particles are moving away from each and will not collide.

Situation 2: $\mathbf{v}_{12} \cdot \mathbf{r}_{12} < 0$ and $(\mathbf{v}_{12} \cdot \mathbf{r}_{12})^2 - \mathbf{v}_{12}^2 (\mathbf{r}_{12}^2 - \sigma^2) < 0$

The two particles are moving toward one another but will not collide.

Situation 3: $\mathbf{v}_{12} \cdot \mathbf{r}_{12} < 0$ and $(\mathbf{v}_{12} \cdot \mathbf{r}_{12})^2 - \mathbf{v}_{12}^2 (\mathbf{r}_{12}^2 - \sigma^2) \geq 0$

This is the necessary and sufficient condition to determine two particles will collide. The quadratic has two roots which imply there are two arrangements, which have the two particles in contact as in the figure. Only the

short-time root

$$\Delta t = \frac{-\mathbf{v}_{12} \cdot \mathbf{r}_{12} - \sqrt{(\mathbf{v}_{12} \cdot \mathbf{r}_{12})^2 - v_{12}^2 (r_{12}^2 - \sigma^2)}}{v_{12}^2} \quad (2.14)$$

is physically possible since the spheres are not impenetrable.

Figure 2.1. Three cases of collision dynamics of two hard spheres

2.3.2 Square-well Model

The square-well potential has been considered as the simplest extension of hard sphere potential containing attractive interactions and can be further considered as a model describing more realistic and physical systems. Due to characteristic attraction, the model could exhibit the phase separation. The

square-well pair potential is given by

$$U(r) = \begin{cases} \infty & r < \sigma \\ -\varepsilon & \sigma \leq r < \lambda\sigma \\ 0 & \lambda\sigma \leq r \end{cases} \quad (2.15)$$

where σ is the hard-core diameter of the particle, $\lambda\sigma$ is the potential-well diameter and ε is the depth of the potential well.

2.3.2.1 Square-well Collision Dynamics

The collision dynamics of square-well particles is similar to the hard spheres except that attractive force acts when two particles enter or escape from the potential well at distance $\lambda\sigma$. The two square-well particles can collide at hard core diameter σ and potential well diameter $\lambda\sigma$. Consider two square-well particles of masses m_1 and m_2 , and momenta $\mathbf{p}_1$ and $\mathbf{p}_2$ before collision. There are 3 cases for collision kinetic:

1. *Hard core collision.*

Two particles collide at the hard core following the same collision dynamics of hard sphere model. A repulsive force acts on the two particles at the direction of the vector joining the centers of these two particles. The impulse can be calculated as

$$\Delta \mathbf{p} = \frac{2m_1m_2}{m_1 + m_2} \frac{\mathbf{v}_{12} \cdot \mathbf{r}_{12}}{\sigma^2} \mathbf{r}_{12} \quad (2.16)$$

2. *Potential well separation*

Two particles are separating and trying to escape from the potential well.

Denote $m_R = 1.0/(1/m_1 + 1/m_2)$, the kinetic energy of the two particles is

$$k_e = \frac{m_R (\mathbf{v}_{12} \cdot \mathbf{r}_{12})^2}{2r_{12}^2} \quad (2.17)$$

The particles escape from the potential well when $k_e > \varepsilon$ with the total kinetic energy reduced by ε . Following the method of hard-sphere kinetic, the momentum change is denoted as $\Delta \mathbf{p} = a \mathbf{r}_{12}$, which gives

$$\mathbf{p}_1^{new} = \mathbf{p}_1^{old} + a \mathbf{r}_{12} \quad (2.18)$$

$$\mathbf{p}_2^{new} = \mathbf{p}_2^{old} - a \mathbf{r}_{12} \quad (2.19)$$

and

$$\frac{1}{2m_1} |\mathbf{p}_1^{old} + a \mathbf{r}_{12}|^2 + \frac{1}{2m_2} |\mathbf{p}_2^{old} - a \mathbf{r}_{12}|^2 = \frac{1}{2m_1} |\mathbf{p}_1^{old}|^2 + \frac{1}{2m_2} |\mathbf{p}_2^{old}|^2 - \varepsilon \quad (2.20)$$

Solving this equation gives us

$$a = \frac{m_R \left(\mathbf{v}_{12} \cdot \mathbf{r}_{12} - \sqrt{(\mathbf{v}_{12} \cdot \mathbf{r}_{12})^2 - \frac{2(\lambda\sigma)^2 \varepsilon}{m_R}} \right)}{(\lambda\sigma)^2} \quad (2.21)$$

and

$$\Delta \mathbf{p} = \frac{m_R \left(\mathbf{v}_{12} \cdot \mathbf{r}_{12} - \sqrt{(\mathbf{v}_{12} \cdot \mathbf{r}_{12})^2 - \frac{2(\lambda\sigma)^2 \varepsilon}{m_R}} \right)}{(\lambda\sigma)^2} \mathbf{r}_{12} \quad (2.22)$$

If $k_e < \varepsilon$, the kinetic energy is not enough to allow the two particles escape from the potential well, an attractive force is acted to push back the particles and the kinetic energy does not change, thus ε is omitted, which gives

$$\Delta \mathbf{p} = \frac{2m_R \mathbf{v}_{12} \cdot \mathbf{r}_{12}}{(\lambda\sigma)^2} \mathbf{r}_{12} \quad (2.23)$$

3. *Potential well approaching.*

Two particles are outside of the potential well and attracted by the potential well. The total kinetic energy increases by ε after attraction, which gives

$$\frac{1}{2m_1} |\mathbf{p}_1^{old} + a\mathbf{r}_{12}|^2 + \frac{1}{2m_2} |\mathbf{p}_2^{old} - a\mathbf{r}_{12}|^2 = \frac{1}{2m_1} |\mathbf{p}_1^{old}|^2 + \frac{1}{2m_2} |\mathbf{p}_2^{old}|^2 + \varepsilon \quad (2.24)$$

Solving the equation gives

$$a = \frac{m_R \left(\mathbf{v}_{12} \cdot \mathbf{r}_{12} + \sqrt{(\mathbf{v}_{12} \cdot \mathbf{r}_{12})^2 + \frac{2(\lambda\sigma)^2 \varepsilon}{m_R}} \right)}{(\lambda\sigma)^2} \quad (2.25)$$

and

$$\Delta \mathbf{p} = \frac{m_R \left(\mathbf{v}_{12} \cdot \mathbf{r}_{12} + \sqrt{(\mathbf{v}_{12} \cdot \mathbf{r}_{12})^2 + \frac{2(\lambda\sigma)^2 \varepsilon}{m_R}} \right)}{(\lambda\sigma)^2} \mathbf{r}_{12} \quad (2.26)$$

2.3.2.2 Collision Time

Let us consider two square-well particles whose mass are m_1 and m_2 , and initial momenta $\mathbf{p}_1$ and $\mathbf{p}_2$, respectively. The potential well diameter is λ and potential depth ε . The two particles collide when the distance equals to the hard core diameter σ or the potential well diameter $\lambda\sigma$. To find the collision time Δt , we have the following situations and those are summarized in Figure 2.2.

The two particles are inside of the potential well. In this case we first try to find if the hard core collision will happen. The collision time is calculated in the same way with hard spheres.

$$\left| \mathbf{r}_2(t + \Delta t) - \mathbf{r}_1(t + \Delta t) \right|^2 = \sigma^2 \quad (2.27)$$

$$v_{12}^2 \Delta t^2 + 2(\mathbf{v}_{12} \cdot \mathbf{r}_{12})(\Delta t) + (\mathbf{r}_{12}^2 - \sigma^2) = 0 \quad (2.28)$$

If we have $\mathbf{v}_{12} \cdot \mathbf{r}_{12} < 0$ and $(\mathbf{v}_{12} \cdot \mathbf{r}_{12})^2 - v_{12}^2(\mathbf{r}_{12}^2 - \sigma^2) > 0$, the two particle will collide with the time

$$\Delta t = \frac{-\mathbf{v}_{12} \cdot \mathbf{r}_{12} - \sqrt{(\mathbf{v}_{12} \cdot \mathbf{r}_{12})^2 - v_{12}^2(\mathbf{r}_{12}^2 - \sigma^2)}}{v_{12}^2} \quad (2.29)$$

If $\mathbf{v}_{12} \cdot \mathbf{r}_{12} > 0$ or $(\mathbf{v}_{12} \cdot \mathbf{r}_{12})^2 - v_{12}^2(\mathbf{r}_{12}^2 - \sigma^2) < 0$, the two particle will miss for the hard core collision but will collide at the potential well. The collision

time can be calculated as

$$\left| \mathbf{r}_2(t + \Delta t) - \mathbf{r}_1(t + \Delta t) \right|^2 = (\lambda \sigma)^2 \quad (2.30)$$

$$v_{12}^2 \Delta t^2 + 2(\mathbf{v}_{12} \cdot \mathbf{r}_{12})(\Delta t) + (\mathbf{r}_{12}^2 - \lambda^2 \sigma^2) = 0 \quad (2.31)$$

$$\Delta t = \frac{-\mathbf{v}_{12} \cdot \mathbf{r}_{12} + \sqrt{(\mathbf{v}_{12} \cdot \mathbf{r}_{12})^2 - v_{12}^2 (\mathbf{r}_{12}^2 - \lambda^2 \sigma^2)}}{v_{12}^2} \quad (2.32)$$

When two particles are outside of the potential well, then look for collision time for the well collision

$$\left| \mathbf{r}_2(t + \Delta t) - \mathbf{r}_1(t + \Delta t) \right|^2 = (\lambda \sigma)^2 \quad (2.33)$$

$$v_{12}^2 \Delta t^2 + 2(\mathbf{v}_{12} \cdot \mathbf{r}_{12})(\Delta t) + (\mathbf{r}_{12}^2 - \lambda^2 \sigma^2) = 0 \quad (2.34)$$

which leads to three cases similar to the hard-sphere collision. The two square-well particles will collide at the potential well diameter if the two conditions $\mathbf{v}_{12} \cdot \mathbf{r}_{12} < 0$ and $(\mathbf{v}_{12} \cdot \mathbf{r}_{12})^2 - v_{12}^2 (\mathbf{r}_{12}^2 - \lambda^2 \sigma^2) < 0$ are satisfied, otherwise the two particles miss for collision. The collision time is

$$\Delta t = \frac{-\mathbf{v}_{12} \cdot \mathbf{r}_{12} - \sqrt{(\mathbf{v}_{12} \cdot \mathbf{r}_{12})^2 - v_{12}^2 (\mathbf{r}_{12}^2 - \lambda^2 \sigma^2)}}{v_{12}^2} \quad (2.35)$$

Figure 2.2. Collision dynamics of two square-well particles

2.3.3 Simulation Algorithm

The general simulation algorithm for hard-sphere and square-well models in the three dimensional space can be divided into three parts: (a) *initialization*, (b) *equilibration*, and (c) *production*. The simplest yet widely used algorithm was devised by Alder and Wainwright[6] when they introduced the first hard sphere molecular dynamics method. The algorithm is summarized below[67]:

Initialization. Initialization assigns initial positions and momenta to the N particles in the system.

1. Choose a number of particles N and number density ρ . Compute the volume $V = N/\rho$ and length of the simulation box $L = V^{1/3}$.
2. Assign initial positions r_i ($i = 1, \dots, N$) to all particles. Typically in a bulk simulation the initial positions are the sites of a FCC lattice. Alternatively, the positions can be obtained from previous simulations. In a simulation of fluids confined in pores of different geometries, the initial positions can be calculated in different methods, which will be discussed in the corresponding chapters.
3. Assign initial velocities v_i ($i = 1, \dots, N$) to the N particles. The velocities can be assigned randomly and directly from the Maxwell distribution. Alternatively, the components of each v_i can be assigned from a uniform distribution on $[-1, 1]$ and scaled to desired temperature and yielding the total momentum of the system as zero

Equilibration. The averages for equilibrium properties must be independent of the initial conditions. Thus one must carefully check if the system has reached equilibration.

4. Run the simulation loop (steps 5-8) over a period of prescribed number of collisions to allow the system to relax from the initial conditions.

Production. After equilibration the program enters the production process. The

properties will be calculated from the configurations generated in this step.

5. Calculate all collision time Δt_{ij} for the $1/2N(N-1)$ pairs of particles. The minimum collision time $\Delta t_{\min}$ determines which pair of particles will collide next.
6. From their current position $\mathbf{r}_k(t)$, advance all spheres through $\Delta t_{\min}$ via free flight.
7. Apply periodic boundary conditions to the particles leaving the primary cell during $\Delta t_{\min}$.
8. Perform collision kinetic and obtain the new velocities of the collision pair of particles i and j .
9. Compute contributions of the current configuration to the equilibrium properties.
10. Iterate step 5-9 over the desired number of collisions. Calculate the final properties and end the simulation.

2.4 Properties Calculation

2.4.1 Pressure

One of the most important properties in this study is the pressure as the function of the number density. The pressure is usually derived from the virial theorem of the pairwise-additive potential.

$$P_{\alpha\beta} = \rho kT + \frac{1}{V} \left\langle \sum_{i=1}^{N-1} \sum_{j>i}^N (\mathbf{r}_{ij})_{\alpha} (\mathbf{f}_{ij})_{\beta} \right\rangle \quad (2.36)$$

where N is the number of molecules, $\mathbf{r}_{ij}$ is the relative position vector between the center-of-mass of molecules i and j , and $\mathbf{f}_{ij} = -\nabla u_{ij}$ is the force between them at the potential energy u_{ij} . The angle bracket indicates usual time average. In the hard-sphere model, the collision of two particles occurs when the distance of two particles equals to hard-core diameter. The forces between two particles, during the collision, have an infinite magnitude but act for an infinitesimal time, thus we do not need to sum over all pairs of particles, instead we need to identify when any of two particles i and j collide. Each pair collision contributes an amount to the average of Eqn. (2.36) when integrated over time.

$$P_{\alpha\beta} = \rho kT + \frac{1}{V t_{sim}} \sum_{collision} (\mathbf{r}_{ij})_{\alpha} (\Delta \mathbf{p}_{ij})_{\beta} \quad (2.37)$$

where t_{sim} is the total simulation time and the sum is over all collision occurring during this period; $\Delta \mathbf{p}_{ij}$ is the difference of momentum before and after the collision between particles i and j .

2.4.2 Bond Order Parameters

To distinguish different solid structures, we use the method of bond order parameters[68]. Measurements of radial distribution functions (RDF) in dense liquids indicate that each atom has roughly 12 particles in its first coordination shell[69]. The clusters of 12 atoms around a central atom corresponding to FCC and HCP crystals are shown in Figure 2.3 *a* and *b*, respectively. Figure 2.3 *c* is

icosahedral packing, which has a significantly lower energy than the others.

Figure 2.3. Three different clusters of 12 atoms surrounding a centre atom: a) FCC cluster b) HCP cluster d) Icosahedron.

The idea of bond order parameters is to capture the symmetry of bond orientation regardless of the bond length. Note that the bond represents the vector joining a pair of neighboring particles, whose distances are less than a cutoff radius. The radius can be altered depending on different definition of neighboring atoms. In our study, it equals to the distance to the minimum length of the first and the second peaks of the radial pair-correlation function $g(r)$, which has an approximate value of 1.5σ . To calculate bond order parameters, we begin with a set of numbers associated with a bond $\mathbf{r}$

$$Q_{lm} \equiv Y_{lm}(\theta(\mathbf{r}), \phi(\mathbf{r})) \quad (2.38)$$

where $\theta(\mathbf{r})$ and $\phi(\mathbf{r})$ are the polar and azimuthal angles of the bond with respect to an arbitrary but fixed reference frame, and $Y_{lm}(\theta(\mathbf{r}), \phi(\mathbf{r}))$ are the usual spherical harmonics. Since the bond between atom i and j can be arbitrarily taken as either $\mathbf{r}_{ij}$ or $\mathbf{r}_{ji} = -\mathbf{r}_{ij}$, only the even l bond parameters Q_{lm} are considered, which

are invariant under inversion of bond orientation. Global bond order parameter can be calculated by averaging $Q_{lm}(\mathbf{r})$ over all bonds in the system,

$$\bar{Q}_{lm} \equiv \frac{1}{N_b} \sum_{bonds} Q_{lm}(\mathbf{r}) \quad (2.39)$$

The average is taken over N_b , which is the number of bonds in the whole system. The Q_{lm} value for a given l can be drastically changed by applying them to a rotated coordinate system. To make the order parameters invariant with respect to rotations of the reference frame, it is important to consider rotationally invariant combinations, such as

$$Q_l \equiv \sqrt{\frac{4\pi}{2l+1} \sum_{m=-l}^l |\bar{Q}_{lm}|^2} \quad (2.40)$$

and

$$W_l \equiv \sum_{\substack{m_1, m_2, m_3 \\ m_1 + m_2 + m_3 = 0}} \begin{pmatrix} l & l & l \\ m_1 & m_2 & m_3 \end{pmatrix} \bar{Q}_{lm_1} \bar{Q}_{lm_2} \bar{Q}_{lm_3} \quad (2.41)$$

where Q_l and W_l are called second-order and third-order invariant, respectively.

The coefficients

$$\begin{pmatrix} l & l & l \\ m_1 & m_2 & m_3 \end{pmatrix} \quad (2.42)$$

in the third-order invariants are Wigner $3j$ symbols. A normalized bond order parameter is defined as

$$\hat{W}_l = \frac{W_l}{\left(\sum_m |Q_{lm}|^2 \right)^{3/2}} \quad (2.43)$$

which, for a given l , is independent of the magnitudes of the Q_{lm} values. The four bond order parameters Q_4 , Q_6 , $\hat{W}_4$, and $\hat{W}_6$ are generally sufficient to identify different structures. The values of these bond order parameters for different structures are listed in Table 2.3.

Table 2.3. Bond order parameters for face centered cubic (FCC), hexagonal close-packed (HCP), simple cubic (SC), body centered cubic (BCC), icosahedron and liquid.

Geometry	Q_4	Q_6	$\hat{W}_4$	$\hat{W}_6$
FCC	0.191	0.575	-0.159	-0.013
HCP	0.097	0.485	0.134	-0.012
SC	0.764	0.354	0.159	0.013
BCC	0.036	0.511	0.159	0.013
Icosahedron	0	0.663	0	-0.170
Liquid	0	0	0	0

Bond order parameters averaged over all bonds can be used to monitor global structural changes. Bond order parameters listed in Table 2.3 vanish in the isotropic fluid phase in the thermodynamic limit, so those quantities can be used as a means to measure isotropic fluid to solid transition.

Another third order invariant W_{446} , which is denoted as

$$W_{446} \equiv \sum_{\substack{m_1, m_2, m_3 \\ m_1 + m_2 + m_3 = 0}} \begin{pmatrix} 4 & 4 & 6 \\ m_1 & m_2 & m_3 \end{pmatrix} \bar{Q}_{4m_1} \bar{Q}_{4m_2} \bar{Q}_{6m_3} \quad (2.44)$$

is extremely sensitive to the FCC structure. W_{446} fluctuates much at the vicinity of 0.0025 for FCC arrangement while other structures have the value of W_{446} in the vicinity of 0. A system that has $W_{446} > 0.0007$ can be recognized as FCC-like whereas those with $W_{446} < 0.0007$ as non-FCC[70].

The aforementioned global bond order parameters are used to characterize the structure of the whole system. In computational studies of fluid-solid phase transitions, it is important to be able to distinguish particles within different local structures. The technique of calculating global bond order parameters can be extended to identify individual solid-like particles, by using the local bond order parameters. First, the complex vector $q_{lm}(i)$ of particle i is defined as

$$\bar{q}_{lm}(i) = \frac{1}{N_b(i)} \sum_{j=1}^{N_b(i)} Y_{lm}(\mathbf{r}_{ij}) \quad (2.45)$$

where $N_b(i)$ is the number of nearest neighbors of particle i , and the integer l and spherical harmonic Y_{lm} have the same definition with global bond order parameters. The local invariants can be constructed from $q_{lm}(i)$,

$$q_l(i) \equiv \sqrt{\frac{4\pi}{2l+1} \sum_{m=-l}^l |\bar{q}_{lm}(i)|^2} \quad (2.46)$$

and

$$\hat{w}_l(i) = \frac{w_l(i)}{\left(\sum_{m=-l}^l |\bar{q}_{lm}(i)|^2 \right)^{3/2}} \quad (2.47)$$

where $w_l(i)$ is given by

$$w_l(i) \equiv \sum_{\substack{m_1, m_2, m_3 \\ m_1 + m_2 + m_3 = 0}} \begin{pmatrix} l & l & l \\ m_1 & m_2 & m_3 \end{pmatrix} \bar{q}_{lm_1}(i) \bar{q}_{lm_2}(i) \bar{q}_{lm_3}(i) \quad (2.48)$$

The parameter W_{446} also has a local version w_{446} which is defined as

$$w_{446}(i) \equiv \sum_{\substack{m_1, m_2, m_3 \\ m_1 + m_2 + m_3 = 0}} \begin{pmatrix} 4 & 4 & 6 \\ m_1 & m_2 & m_3 \end{pmatrix}^- \bar{q}_{4m_1}(i) \bar{q}_{4m_2}(i) \bar{q}_{6m_3}(i) \quad (2.49)$$

Unlike the global bond order parameters which vanish for the fluid phase, the local bond order parameters have large values not only in solid but also in the liquid phase.

2.4.3 2D Hexagonal Order Parameter

In addition to the bond order parameters Q_4 , Q_6 , $\hat{W}_4$, $\hat{W}_6$ and W_{446} which capture the order of a system in three directions, we have also utilized the 2D hexagonal order parameter Φ_6 defined as

$$\Phi_6 = \left| \frac{1}{M} \sum_{i=1}^M \frac{1}{N_i} \sum_{j=1}^{N_i} \exp(i6\theta_{ij}) \right| \quad (2.50)$$

where M is the number of particles in the 2D simulation, N_i is the number of nearest neighbors of particles i . We define the nearest neighbors as those particles j within a distance 1.3σ from particles i , and θ_{ij} is the angle between two neighboring particles i and j and an arbitrary but fixed axis. For a perfect hexagonal plane, the value of Φ_6 is unity, but far from unity for a disordered phase.

2.4.4 Structure Factor

The structure factor $S(\mathbf{k})$ in 3-dimensionsal phase is defined as[71]

$$S(\mathbf{k}) = N^{-1} \left| \sum_{i=1}^N \exp(i\mathbf{k} \cdot \mathbf{r}_i) \right|^2 \quad (2.51)$$

where N is the number of particles, $\mathbf{k} = (2\pi/L)\mathbf{n}$ is a reciprocal lattice vector for the periodic unit cell, with $\mathbf{n}$ the vector with integer elements and L the length of simulation box, and $\mathbf{r}_i$ is the position of particle i . To calculate $S(k)$, where $k = |\mathbf{k}|$ is the magnitude of the reciprocal lattice vector $\mathbf{k}$, all the reciprocal lattice vectors inside a spherical shell of thickness $2\pi/L$ are averaged. The structure factor for crystalline structure would show a series of peaks at regular intervals. On the contrary, for fluid-like and disordered solid structures, the structure factor would show smooth behavior.

2.5 Simulation Environment

To conduct our studies we apply the programming package *Etomica*.^[72, 73] *Etomica* is an API for the construction of molecular simulation written in the object-oriented Java programming language. The API is a collection of building block classes that can be assembled to perform complex computation in a form of simulation. All simulations in the study are extension of *Etomica*, which contains branches of java classes with respect to species of molecules, the simulation space, the phase, and the potentials or molecular interactions. The *Etomica* simulation API also has classes that perform MD or MC simulation, control the process of the simulation, and meters to collect the properties of the system. The OpenGL technology is introduced to provide 3D visualization. The main components of *Etomica* API are shown below:

Simulation: Each simulation is formed from a single *Simulation* class, which

serves as a point of reference for all elements.

Space: The *Space* class defines all features of physical space in which the simulation is performed. It contains methods of generating one, two, or three dimensions spaces and its boundary.

Species: The *Species* class defines and creates the atoms and molecules used in the simulation. A molecule is just a data structures holding information such as what type and how many atoms it contains, where the atoms are and how fast they are moving.

Potential: The *Potential* class defines how the atoms interact with each other. There are two fundamental types of potential, soft potential and hard potential. Soft potential can report an energy, force, virial, etc, while hard potential, which have impulsive forces, can report the energy and the collision force and virial.

Phase: The *Phase* class collects all the atoms that interact with each other. Most simulations consist of a single phase, but there are many circumstances in which more than one phase is appropriate. This class handles both cases.

Integrator: The *Integrator* class is responsible for generating configurations of the molecules and their movement. Typically, an integrator will do this by applying a molecular dynamics or Monte Carlo algorithm.

Controller: The *Controller* class acts to control the simulation process, for example, setting the simulation in motion and determining when it ends.

Meter: The *Meter* class is responsible for collection data from the simulation.

Displays: The *Display* class is responsible for presenting information to the user with Graphic User Interface (GUI) platform.

Device: The *Device* class in graphical element that permits the user to interact with the simulation on-the-fly.

Our simulations can be performed in graphic or non-graphic modes. Usually, coding and testing of small systems are performed on the PC level, which operates under *Windows* operating system. We use *eclipse*, which is a Java Integrated Development Environment (IDE) developed by IBM and the IDE provides us very much freedom to manipulate *Etomica* package. A screenshot of the simulation system is shown in Figure 2.4. Simulations of large scale are performed in a computer cluster running *Linux* operating system and *Sun Grid Engine (SGE)* for distribution of simulation jobs.

Figure 2.4. Screenshot of the simulation environment based on eclipse java IDE

Chapter 3

Bulk Hard-Sphere Fluids

3.1 Introduction

The hard-sphere model has received much attention despite its simplicity. It can serve as a useful model for a number of physical applications such as simple liquids, glasses and colloidal systems. Many complex dense molecular systems can be reduced and approximated as hard spheres since the short range repulsive interaction is the primary factor to determine spatial arrangement of the particles. A lot of studies have shown evidence for the existence of a disorder-to-order phase transition for hard-sphere systems. The equation of state splits into three branches where the reduced pressure P^* is plotted as the function of reduced number density ρ^* . The fluid branch begins from $\rho^* = 0$ until the freezing density at $\rho^* \approx 0.943$. With further increase of density, the pressure does not change, which shows a horizontal portion at which both fluid and solid can coexist until the melting point at $\rho^* \approx 1.041$. The curve continues above the melting point and ends at the close-packed FCC crystal at the density $\rho^* = 1.414$.

To understand the existence of phase transition in hard-sphere systems, one must look into the structural difference in the fluid and solid states. At low density, the system contains many disordered states, which are thermodynamically stable. As the density increases, the disordered configurations are less allowable and at some point the ordered configurations

dominates, and the system freezes. To understand the process, we have studied the systems initially packed as face centered cubic (FCC), hexagonal close-packed (HCP) and body centered cubic (BCC) structures. The equations of state of these systems are precisely determined via MD simulations and the structural variations are monitored by bond order parameters, radial distribution functions, and structure factors.

3.2 Simulation Methodology

3.2.1 Initial Positions

The positions of the hard spheres can be assigned from the end of an earlier run, but more effectively, we may locate the atoms on a regular lattice structure into which the substrate of interest crystallizes.

Here we discuss how to construct the FCC and BCC lattices in our simulations. A space lattice is constructed by replicating a fundamental arrangement of atoms called the unit cell, which prescribes the locations of the smallest number of atoms n needed to define the symmetry of the lattice. The unit cell of FCC and BCC lattices are cubic structures, each side of the unit cell has length a , which is called the lattice constant. Therefore a cubic unit cell composed of identical atoms, the density is

$$\rho = \frac{n}{a^3} \quad (3.1)$$

where $n = 4$ for FCC lattice and $n = 2$ for BCC lattice. The 4 location vectors for the FCC unit cell are

$$\begin{aligned}
\mathbf{r}_1 &= (0, 0, 0) \\
\mathbf{r}_2 &= (0, \frac{1}{2}a, \frac{1}{2}a) \\
\mathbf{r}_3 &= (\frac{1}{2}a, 0, \frac{1}{2}a) \\
\mathbf{r}_4 &= (\frac{1}{2}a, \frac{1}{2}a, 0)
\end{aligned} \tag{3.2}$$

and the 2 location vectors for the BCC unit cell are

$$\begin{aligned}
\mathbf{r}_1 &= (0, 0, 0) \\
\mathbf{r}_2 &= (\frac{1}{2}a, \frac{1}{2}a, \frac{1}{2}a)
\end{aligned} \tag{3.3}$$

Full FCC and BCC lattices can be built from these unit cells by translating these corresponding vectors in the unit cell through the distance of the lattice constant a in each of the three directions (i.e. x , y , and z). The total number atoms N of an FCC lattice is $N = 4I^3$ and for BCC lattice is $N = 2I^3$, where I is the number of unit cells along one dimension of the cubic box.

3.2.2 Simulation Details

The MD simulations were first performed in the canonical (NVT) ensemble, where the number of particles N , the volume V and the temperature T are fixed during simulation. The temperature was kept constant by simple momentum rescaling at the end of each time step. The time step Δt^* was set to 0.1 and the temperate T^* was fixed at 1.0. Note that the symbol $*$ represents the reduced unit. For FCC structure, I was set to 8, where $N = 4 \times 8^3 = 2048$. For the BCC structure, I was set to 10, where $N = 2 \times 10^3 = 2000$. We have also conducted simulations of double and half system sizes and carefully checked that the system size we used was enough to avoid finite size effects. The total time steps

for equilibration were set to 2×10^5 and once the system reached equilibrium, another same number of steps were run in the microcanonical (NVE) ensemble to produce data. The pressure tensor was collected via Eqn. (2.37) for each collision of particles. The radial density distribution function $g(r)$, global bond order parameters Q_4 , Q_6 , $\hat{W}_4$, $\hat{W}_6$ and W_{446} , local bond order parameter w_{446} , and structure factor $S(k)$ were calculated and updated at the end of each time step.

3.3 Results and Discussion

3.3.1 Equation of State

In the fluid phase, Carnahan and Starling[74] proposed the following equation of state:

$$Z = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3} \quad (3.4)$$

where $\eta = \rho \sigma^3 \pi/6$ is the packing fraction. Boublik and Nezbeda[75] refined the equation as follow:

$$Z = \frac{1 + \eta + \eta^2 - b_1 \eta^3 - b_2 \eta^4 - b_3 \eta^5}{(1 - \eta)^3} \quad (3.5)$$

with $b_1 = 0.764314$, $b_2 = 0.151532$, and $b_3 = 0.654551$. More recently, Speedy[76] proposed another approximation for the fluid phase

$$Z = \frac{P\beta}{\rho} = 1 + \frac{x + 0.076014x^2 + 0.019480x^3}{1 - 0.548986x + 0.075647x^2} \quad (3.6)$$

For the solid phase, Speedy[77] proposed the following equation of state:

$$Z = \frac{3}{1-z} - a \frac{z-b}{z-c} \quad (3.7)$$

where $z = \sigma^3 \rho / \sqrt{2}$ and $a = 0.5921$, $b = 0.7072$ and $c = 0.601$ for the FCC crystal.

In Figure 3.1, we compare the predictions of the equation of state with the results from our MD simulations for a long range of densities.

Figure 3.1. Reduced pressure P^* as the function of average density ρ^* for the hard sphere system. The open circles are data from MD simulations of this work. The red solid line is analytical approximation of Carnahan-Starling for the fluid phase and blue line is the EOS proposed by Speedy for the FCC crystal. The black line marks the coexistence tie-line at which the fluid and

solid phase show equal pressure, temperature, and chemical potential.

As can be seen in Figure 3.1, our results from the MD simulations match the empirical equation of state perfectly. A discontinuity of the equation of state is observed between $\rho^* = 0.94$ and $\rho^* = 0.95$. The equation of state has different behavior at the different branches of the discontinuous point and match the empirical equation of state of fluid and solid, respectively, which implies that freezing happens at this density. Phase coexistence is not observed in this system as the FCC at $\rho^* > 0.95$ is thermodynamically stable. To locate the fluid-phase coexistence densities, one may find the chemical potential and the pressure of the two phases. To calculate the chemical potential of the fluid phase, the equation of state is integrated from the dilute gas limit, which yields the Helmholtz free energy as the function of density:

$$\frac{F(\rho)}{Nk_B T} = \frac{F^{id}(\rho)}{Nk_B T} + \frac{1}{k_B T} \int_0^\rho d\rho' \left(\frac{P(\rho') - \rho' k_B T}{\rho'^2} \right) \quad (3.8)$$

where N is the number of particles, k_B is the Boltzmann constant, T is temperature, F^{id} is the free energy of an ideal gas, and P is the pressure. The chemical potential is calculated as follows,

$$\beta\mu(\rho) = \frac{\beta G}{N} = \frac{\beta F}{N} + \frac{P}{\rho k_B T} \quad (3.9)$$

The Helmholtz free energy per particles of the ideal gas at density ρ is given by

$$\beta f^{id} = \frac{F^{id}(\rho)}{Nk_B T} \approx \ln \rho \Lambda^3 - 1 \quad (3.10)$$

where Λ is the de Broglie thermal wavelength. The chemical potential in the solid phase cannot be calculated directly from Eqn. (3.9) since the integration path is not reversible over strong first-order phase transition. Frenkel and Ladd[36, 50] proposed a method of coupling the particles harmonically to their lattice sites so that the solid can be transformed into an Einstein crystal reversibly. The potential energy with a coupling parameter λ for a hard-sphere solid is given by,

$$U(\lambda) = U_0 + \lambda U = U_0 + \lambda \sum_{i=1}^N (r_i - r_{0,i})^2 \quad (3.11)$$

where r_i is the position of a given particle i and $r_{0,i}$ is the lattice position, U_0 is the original hard-sphere potential. The free energy difference between the systems with coupling parameter λ and the hard-sphere solid is then given by,

$$F_{HS} = F(\lambda_{\max}) - \int_0^{\lambda_{\max}} U(\lambda) d\lambda \quad (3.12)$$

To this end, we use the coexistence pressure $P = 11.567$ and the chemical potential $\mu = 17.071$ from ref. [36] and draw the coexistence tie-line in Figure 3.1. Our own estimations were very close to those values. (not shown here)

The MD simulation results of HCP and BCC together with the results of FCC for comparison is shown in Figure 3.2.

Figure 3.2. Reduced pressure P^* as the function of density ρ^* for FCC, HCP and BCC structures. The open symbols are data from MD simulations. The solid lines are the same as Fig. 3.1.

As can be seen from Figure 3.2, the results of HCP is very close to that of FCC. Recent studies have shown that the FCC structure to be more stable at melting point than HCP structure by the free energy difference of the order of $10^{-3}k_B T$. The BCC structure seems unstable at the density larger than the freezing density of FCC and HCP. The pressure is higher than that of FCC and HCP structures at the same density larger than 0.94.

3.3.2 Structure Characterization

The hard-sphere system is the simplest model to exhibit freezing/melting

behavior. At high densities hard-sphere systems have solid-like behavior: long range order and small self-diffusion coefficients. At low densities they have fluid-like behavior: lack of long range order and moderate self-diffusion. Due to the absence of attractive forces, the freezing process is generally a geometric structure rearrangement from disorder to order.

In Figure 3.3, we plot the radial distribution function (RDF) $g(r)$ for the densities 0.90, 0.96, 1.00, 1.04 and 1.12 for the FCC structure. For the low density $\rho^* = 0.90$ we observe fluid-like behavior. The $g(r)$ has smooth peaks at $r = 1.0, 2.0$, and 3.0 , and has a long tail where $g(r)$ decays to the value of 1.0. At higher density (e.g. $\rho^* = 0.96$), $g(r)$ develops small peaks below smooth peaks at $r = 2.0$ and $r = 3.0$, and at higher densities (e.g. $\rho^* = 1.00$ and 1.04), these small peaks increase to distinct peaks at $\rho^* = 1.12$. The development of the radial distribution function shows how the system is frozen with long range order developed in the system when the density increases.

Figure 3.3. Radial distribution functions $g(r)$ of the hard spheres in FCC structure at different densities.

A comparison of the radial distribution functions for the FCC, BCC and HCP structures at the density $\rho^* = 1.26$ is given in Figure 3.4. The RDFs of FCC and HCP are almost overlap at $r < 2.0$, though have slight difference in values. The RDFs can only give us rough idea about the particle distribution. It is difficult to distinguish fluid and solid and different structures only by comparing the RDFs, especially when different structures are mixed.

Figure 3.4. Radial distribution functions $g(r)$ for the FCC, BCC, and HCP structures at the density $\rho^* = 1.26$.

Figure 3.5 shows the structure factor $S(k)$ for the FCC structure at fluid (i.e. *a*) and solid (i.e. *b*) phases. The behavior of $S(k)$ is distinct at different phases. The solid structure ($\rho^* = 0.96, 1.00, 1.04$ and 1.12) shows the corresponding spikes on the $S(k)$ curves. In comparison, the structure factors of fluid ($\rho^* = 0.90$ and 0.94) structure have smooth curves. It is clear that the phase transition from fluid to solid is correlated with the structure transformation from disorder to order.

Figure 3.5. Structure factor $S(k)$ for the bulk hard-sphere system in FCC structure at different densities.

The bond order parameters as the function of density are shown in Figure

3.6 for the FCC, BCC and HCP structures. As can be seen from Figure 3.6, all five bond order parameters are near zero at the fluid branch, Q_4 , Q_6 and W_{446} of the FCC and HCP structures show sharp increases when crystallization happens and the values continuously increase with respect to density towards the corresponding values of the perfect FCC and HCP crystal. The BCC structure has similar increase of Q_4 and Q_6 , but the values do not increase continuously with respect to density, which implies that the BCC structure in such densities is not stable. We notice that the HCP structure shows the increase of W_{446} , but the value is much smaller than that of the FCC. Even the value of W_{446} at $\rho^* = 1.3$ is smaller than the value of W_{446} of the FCC at $\rho^* = 0.95$, at which crystallization happens for both the structures. This indicates that W_{446} can distinguish the FCC structure from other structures. The values of $\hat{W}_4$ almost invariant for the FCC and HCP in their solid phase and equal to their corresponding perfect values of -0.159 and 0.134, respectively. $\hat{W}_6$ of the FCC in the solid phase shows similar behavior with $\hat{W}_4$ (i.e. the value is almost invariant at the value of -0.013), while for the BCC, $\hat{W}_6$ changes a little with increase of density, but finally reaches the perfect value of -0.012 at sufficiently high density. The value of $\hat{W}_4$ of the BCC is close to the perfect value of 0.159 at density $\rho^* > 1.04$, which is the melting density of the stable hard-sphere solid, but still, the value fluctuates when the density increases. $\hat{W}_6$ of the BCC is far from the perfect value of 0.013 at any density.

As discussed above, the bond order parameters serve well to determine the existence of crystallization of hard-sphere systems by sharp change of the

values and enable us to distinguish different crystal structures.

Figure 3.6. The bond order parameters Q_4 , Q_6 , $\hat{W}_4$, $\hat{W}_6$ and W_{446} as a function of density for the hard-sphere systems in FCC, BCC and HCP structures.

3.4 Conclusion

In this chapter, the equations of state of the bulk hard-sphere fluids are studied. Different initial packings of particles are investigated for the densities from dilute fluid to solid. The results of the equation of state from molecular dynamics simulations perfectly reproduce the literature data and match the analytical approximations. The structure of the bulk hard-sphere systems are characterized using various tools including radial distribution functions, bond order parameters and structure factors. We found that although all these tools perform well in distinguishing fluid and solid structures, the bond order parameters are extremely sensitive to the different structures.

Chapter 4

Hard Sphere Fluids Confined in Cylindrical Hard Pores

4.1 Introduction

It is well recognized that fluids confined in nano- to micrometer pore sizes exhibit different properties and behavior compared to bulk fluids at the same thermodynamic conditions[78-82]. An explanation to this phenomenon can be found from understanding confining effects towards the structural arrangement and the movement of molecules, which are much restricted than in the bulk [65, 83]. In past decades many studies on confinement have been done in porous media and carbon-nanotube (CNT). It has been shown that even with a generalized pore shape, the fundamental knowledge of fluid-pore systems can be captured for realistic systems [62, 84, 85].

In correspondence with the growing demands for understanding solid phase-related problems in cylindrical confinement, there exist some studies, which use the hard cylindrical wall with hard-sphere model for the fluids. Several numerical results provide evidences on the existence of fluid-solid phase transition in both for bulk[5, 86-88] or confined systems[64] even in the absence of attractive interactions. The hard cylindrical confinement provides the system under effects of dominant influence of entropy, thus leads one to focus on the relation of the phase-transition and the structure of confined particles with varying pore sizes. Moreover, this simple model resembles realistic colloidal

particles[89-91], and peapod-related systems (e.g. C_{60} encapsulated in CNT) that can be described by quasi one-dimensional approach in statistical mechanics[92].

Mon and Percus[93] performed *NPT* Monte Carlo (MC) simulations of confined hard-sphere fluid to obtain the effect of narrow pore on the equation of state (i.e pressure vs. density). They found a non-monotonic change of the equation of state caused from various structures of confined particles. Later, theoretical quantification for hard-sphere fluids behavior in very narrow pore was established[94]. In recent years, Gordillo *et al.* [64]observed the onset of the freezing shown by a sharp change of the density at certain radius of pores via same *NPT* MC method, and elucidated that the cause for this behavior was due to microstructural transformations. Koga and Tanaka[83] studied Lennard-Jones (LJ) confined fluids analogous to argon atoms trapped in single-walled carbon nanotube via molecular dynamics (MD). Dependence of temperature and spontaneous structures of soft-sphere particles was examined with respect to variation of phases.

The aforementioned works generally focused on narrow range of pores, but we wish to extend the idea of pore-size dependence on hard-sphere fluid-solid model with asymptotic increase of pore-size range up to 15σ , where σ is the diameter of the hard sphere, using collision-based MD method. Note that we use the term fluid-solid phase transition or phase transition to identify transition of confined fluids from disordered (i.e. fluid-like) to ordered (i.e. solid-like) states. The rest of the chapter is organized as follows: In section 4.2 we briefly introduce the fluid and boundary model in our simulation and the details of simulation

conditions in this work. Section 4.3 presents the results and discussion followed by conclusion in section 4.4.

4.2 Simulation Models and Details

In this work, the fluid-fluid interaction is represented by the hard-sphere potential,

$$u_{f-f}(r_{ij}) = \begin{cases} 0 & r_{ij} \geq \sigma \\ \infty & r_{ij} < \sigma \end{cases} \quad (4.1)$$

where r_{ij} is the distance between two particles. The cylindrical pore is then modeled by creating an inscribed cylindrical boundary in a rectangular simulation box so that fluid particles are confined in the cylindrical shape. The cylindrical pore is considered perfect rigid and has no slip, *i.e.* when a particle collides at the wall, the normal component of its momentum turns into its opposite direction with the same magnitude while the tangential component is invariant. The fluid-wall interaction is represented by the following equation,

$$u_{f-w}(r) = \begin{cases} 0 & r \geq 0.5\sigma \\ \infty & r < 0.5\sigma \end{cases} \quad (4.2)$$

where r is the distance from the wall boundary to the center of the particle. Periodic boundary condition is applied along the pore axis, which is set to z direction (See Figure 4.1).

Figure 4.1. Screenshots of the simulations at high densities, at which solid structures can be observed. The cross section and side views are shown for different pore sizes for $D = 1.7$ (quasi-one dimensional system), 2.2 and 2.5 (one layer), 3.01 3.1 3.2 3.5 3.6 3.7 3.9 4.0 and 4.5 (two layers), 5.0 6.0 7.0 8.0 10.0 and 12.0 (3 or multi layers).

The units in this work are simulation units, which use *amu* for mass, Å for length, and *ps* for time. Since we take unity for hard-sphere diameter σ , the number density ρ^* (i.e. $\rho\sigma^3$) becomes dimensionless. All length scales are in units of σ . Other reduced units are pressure $P^* = \beta P \sigma^3$, and time $t^* = t/[\sigma(m/kT)^{0.5}]$. We have performed a series of MD simulations in the microcanonical (*NVE*) ensemble, where N is the number of particles, V is the volume of simulation box and E is energy, using *Etomica*[72, 73]. The reduced time step Δt^* was set to 0.01. The reduced temperature T^* was fixed at 1.0, as it has no effects to the transition behavior in the hard-sphere system. For pore diameters less than 4.0σ the simulation was conducted with the system size of 1000 particles. 2000 or more particles were used for pores larger than 4.0σ to avoid finite size effects. Simulations of double system size were conducted and revealed no significant difference in properties compared to those revealed in smaller system. The total time steps for equilibration were set to 10^6 at constant temperature and once the system reached equilibrium, another same number of steps were run in the *NVE* ensemble to produce data. Note that we omit σ in the length unit hereafter. For P_{zz}^* (i.e. axial pressure), we use the pressure tensor equation obtained from collision-based virial theorem[95]. Since the system of interest is not under effect of shear stress, we consider only the main diagonal terms in the pressure tensor, where P_{xx}^* and P_{yy}^* (e.g. same magnitude in average) are in the radial direction while P_{zz}^* is in the axial one.

It is generally very difficult to simulate high density systems mainly due to the difficulty of constructing the random and spontaneous systems above the

freezing density. The artificially constructed initial packing at high density may affect the properties of the system. The initial configuration may be at the jammed state that could not be changed to other possible configurations at the same density. A study of spontaneous close-packed structures of hard-sphere particles in cylindrical shape at $T^* = 0$ was done by Pickett *et al.*[65], who found different close-packed configurations of particles in narrow cylindrical shape (*i.e.* diameter smaller than 2.2). Another study of close-packed structure of confined LJ systems was conducted by Koga and Tanaka[83]. Spontaneous close-packed structure of particles in larger pores becomes severely complex and remains an unsolved problem. To obtain high density, one solution is starting the simulation at random fluid-like structure and carefully compress the system to high density using the NPT MC method. However, by the NPT scheme, compressing the system from low density to high usually lead a system to a jammed state at high density somewhere above melting or to a metastable state for worse case. This might have been an issue for Gordillo *et al.*[64], who could not observe the freezing at $D = 2.18$, while we found it at 2.17. Also, their simulations ended at $P_{zz}^* = 20.0$, which is lower than the coexistence pressure we found for $D = 2.18$. We suspect that they could have not performed simulations at higher pressure due to low probability of volume-decrease; the system did not go through chirally ordered solidification. To this end, we realized that the NPT scheme may not be suitable for accurate determination of the fluid-solid transition. Thus we develop our own scheme to construct the initial configurations.

Here we give a brief description of this simplified scheme. In radial direction, the particles are packed into layers of regular polygons with different

shape. Note the radius of i th layer within pore diameter as r_i and the number of sides of a polygon as S_i . We begin with the outer layer. For a pore diameter D , the maximum accessible distance of the center of a particle to the center of cylinder is $(D-1)/2$, then $r_n = (D-1)/2 - \delta$, where n denotes the maximum number of layers and δ is a small number (i.e. 0.001 or smaller), which can be modulated to position the particles radially so that the surface of the particle at the outmost layer do not overlap with the cylindrical wall surface. In the next step, we calculate the maximum possible number of sides S_n of a regular polygon, whose length of side is 1.0 and circumradius is smaller than r_n . Then we lay the center of particles into a regular polygon of S_n side and circumradius r_n . The $(n-1)$ th layer is packed with $r_{n-1} = r_n - 1.0 - \delta$ and the same procedure is repeated until the inner-most layer is reached. If the radius of the inner-most layer r_1 is not large enough to hold a polygon shape or layer of two atoms, we then pack the particles into a zig-zag structure. In the axial direction, the regular polygons are stacked with the structure $ABAB\dots$, in which, A and B have the same shape, while B rotates with an angle of π/S_i against A . The distance of A and B is set to 0.87 (i.e. slightly larger than $\sqrt{3}/2$, to avoid the overlap of particles and assure enough density). Note that this scheme has some shortcomings; first, it does not produce extremely high density (i.e. near close-packed density in the bulk), and second, at high density, as the packing is not spontaneously constructed, the properties obtained from these initial packing may be specific beyond the melting point. Nevertheless, this compromising solution of packing structure serves our purpose, which predicts the target fluid-solid transition ranges of density and pressure of our interest.

The microscopic structure of the system is monitored by the one-body radial density profile $\rho(r^*)$ and the axial pair distribution function $g(z^*)$, where $r^* = r/\sigma$ and $z^* = z/\sigma$, respectively. For the fluid confined in cylindrical pores, the radial density profile $\rho(r^*)$ is obtained by dividing the pore into n concentric cylindrical shells with same thickness $\Delta r = (D-1.0)/2n$, then sample the number of particles in each shell divided by the shell volume. Thus, the segment of $\rho(r^*)$ can be expressed as,

$$\rho(r_i/\sigma) = \frac{\langle N_i \rangle}{\pi \left((r_i/\sigma)^2 - (r_{i-1}/\sigma)^2 \right) L} \quad (4.3)$$

where N_i is the number of particles, whose distances to the pore center are in the range r_{i-1} to r_i , and $r_i = \Delta r \times i$. L is the length of cylindrical pore. A simple modification from the pair correlation function based on the spherical coordinate can lead to the axial pair distribution function, which is extracted from the following equation,

$$\int_{z^*=0}^{z^*=\infty} \rho^* g(z^*) \pi \left(\frac{R}{\sigma} \right)^2 dz^* \approx N \quad (4.4)$$

where N is the total number of particles, $\rho = N/V$ is the number density, and R is the radius of the cylindrical pore. The upper limit of Z^* is changed to the axial length of the simulation box, L in calculation. A normalization factor (i.e. $N\rho\pi R^2 L$) has been used to present the results in this study.

4.3 Results and Discussion

It has been generally considered that a purely one-dimensional system with short-ranged interactions cannot have a phase transition at finite temperature[96]. Hard-sphere particles confined with pore diameters less than 2.0 can be considered as such kind of system, as each particle can only have two unchangeable neighbors and the motions of particles are restricted to one dimension, the axis of the cylindrical core (see Figure 4.1 for snapshots of confined structures at different pore sizes). Figure 4.2 presents the equation of state of the aforementioned system. We observe that for $D = 1.1$, P_{zz}^* is lower than the bulk value (i.e. Carnahan and Starling[74] and Speedy[77]) at the same density. This is due to fewer collisions between particles, which can be considered as a major confining effect; the frequency of occurrence of inter-collision between particles is comparable to that of the particle-wall collision. For other pore sizes (i.e. $D = 1.3, 1.5, 1.7$ and 1.9), the axial pressures almost overlap with the bulk value at low density, and as density increases, they greatly deviate from the bulk value and diverges to the infinite at the close-packed structures corresponding to their pore sizes. We particularly observe that the dependence of the axial pressure on the pore size is non-monotonic. Over densities higher than 0.4, it is clear that the axial pressure increases with the pore diameter from 1.1, reaches its maximum around 1.7, and then drops as the diameter increases to 1.9. This behavior indicates the structural change of the confined particles, which can be easily observed by the axial pair distribution function $g(z^*)$ as shown in Figure 4.3. We did not observe any discontinuous points indicating the occurrence of the phase transition in these

pore sizes.

Figure 4.2. The axial pressure P_{zz}^* vs. the average density ρ^* of confined hard-spheres in the cylindrical hard pore. The pore diameters are in the range from 1.1 to 1.9. The solid line for Carnahan-Starling's equation of state²⁵ is plotted for comparison. Error is smaller than the size of symbols.

Figure 4.3. Axial distribution function $g(z)$ at $D = 1.7$. The different lines correspond to the densities from low to high, which show no distinct difference in shape, thus, no internal structure rearrangement from disorder to order.

The axial pressure with respect to the average number density is presented in Figure 4.4 for the pore sizes ranged from 2.17 to 2.5. Such systems consist of only one cylindrical layer of particles of twisted helixes or simple regular polygon shapes – triangle and square (See Figure 4.1).

Figure 4.4. The axial pressure P_{zz}^* vs. the average density ρ^* of confined hard-spheres in the cylindrical hard pore. The pore diameters are in the range from 2.17 to 2.5. The solid lines in different phases are obtained from the equation of states for fluids and solids (i.e. face-centered-cubic hard-sphere crystal) from Carnahan-Starling and Speedy, respectively. Error is smaller than the size of symbols.

Compared to the case $D \leq 1.9$, these systems show higher packing over unit volume. The axial pressure is always larger than the bulk value over the density of interest; the inter-collision between particles is more rigorous than the particle-wall collision. The smallest pore size at which the phase transition of hard-sphere fluids we observed is $D = 2.7$. Due to the severe sensitivity of the pore size on the phase transition, we asymptotically increase the diameter to

capture the transition of the fluid-solid coexistence region. Note that the *NPT* MC method is not easily able to obtain the clear phase transition with the same accuracy. While the pore size gradually increases until 2.2, the axial pressure decreases in a non-monotonic manner, but the freezing and melting densities linearly decrease with nearly same range of the coexistence region (i.e. weak dependence on pore size). We observe the fluid-like (i.e. disordered) structure below the freezing density transforms to the solid-like (i.e. series of triangular polygons in the axial direction) through forming a twisted helical structure at coexistence. Typical pair distribution functions at $D = 2.2$ are presented to show the confined structures at different phase branches in Figure 4.5; fluid, around freezing, in coexistence, around melting, and solid branch. Note that appearance of small and irregular shape of peaks among regular peaks at coexistence, which indicates helical shape of the confined particles. Over this range of pore sizes, the confined particles show the similar structures except at $D = 2.5$. The freezing and melting densities shift to high with a shorter coexistence region but with the same pressure as in $D = 2.2$ (i.e. similar inter-collision numbers). We attribute this phenomenon to a structural change, in which indeed the tomogram of the confined particles depicts a square (See Figure 4.1).

Figure 4.5. The axial distribution function $g(z^*)$, where $z^* = z/\sigma$, at $D = 2.2$. The different lines correspond to the densities at fluid branch ($\rho^* = 0.77$), around freezing density ($\rho^* = 0.80$), within fluid-solid coexistence ($\rho^* = 0.85$), around melting density ($\rho^* = 0.88$) and solid branch ($\rho^* = 0.90$).

The axial pressures in the systems of two cylindrical layers of particles are presented in Figure 4.6. Such systems involve the interactions of particles between different layers, thus render the phase-transition behavior much more complex.

Figure 4.6. Axial pressure P_{zz}^* vs. the average density ρ^* of confined hard-spheres in the cylindrical hard pore. The pore diameters are in the range from 3.01 to 4.5. The solid lines are the same shown in Figure 4.2. Error is smaller than the size of symbols at fluid and solid phases, but twice the symbols size at coexistence.

Similar to the one layer case, the pressures in these pores are larger than the bulk value at the same density. However, one can expect the oscillatory behavior of the equation of state, which may heavily rely on the confined structure of the particles. Observed by Figure 4.1 and Figure 4.7, the outer-layer particles are aligned following loosely elongated helical shape along the axial direction so that the inner-layer particles form zig-zag (i.e. well-fitting of the inner-layer particles onto the contacting surface of the outer-layer particles) at $D = 3.01$, the

outer layer is recoiled to form a more compact helical shape, which makes the inner-layer particles aligned in a line at $D = 3.1$, and then the hexagonal shape of the outer-layer particles are formed throughout the axial direction with the inner-layer particles form in a line at $D = 3.2$. Indeed, we found the oscillatory values of coexistence pressure and densities. For $D = 3.01$, we observed a wide coexistence region (i.e. from $\rho^* \approx 0.870$ to 0.935 , indicating a large shift towards the bulk phase-transition region, compared to the case of $D = 2.5$) and the coexistence pressure is about 11.9 , which is quite close to the coexistence pressure in the bulk. A little increase of the diameter to 3.1 largely shifts the coexistence region (i.e. from $\rho^* \approx 0.950$ to 0.991) and the coexistence pressure is around 20.2 , but at $D = 3.2$, the coexistence region drops back again (i.e. from $\rho^* \approx 0.863$ to 0.892) with the pressure at around 11.1 . As the pore size continuously increases, we found that the system exhibits the oscillatory behavior of the equation of state with the narrow phase-transition region. In particular, over the pore range from 3.5 to 4.5 , the largest coexistence pressure was found at $D = 3.6$ due to a probable occurrence of the closed-packed structure as similarly found in $D = 3.1$. Most interestingly, the phase transition disappears at $D = 3.7$. We speculate that the system is in the jammed configuration, which can be indirectly seen from very low density for the inner-layer and high one for the outer-layer, which forms a concrete octagon shape. We have also not seen clear phase transitions at $D = 3.9$ and 4.0 .

Figure 4.7. Radial density profiles $\rho(r^*)\sigma^3$, where $r^* = r/\sigma$, for the pores in the range from $D = 3.01$ to 4.5 . The profiles show the different positions formed by the two layers of particles within the pores.

For the systems with 3 or more layers, the pressure is close to the bulk fluid phase value and the phase transition generally happens below the freezing density of the bulk system. The equation of states are presented in Figure 4.8 and typical axial pair distribution functions for fluid and solid are presented in Figure 4.9 to show the relative structures of the confined particles between small ($D = 3.01$ and 3.5) and large ($D = 6.0$) pores.

Figure 4.8. The axial pressure P_{zz}^* vs. the average density ρ^* of confined hard-spheres in the cylindrical hard pore. The pore diameters are in the range from 5.0 to 15.0. The bulk lines are the same as Figure 4.1 and Figure 4.4. Error is smaller than the size of symbols at fluid and solid phases, but twice than that of the symbols at coexistence.

Figure 4.9. The axial pair distribution function $g(z^*)$, where $z^* = z/\sigma$, for the pores $D = 3.01, 3.5$ and 6.0 at fluid branch and solid branch, respectively.

Fluid-solid coexistences are clearly observed for $D \geq 6.0$ while those are absent (or not clear) in $D = 5.0$ and 5.5 . The freezing and melting points shift to higher densities and the coexistence pressure rises as the pore size increases from $D = 6.0$ to 8.0 . For $D \geq 10$, we found that the coexistence pressure is very close to the bulk value but with a shorter range of the coexisting region. We do not observe a strong oscillatory behavior of the equation of state over this range of the pore sizes indicating less effect of the different packing-structures. The values of the freezing and melting densities are presented in Table 4.1 with respect to the coexistence axial pressures depending on the pore sizes at the phase transitions. In these large pores, each layer could be regarded as a

hexagonal plane rolls into cylindrical pore in general. As the pore size increases, atoms are less directly affected by the wall boundary so that the bulk structure might be locally formed in the vicinity of the cylinder axis, however we do not specify a notable threshold to distinguish whether the particles follow the behavior of the bulk system or highly confined one. Lastly, we provide relative axial pressures with respect to those at bulk depending on pore sizes when the density of system is below 0.7 in Figure 4.10. At very low densities from 0.1 to 0.2, the pressures monotonically reduce towards those at bulk as pore sizes increase. As density increases, we observed that the range of pore size for the non-monotonic behavior of the relative pressure becomes larger and the pressures cross over to those at lower densities. This phenomenon indicates the considerable structural rearrangements started even at liquid-like densities. The non-monotonic behavior of the relative pressure spreads over larger pore size as the density increases, thus complex cross-over of the equation of state happens at coexisting and solid-like regions as shown in this work.

Table 4.1. Estimated data of densities at freezing (ρ_f^*) and melting (ρ_m^*) and coexistence axial pressure ($P_{zz,coe}^*$) for various pore sizes. The coexistence pressure is calculated by averaging the values in the coexistence region. The freezing and melting densities are then estimated by fitting the second-order polynomials to fluid and solid branches, respectively. The values shown in parentheses represent errors in the last digits.

Diameter	ρ_f^*	ρ_m^*	$P_{zz,coe}^*$
2.17	0.852(1)	0.935(1)	26.1(2)
2.18	0.832(1)	0.914(2)	20.6(1)
2.19	0.813(2)	0.895(4)	17.2(3)
2.2	0.803(1)	0.878(2)	14.91(9)
2.5	0.826(2)	0.893(3)	14.8(4)
3.01	0.870(4)	0.935(3)	11.9(2)
3.1	0.950(1)	0.991(2)	20.2(4)
3.2	0.863(2)	0.892(1)	11.1(1)
3.5	0.852(2)	0.893(2)	13.9(2)
3.6	0.870(1)	0.909(1)	14.8(1)
4.5	0.897(5)	0.929(7)	12.9(6)
6.0	0.858(2)	0.879(6)	9.73(6)
7.0	0.865(3)	0.899(4)	9.8(1)
8.0	0.883(3)	0.911(6)	10.4(1)
10.0	0.903(4)	0.947(8)	11.0(2)
12.0	0.922(1)	0.983(9)	11.7(4)
15.0	0.922(4)	0.961(3)	11.5(1)

Figure 4.10. The relative axial pressure (i.e. P_{zz}^* / P_{bulk}^*) vs. the diameter of pore for dilute to dense fluids.

4.4 Conclusion

In this chapter, we consider hard-sphere fluids confined within hard cylindrical pores to capture the effects of confinement on the phase transition. We determined the equation of state in the cylindrical pores with a wide range of pore sizes via the *NVE* MD method. Besides agreement with others[64, 93, 94] in that the behaviors of the equation of states highly depend on the pore size when it is narrow, we found that little variations of the pore diameter dramatically change the freezing and melting process; large shifts on the freezing and melting densities as well as on the coexistence pressure and the degree of property dependence on the pore size become weaker as the pore diameters increase. We did not observe the phase transition in the pore diameters

less than 2.0 while the transition is observed for the pore diameters larger than 2.16, in agreement with Gordillo *et al.* (i.e. $1 + 2\sqrt{3}/3$)[64]. We presented detailed data for the coexistence of fluid-solid phase and tracked structural changes during the onset of the fluid-solid transition. Our results suggest that none of the properties considered show monotonic dependences on the pore size, mainly due to the diversity of hard-sphere packing structures with respect to different pore size. Indeed, certain pore sizes make the systems without any clear phase transitions, but one can consider other spontaneous packing structures, which we leave for a future work.

Chapter 5

Square-Well Fluids Confined in Narrow Cylindrical Hard Pores

5.1 Introduction

The square-well (SW) interaction potential plays an important role in the study of fluids as it is the simplest model containing both attractive and hard-core repulsive interactions. The thermophysical and structural properties of this model have been studied for many years in both theory and computer simulations due to practical similarities. Many results are available for vapor-liquid phase behaviors for the SW model[78, 97-99]. There are several techniques to determine the vapor-liquid coexistence, such as Gibbs ensemble Monte Carlo(GEMC)[25], Gibbs-Duhem integration (GDI)[34, 35], grand-canonical transition-matrix Monte Carlo (GC-TMMC)[78, 100]. Less is known about the fluid-solid behavior. Pagan and Gunton[101] used the free energy calculation and GDI to determine the fluid-solid coexistence and the metastable fluid-fluid coexistence for a short range SW model. Later, Liu *et al.*[32] combined GEMC with aggregation-volume-biased method in conjunction with GDI to develop the full vapor-solid, vapor-liquid, and liquid-solid phase diagrams of the SW model. The aforementioned studies indicates that the phase behavior of colloidal particles depends sensitively on the range of interaction, as has been known since the work of Gast *et al.*[102]. So far, the studies of the fluid-solid coexistence have mainly focused on the bulk systems as shown previously.

On the other hand within some confinements[3, 103, 104], the fluid-solid properties may exhibit significant deviation from the bulk ones due to geometrical size effects and the interaction of particles with confining walls. A previous study[105] indicates a strong dependence of the fluid-solid coexistence of hard sphere fluids on the pore size and it is expected that both the range of interaction and pore size have significant effects to the fluid-solid behavior. Another important factor in studying the behavior of model fluids is the structure. Several studies have investigated the ordering of particles under cylindrical confinement[64-66, 79, 106]. The structure of confined fluids is highly dependent on the pore diameter and it seems there is no simple and continuous dependence, which can be generalized. Here we focus on narrow pores, which can only hold one cylindrical layer of particles, and are of great theoretical and experimental interest, as in such systems the particles can be self assembled to form single helical or twisted helical structures. The systems resemble colloids confined in very narrow channels for constructing nanowires[107-109], and peapod-related system such as C_{60} encapsulated in CNT[92, 106]. Also, better and more understanding of the fluid-solid behavior and structure of these systems ultimately help to find practical nano-applications in capillarity, lubrication, gas purification and storage, fabrication of nanofluidic devices, and provide important insights on the self-assembly helical structure, which is commonly found in the nature.

To this end, we elucidate the fluid-solid behavior and structure of the SW fluids under narrow cylindrical confinement using molecular simulations and modeling methods to investigate the effect of range of interaction and narrow pore sizes. The pore sizes are chosen to hold only one cylindrical shell of

particles in such systems, which have small interface and fraction of particles due to small cross section. The free energy gap during the fluid-solid transition is small enough to ensure the equilibrium of the coexisting phases in the same simulation box, thus this makes a direct simulation of equilibrium of fluid and solid phases in one simulation box possible. The rest of this chapter is organized as follows; in the next section we briefly describe our systems and methods used for obtaining the equation of state and methods to characterize the structure of the confined SW fluids. Section 5.3 describes the details of simulation conditions considered in this work. Section 5.4 presents the results and discussion followed by the conclusion in section 5.5.

5.2 Methodology

We consider the system of SW particles confined in narrow cylindrical hard pores of diameter D . The particles are first arranged in cylindrical shell of triangular or square shape for $D = 2.2\sigma$ and 2.5σ , respectively, where σ is the diameter of the confined particles. To obtain the accurate equation of state along an isotherm from fluid to solid including the coexistence regime, we have run series of molecular dynamics (MD) simulations. Once the equation of state is known, the fluid isotherm is fitted to a convenient fitting function of the form[110],

$$\beta P = \frac{\rho}{1 - a\rho} + b \left(\frac{\rho}{1 - a\rho} \right)^2 + c \left(\frac{\rho}{1 - a\rho} \right)^3 \quad (5.1)$$

where ρ is the number density and $\beta = 1/kT$ is the inverse temperature, where T and k are the temperature and the Boltzmann constant, respectively. The solid

isotherm is fitted to a second order polynomial equation in the form of $\beta P = a + b\rho + c\rho^2$. The pressure values within the coexistence regime are averaged; the pressure at which both phases are in equilibrium are determined, then the freezing and melting densities are obtained by solving the equation of state for both phases at this pressure. We separately performed the isobaric-isothermal Monte Carlo simulations (NPT MC) and compared the results to those of MD. The comparison indicates that MD is more efficient to evaluate the phase coexistence in such systems.

In this work, the pressure components of the SW fluid confined in the cylindrical pore using MD is obtained by using the virial theorem of the pairwise-additive potential,

$$P_{\alpha\beta} = \rho kT + \frac{1}{V} \left\langle \sum_{i=1}^{N-1} \sum_{j>i}^N (\mathbf{r}_{ij})_{\alpha} (\mathbf{f}_{ij})_{\beta} \right\rangle \quad (5.2)$$

where N is the number of molecules, $\mathbf{r}_{ij}$ is the relative position vector between the center-of-mass of molecules i and j , and $\mathbf{f}_{ij} = -\nabla u_{ij}$ is the force between them at the potential energy u_{ij} . The angle bracket indicates the time average of MD or the ensemble average of MC. In the square-well model, the collision of two particles occurs when the distance of two particles equal to hard-core. The forces between two particles, during the collision, have an infinite magnitude but act for an infinitesimal time. Each pair collision contributes an amount to the average of Eqn. (5.2) when integrated over time, while the particle-wall collision has no contribution to the spreading pressure,

$$P_{\alpha\beta} = \rho kT + \frac{1}{V t_{sim}} \sum_{collision} (\mathbf{r}_{ij})_{\alpha} (\Delta \mathbf{p}_{ij})_{\beta} \quad (5.3)$$

where t_{sim} is the total simulation time and the sum is over all collision occurring during this period; $\Delta \mathbf{p}_{ij}$ is the difference of momentum before and after the collision between atom i and j .

The microstructure of the system is monitored by the one-body radial density profile $\rho(r)$, the axial pair distribution function $g(z)$, bond order parameters Q_6 and 2D hexagonal order parameter Φ_6 . Of these three functions, the first two are used to monitor the radial and axial distribution of particles, respectively, and Q_6 and Φ_6 are used to monitor the global order of the system. The reduced radial density profile $\rho^*(r)$ is obtained by dividing the cylindrical pores into n concentric cylindrical shells with the same thickness then sample the number of particles divided by the shell volume. Thus, the definition of $\rho^*(r)$ can be expressed as,

$$\rho^*(r_i) = \frac{\langle N_i \rangle}{\pi (r_i^2 - r_{i-1}^2) L} \sigma^3 \quad (5.4)$$

where N_i is the number of particles, whose distance to the pore axes are in the range of r_{i-1} to r_i , with $r_i = \Delta r \times i$, and Δr the thickness of the cylindrical shell. L is the length of the cylindrical pore. The axial pair distribution function $g(z^*)$ is modified from the pair correlation function, which is extracted from the following equation,

$$\int_{z^*=0}^{z^*=\infty} \rho^* g(z^*) \pi R^{*2} dz^* \approx N \quad (5.5)$$

where N is the total number of particles, $\rho^* = \rho\sigma^3$ is the reduced density, $z^* = z/\sigma$ is the reduced axial distance and $R^* = R/\sigma$ is the reduced pore radius. The upper limit of z^* is changed to the axial length of the simulation box, L/σ in calculation. The global order of the system indicates whether a system is fluid-like or solid like and is characterized by the bond order parameters introduced by Steinhardt *et al.*[111] To calculate bond order parameters, we start from the spherical harmonic associated with every bond $\mathbf{r}_{ij}$ in the system. Here a bond is not chemical bond but a vector joining two neighboring atoms, whose distance is less than a cut off radius. The quantity is defined as[112],

$$Q_{lm} = Y_{lm}(\theta(\mathbf{r}_{ij}), \phi(\mathbf{r}_{ij})) \quad (5.6)$$

where Y_{lm} is the spherical harmonic, and θ and ϕ are polar and azimuthal angles of the bond with respect to a fixed coordinate frame, which can be arbitrarily chosen. The global bond order parameter Q_l , which is rotationally invariant, is then defined as follow,

$$Q_l \equiv \left(\frac{4\pi}{2l+1} \sum_{m=-l}^l |\bar{Q}_{lm}|^2 \right)^{1/2} \quad (5.7)$$

where $\bar{Q}_{lm}$ is the average of Q_{lm} 's over all bonds in the system. In this study we use Q_6 , of which $l = 6$ as the order parameter. Q_6 is very sensitive to the global structure, which significantly increases when the ordered structure appears and vanishes for the isotropic fluid.

In addition to the bond order parameter Q_6 which captures the order of a system in three directions, we have also utilized the 2D order parameter Φ_6 defined as

$$\Phi_6 = \left| \frac{1}{M} \sum_{i=1}^M \frac{1}{N_i} \sum_{j=1}^{N_i} \exp(i6\theta_{ij}) \right| \quad (5.8)$$

where M is the number of particles in the same cylindrical layer, N_i is the number of nearest neighbors of particles i . We define the nearest neighbors as those particles j within a distance 1.3σ from particles i , and θ_{ij} is the angle between two neighboring particles i and j and an arbitrary but fixed axis. The cylindrical layer is unrolled into a flat plane so that the 2D order parameter can be applied. The value of Φ_6 equals to 1 for a perfect hexagonal plane, but far from 1 for a disordered phase.

5.3 Simulation Models and Details

In this work, the fluid-fluid interaction is represented by the square-well potential,

$$u_{f-f} = \begin{cases} \infty, & 0 < r_{ij} < \sigma \\ -\varepsilon, & \sigma \leq r_{ij} < \lambda\sigma \\ 0, & \lambda\sigma \leq r_{ij} \end{cases} \quad (5.9)$$

where $\lambda\sigma$ is the potential-well diameter, and ε is the depth of the energy well. The cylindrical pore is represented by the one body potential,

$$u_{w-f} = \begin{cases} \infty, & r < \sigma / 2.0 \\ 0, & r \geq \sigma / 2.0 \end{cases} \quad (5.10)$$

where r is the distance from the center of particle to the wall. In MD simulation, the wall acts as perfect rigid cylindrical surface. During the simulation, normal component of the momentum of the particle colliding with the wall is reversed while keeping the same magnitude. The periodic boundary condition is applied along the pore axis, which is chosen as z direction. We adopt the values of the units such that σ and ε are unity. All length scales are in unit of σ and other reduced units used in the work are the temperature $T^* = kT/\varepsilon$, pressure $P^* = P\sigma^3/\varepsilon$, and time $t^* = t/[\sigma(m/\varepsilon)^{0.5}]$. Note that the superscript asterisk will be omitted in the text below for the sake of convenience.

The MD simulations are first performed in canonical ensemble (NVT), i.e., during the simulation, the number of particles, the volume of simulation box, and the temperature are kept constant. The temperature was kept constant by simple momentum scaling, with all momenta multiplied by an appropriate factor at the end of each time step Δt so that the total kinetic energy of the system remains constant. The time step, Δt , was fixed at 0.05. The only effect of the time step is to determine the frequency of updating the properties measured in the simulation and rescaling the momenta to the desired temperature. The equilibrium period was set to follow two steps. We first set the simulation at $T = 10.0$ to ensure the particles are fully distributed in the cylindrical pore. Then the system was quenched to the target temperature. The total time steps for these two steps were set to 5×10^4 and we switched the simulation to microcanonical ensemble (NVE) to collect the equilibrium data. The time step for production

was taken as 2×10^5 and we repeated each simulation five times. Longer simulations were performed for the coexistence regime. The simulations were conducted with the system size of 1000 particles and we carefully checked that the system size is sufficient to avoid finite-size effect in our system. For the NPT MC simulations, the change in volume was made by changing the length of the cylinder keeping the diameter fixed. We performed N trials of displacing a randomly chosen particle followed by one trial of changing the pore length. The initial configuration was set to the random configuration at $\rho = 0.7$. For NPT simulations, equilibrium and production cycles were set to 5×10^5 in most cases.

5.4 Results and Discussion

In Figure 5.1 we compare the equation of state of the SW fluid confined in a cylindrical pore of $D = 2.2$ obtained by MD and NPT MC. The MD simulations were first performed to obtain the pressure as a function of density. The values of pressure were then used as the input for the NPT MC simulations. Both results show good agreements on the fluid and solid branches. The discontinuity on the equation of state, which is observed from both methods, is indicative of the fluid-solid transition. This comparison indicates that both methods are accurate enough to determine the equation of state at both fluid and solid branches. However for determining the fluid-solid coexistence regime, we find that MD is better than NPT MC, as MD not only has much smaller relaxation time, which enables us accurately to determine the coexistence

density regime and coexistence pressure, while NPT MC generally cannot pinpoint these properties in such accuracy.

Figure 5.1. Comparison of the equation of state (P_{zz} vs. ρ) of the SW molecules of $\lambda = 1.5$ confined in cylindrical hard pore of $D = 2.2$ at $T = 1.0$ obtained by NPT MC and MD simulations, which are represented by square and circle symbols, respectively. The solid line indicates the fit of result at fluid branch using Eq. (1), and the dash line is the second order polynomial fit to the solid branch. Error bars are the standard deviation of 5 independent runs.

Figure 5.2 presents the equation of state of the SW fluid confined in the pore of $D = 2.2$ for $\lambda = 1.5$ at different temperatures. The result of hard sphere

is plotted for a comparison as the infinite temperature limit ($\beta \rightarrow 0$), where the square-well potential is reduced to the hard-sphere one. We can observe that for all temperatures studied, βP_{zz} 's are lower than that of hard sphere over the densities of interest, which indicates that the attractive forces actually affect the system to be frozen at lower pressures. The equation of state at high temperature is always above that of low temperature including the fluid-solid coexistence branch. The coexistence spreading pressure becomes lower as the temperature reduces, which is also same for the fluid branch, and the coexistence range becomes larger as the temperature decreases due to the early start of the freezing at low temperature. Note that the relative differences in the coexistence spreading pressures would be dramatically larger if β is excluded from the figure, thus the effect of the temperature is considered to be large on the coexistence spreading pressure for $\lambda = 1.5$. Nevertheless, we found that the melting densities are almost invariant over the variation of the temperature.

Figure 5.2. The equation of state (βP_{zz} vs. ρ) of the SW molecules of $\lambda = 1.5$ confined in a cylindrical hard pore of $D = 2.2$ at different temperatures 0.5, 0.8, 1.0, 2.0 and 5.0. The result of hard spheres confined in the same pore size is shown for comparison.

With the same conditions of the system, the range of the interaction is decreased and Figure 5.3 presents the results of $\lambda = 1.2$, 1.3 and 1.4 for $D = 2.2$. For a shorter attractive range $\lambda = 1.2$, the equation of state at high temperature is apparently above that of low temperature at the fluid branch, however at $\rho >$

0.7, the differences of the equations of states at different temperatures vanish and those are observed to coincide at the solid and fluid-solid coexistence branch. Note that if β is omitted from Figure 5.3, the reduced coexisting pressures show some differences, but not as dramatic as in the case of the longer interaction range $\lambda = 1.5$ in this pore size. Consequently, freezing and melting densities change little with the temperature at this short attractive range, which is shown from Figure 5.4. The equations of states for $\lambda = 1.3$ and 1.4 show the similar behavior of $\lambda = 1.2$, yet the fluid pressure slightly increases as λ increases from 1.2 to 1.4 at the same density, while the fluid-solid coexistence branch and solid branch are insensitive to the well extent.

Figure 5.3. The equation of state (βP_{zz} vs. ρ) of the SW molecules of $\lambda = 1.2$ confined cylindrical hard pore of $D = 2.2$ at different temperatures 0.5, 0.8, 1.0 and 2.0, and $\lambda = 1.3$ and 1.4 at $T = 1.0$. The result of hard sphere is shown for comparison.

Figure 5.4. The temperature-density fluid-solid phase diagram of the SW molecules confined in a cylindrical hard pore of $D = 2.2$ for the short range $\lambda = 1.2$ and the long range $\lambda = 1.5$, using molecular dynamics simulation described in the text.

With a slight increase of the pore size, the structure of the system is significantly changed from at most 3 coplanar molecules in $D = 2.2$ to 4 coplanar molecules in $D = 2.5$. Figure 5.5 shows the equation of state for the pore diameter $D = 2.5$. We found that, all equations of states of $\lambda = 1.5$ in $D = 2.5$ at different temperatures are close to each other to that of hard sphere except at the coexistence branch (i.e. slightly higher than that of hard sphere) while the case of $\lambda = 1.5$ in $D = 2.2$ shows large deviations of the equations of states at different temperatures. When the attractive range is increased to

$\lambda = 1.65$ in $D = 2.5$, the behavior of the equation of state becomes similar to the case of $\lambda = 1.5$ in $D = 2.2$. It is shown that there exist some scale-up effect between the pore size and the interaction range in behavior of the equation of state even with the variation of the structure (i.e triangular to square shape, See Figure 5.10). The detailed coexistence properties are listed in Table 5.1.

Figure 5.5. The same equation of state as in Figure 5.3 for $D = 2.5$ and $\lambda = 1.5$ at $T = 0.8, 1.0$ and 2.0 , $\lambda = 1.65$ at $T = 1.0$ and 2.0 . The equation of state of hard spheres confined in $D = 2.5$ is shown for comparison.

Table 5.1. Fluid-solid coexistence data estimated from MD simulation of SW molecules confined in cylindrical pore with various well diameter under narrow pore sizes. The subscripts f and s represent fluid and solid, respectively. The number(s) in parentheses represent the error in the last digit(s).

	T	ρ_f	ρ_s	P_{zz}
$D = 2.2$				
$\lambda = 1.2$	0.5	0.8049(3)	0.8941(3)	7.27(4)
	0.8	0.8053(2)	0.8924(3)	11.69(4)
	1.0	0.8053(4)	0.8922(4)	14.69(8)
	2.0	0.8042(4)	0.885(1)	29.5(1)
	5.0	0.803(1)	0.885(1)	74.2(6)
$\lambda = 1.3$	1.0	0.7991(4)	0.8837(4)	14.93(7)
$\lambda = 1.4$	1.0	0.799(2)	0.867(1)	14.4(2)
$\lambda = 1.5$	0.5	0.753(2)	0.872(2)	3.14(3)
	0.8	0.757(3)	0.877(1)	7.01(13)
	1.0	0.765(1)	0.877(1)	9.90(4)
	2.0	0.784(2)	0.877(1)	24.4(3)
	5.0	0.7964(3)	0.882(1)	68.8(1)
HS	1.0	0.803(1)	0.878(2)	14.91(9)
$D = 2.5$				
$\lambda = 1.5$	0.8	0.836(2)	0.906(1)	13.69(35)
	1.0	0.836(1)	0.905(1)	16.56(20)
	2.0	0.8347(7)	0.9016(8)	31.13(15)
$\lambda = 1.65$	1.0	0.756(5)	0.9045(4)	7.33(29)
	2.0	0.803(1)	0.9019(2)	21.77(10)
HS	1.0	0.826(2)	0.893(3)	14.8(4)

Figure 5.6 shows the bond order parameter Q_6 as the function of density in the pore size $D = 2.2$. Q_6 is found to be non-zero for dilute fluid due to a confinement effect; the system with a random set of bonds has a Q_l value of $1/\sqrt{N_b}$ but not zero[113] as within the tight confinement, the direction of bonds joining each pair of atoms is not stochastic but has limited orientations. An interesting phenomenon has been observed with the increase of the density of the fluid. Q_6 increases to reach a value around 0.15 at the density around 0.75. Similar behavior is found for Φ_6 with slight increase within this density range as shown in Figure 5.7. However, the equation of state shows that the system is still in the fluid phase at this density. Since the particles form a structure of spiral tetrahedra along the pore axis, an ordered structure is created even for the fluid phase under narrow confinement. With further increase of the density, Q_6 and Φ_6 decrease to a minimal value and increase sharply. Over this density range, the phase transition can be associated with the structure of spiral packing of tetrahedra transforming to triangular packing of three particles rotated with an angle of $\pi/3$ against the nearest layer of the triangular particles along the pore axis. (See Figure 5.10).

Figure 5.6. The bond order parameter Q_6 as the function of density for the SW molecules confined in a cylindrical hard pore of $D = 2.2$ at different temperature and potential range. Symbols square, circle and triangle represent system at $T = 1.0$ and $\lambda = 1.2$, $T = 1.0$ and $\lambda = 1.5$, $T = 2.0$ and $\lambda = 1.5$, respectively.

Figure 5.7. The 2D bond order parameter Φ_6 as the function of density for the SW molecules confined in a cylindrical hard pore of $D = 2.2$ at $T = 1.0$ and the potential range $\lambda = 1.2$.

To understand the structure in details, the axial distribution function $g(z)$ and the density profile $\rho(r)$ are studied as shown in Figure 5.8 and Figure 5.9. Also, the snapshots of all systems of interest are presented in Figure 5.10 for convenient view.

Figure 5.8. Axial pair distribution function $g(z)$ for the SW molecules confined in cylindrical pore of $D = 2.2$ at $T = 1.0$ and $\lambda = 1.2$, at different average densities, 0.30 (dilute fluid), 0.75 (dense fluid), 0.80 (around freezing density), 0.85 (within fluid-solid coexistence), 0.89 (around melting density), 0.92 (solid).

Figure 5.9. Radial density profiles $\rho(r)$ for the same system as in Figure 5.8.

At the density 0.3, $g(z)$ shows a peak at $z = 1.0$ and a valley at $z = 1.2$, which happen to be the hard core diameter and the potential well extent, respectively and it quickly decays to 1.0 as z increases, thus the system does not have a long range order at this density. For $\rho = 0.75$ and 0.80, two peaks appear at $z < 1.0$, followed by the peaks periodically appeared at the interval of about 0.33, and the value of $g(z)$ at $z = 0$ is nearly zero. The two bond order parameters suggest that there is a partial ordered phase of spiral packing of tetrahedra appearing around this density range. Indeed, the position of peaks at $g(z)$ matches with the axial distance of the peaks of the tetrahedron. For density

0.85(within coexistence), 0.89(around melting point), and 0.92 (solid phase), a sharp peak appears at $z = 0$, and the peak at $z = 1.0$ moves to $z \approx 0.87$, followed by series of peaks periodically appeared at the interval about 0.87. This phenomenon indicates that the tetrahedral packing is transformed to triangular packing. Note that for the density within coexistence, there exist two small peaks between the sharp peak at $z = 0$ and $z \approx 0.87$, which indicates that both tetrahedral and triangular packings are coexisting in the system. There is no distinct discontinuity in $\rho(r)$ as density increases, however $\rho(r)$'s vary near to the wall at low densities, which indicates that the particles are loosely packed and even makes the pocket of particles at the lowest density of interest. This behavior is attributed to the entropic dominance on the system, that particles spontaneously move to the more accessible space to maximize the entropy of the system. In the narrow pore, which can hold only one layer of particles at a plane perpendicular to the z direction, the attractive force has little impact to the radial density profile and the behavior of $\rho(r)$ is similar to that of hard sphere systems confined in hard pores discussed by Duran-Olivencia *et al.*[66]. Similar behavior was also observed in $D = 2.5$, as seen in the $g(z)$ function shown in Figure 5.11, where three peaks are observed at $z < 1.0$ at $\rho = 0.80, 0.83$ and 0.85 indicating a twisted helical structure, and disappear at $\rho = 0.90$ and 0.95 , where the structure is transformed to a square shape consisting of four particles sharing the same z against another nearest square layer by rotating an angle of $\pi/4$.

Figure 5.10 Snapshots for the SW molecules confined in the narrow cylindrical pores of $D = 2.2$ (a to d), and $D = 2.5$ (g to i) at different average densities: a , $\rho = 0.3$ (dilute fluid), b , $\rho = 0.75$ (dense fluid, spiral packing of tetrahedron), c , $\rho = 0.85$ (fluid-solid coexistence), d , $\rho = 0.92$ (solid, triangular packing), g , $\rho = 0.3$ (dilute fluid), h , $\rho = 0.85$ (fluid-solid coexistence) and i , $\rho = 0.95$ (solid, square packing). The tetrahedral, triangular, and square packings are shown in e , f and j , respectively. Two different structures are found in the corresponding coexistence densities in $D = 2.2$ ($c-1$ and $c-2$) and $D = 2.5$ ($h-1$ and $h-2$).

Figure 5.11. Axial pair distribution function $g(z)$ for the SW molecules confined in cylindrical pore of $D = 2.5$ at $T = 1.0$ and $\lambda = 1.5$, at different average densities, 0.30(dilute fluid), 0.80 (dense fluid), 0.83 (around freezing density), 0.85 (within fluid-solid coexistence), 0.90 (around melting density), 0.95 (solid).

5.5 Conclusion

In this chapter we have studied the fluid-solid phase behavior of square-well fluids confined in narrow cylindrical pores using molecular simulation methods. The full equation of state including a fluid phase, a solid phase and a fluid-solid coexistence was accurately calculated for a wide range of temperature and various attractive ranges for the pore diameter $D = 2.2$ and 2.5 . Based on our experience in the work and the comparison with NPT MC simulation, we consider the MD method to be a good choice to determine the equation of state, especially for the fluid-solid coexistence. We found that there is a threshold of the attractive range λ , below which the fluid-solid behavior varies little with respect to temperature and close to that of hard spheres under same thermodynamic condition. In addition to the fluid-solid coexistence calculation, we also present the structure properties of the system from dilute fluid to solid. In particular, we found a partially ordered structure in the dense fluid due to the strong confining effect of the boundary; the mix of triangle and square shapes of the SW particles was observed.

Chapter 6

Hard Sphere Fluids Confined in Spherical Hard Pores

6.1 Introduction

In the previous chapters we have studied the systems in which the number density $\rho = N/V$ can keep constant with varied system sizes. This approach has been possible due to periodic boundary conditions in three directions (bulk) and one direction (cylindrical pore). In recent years, studies of finite systems in spherical confinement in $3D$ [114-119] and circular confinement in $2D$ [120-122] have become popular, since nanoscale systems are of finite volume. In these systems the fluid properties are far from bulk ones. It is clear that the properties of those finite size systems strongly depend on the system size and the thermodynamic limit is no longer valid.

This chapter introduces molecular simulation studies on the phase transition (i.e. if any) in the complete confined systems consisting of N particles in a perfect rigid spherical pore by varying densities gradually. In this case, the number of particles is fixed once the radius of spherical pore and the number density is given. Periodic boundary condition can not be applied. We performed MD simulations for a wide range of densities. The reduced radii of the confining spherical pores are $R = 5.0, 6.0, 6.5, 7.0, 7.5$, and 8.0 .

6.2 Simulation Models and Details

The models considered in this chapter are hard sphere interactions among particles and their hard-wall interaction with a rigid and structureless spherical pore. Thus the fluid-fluid interaction is represented:

$$u_{f-f}(r_{ij}) = \begin{cases} 0 & r_{ij} \geq \sigma \\ \infty & r_{ij} < \sigma \end{cases} \quad (6.1)$$

where σ is the diameter of a particle and r_{ij} the distance between two particles.

The spherical pore is created by adding a spherical boundary inside of a cubic simulation box, where the particles are initially packed inside the boundary. The fluid-wall interaction is considered perfect elastic collision. The fluid-wall interaction is represented by the following equation,

$$u_{f-w}(r) = \begin{cases} 0 & r \geq 0.5\sigma \\ \infty & r < 0.5\sigma \end{cases} \quad (6.2)$$

where r is the distance from the center of a particle to the spherical boundary. To deal with the particle collision with the spherical pore using MD simulation, we follow the same idea in Chapter 2 of two hard-spheres kinetic. Consider the spherical boundary of center $\mathbf{r}_0 = (x_0, y_0, z_0)$ and radius R . The equation of this spherical boundary is

$$(x - x_0)^2 + (y - y_0)^2 + (z - z_0)^2 = R^2 \quad (6.3)$$

Now consider a particle at the position $\mathbf{r}$ and has the velocity $\mathbf{v}$. The

collision time Δt to the spherical pore is calculated by

$$|\mathbf{r}(t + \Delta t) - \mathbf{r}_0|^2 = \left(R - \frac{\sigma}{2}\right)^2 \quad (6.4)$$

where $\mathbf{r}(t + \Delta t) = \mathbf{r}(t) + \mathbf{v}(t)\Delta t$ and σ is the diameter of the particle. The equation leads to the quadratic equation

$$v^2 \Delta t^2 + 2(\mathbf{r} - \mathbf{r}_0) \cdot \mathbf{v} \Delta t + (\mathbf{r} - \mathbf{r}_0)^2 - \left(R - \frac{\sigma}{2}\right)^2 = 0 \quad (6.5)$$

Solving equation 6.5 gives us

$$\Delta t = \frac{-(\mathbf{r} - \mathbf{r}_0) \cdot \mathbf{v} + \sqrt{[(\mathbf{r} - \mathbf{r}_0) \cdot \mathbf{v}]^2 - v^2 \left[(\mathbf{r} - \mathbf{r}_0)^2 - \left(R - \frac{\sigma}{2}\right)^2 \right]}}{v^2} \quad (6.6)$$

The collision happens when the distance of the center of particle to the center of spherical pore equal to $R - \sigma/2$, the normal component of the momentum turns to its opposite after collision.

To pack the particles into the spherical pore, we first construct the FCC lattice at very high density (i.e $\rho = 1.413$) in a cubic simulation box. Then the spherical boundary of radius R is created in the cubic box sharing the same center of the cubic simulation box. Those particles of which distances to the center are larger than R are deleted (See Figure 6.1). In the simulations of bulk and cylindrical pore confinement we can adjust the length of the simulation box to meet the density requirement at a given number of particles. However, the spherical pore is a close system, in which the number of particles is fixed once

the density and radius of pore is given. In this case, we need to calculate the number of particles for a given density and delete those additional particles. The number of particles N for the density ρ in a spherical pore of radius R is given by

$$N = \frac{4}{3} \rho \pi R^3 \quad (6.7)$$

We first performed the MD simulations in the canonical (NVT) ensemble, during which the number of particles N , volume V , and temperature T were invariant. The reduced temperature T^* was set to 1.0 and kept constant by simple momentum recalling at the end of each time step. The reduced time step Δt^* was set to 0.1. The number of particles was calculated via Eqn (6.7) for a given density and pore radius. The total time steps for equilibration was set to 2×10^5 and once the system reaches equilibrium, all meters were reset, followed by another same number of steps run in microcanonical (NVE) ensemble to produce data. Statistical sampling errors were estimated by conducting at least 5 independent runs.

Figure 6.1. Screenshots of constructing simulations of hard spheres confined in spherical hard pores: a) FCC packing at high density; b) delete particles outside of spherical pore; c) randomly delete additional particles to meet the density; d) simulation in equilibrium.

6.3 Results and Discussion

6.3.1 Equation of state

In Figure 6.2 we show the equation of state corresponding to the hard-sphere fluids confined in hard spherical pores of reduced radii $R = 5.0, 6.0, 6.5, 7.0, 7.5$ and 8.0 , where the y axis represents the reduced pressure and the x axis represents the reduced density. The errors are of the size in the symbols and are not shown in Figure 6.2 for simplicity. The solid lines at the fluid and solid branches are Carnahan-Starling equation of state for hard-sphere fluid and Speedy's equation of state for hard-sphere FCC crystal, respectively. It can be seen that for all densities considered in these pores, the pressures are always higher than the bulk. The equations of state of the hard-sphere fluids confined in spherical hard pores at the fluid branch shift a little compared with that of the bulk. Of all the pore sizes studied, the pressure calculated almost overlap at the density from 0.1 to 0.8 , and the deviation becomes larger at density over 0.8 . In all cases studied, we can observe small discontinuity of the equation of state, which splits the equations of state into fluid-like and solid-like branches.

Figure 6.2. Equation of state for hard spheres confined in hard spherical pores of radii $R = 5.0, 6.0, 6.5, 7.0, 7.5$, and 8.0 . Solid lines indicate the same quantity for the bulk hard sphere system.

6.3.2 Structure Characterization

6.3.2.1 Density Profiles

The normalized radial density profiles $\rho^*(r^*)/\rho^*$ (where $\rho^*(r^*)$ is the reduced local density at r^* and ρ^* is the reduced average density, respectively) for the pore of $R = 5.0$ are shown in Figure 6.3. From top to bottom we can observe distinct behaviors of the normalized radial density profile. At the low densities 0.1 and 0.3 , the local densities are very close to the average density at $r < 3.5$, which means that the particles are uniformly distributed in this regime.

The local densities increase near the hard wall and develop layered distributions at the average density of 0.5. The normalized local density near the hard wall increases dramatically as the average density increases. At $\rho = 0.10$, the normalized reduced local density is 1.77, which increases to 2.82 for $\rho = 0.30$, and reaches 4.78 for $\rho = 0.50$. For these average densities, the behavior of the system is close to the that of the bulk. For the average densities 0.80 and 0.94, the system has developed strong layered distributions. For $R = 5.0$, 5 layers of particles are observed as shown by the peaks on the reduced radial density profiles, which become sharper when the average density increases. Such layering behavior is commonly observed in confined systems. Different numbers of layers are found for different pore sizes, as shown in Figure 6.4. Even at the same average density, the peaks become flatter for larger pores, which means that the behavior is closer to bulk when pore size increases, as also shown on the equations of state. At higher densities of 0.98 and 1.06, the reduced radial density profiles become complex at $r < 4.0$, which do not show general layering distribution as observed at $\rho = 0.80$ and 0.94. We speculate that at these densities, the structure at $r < 4.0$ is closer to the FCC structure, with a spherical shell surrounding it.

Figure 6.3. Normalized radial density profiles of hard spheres confined in spherical hard pore of radii $R = 5.0$ at different average densities.

Figure 6.4. Radial density profiles of hard spheres confined in hard spherical pores of $R = 6.0, 6.5, 7.0, 7.5,$ and 8.0 at average density $\rho = 0.90$.

6.3.2.2 Bond-orientational Analysis

In Figure 6.5 we present the bond order parameters in the spherical pore of radius $R = 8.0$ as the function of densities in the range from $\rho = 0.85$ to 1.15 . The upper limit is much higher than the freezing density of the bulk hard-sphere system. The results are shown for all particles (square), exclusive of the first layer (circle), and exclusive of the first and second layers (triangle) to check the effects of the hard wall to the overall microstructure of the system. As can be seen on the Figure 6.5, Q_4 , Q_6 and W_{446} are near zero at the fluid phase and increase sharply when freezing happens at $\rho \approx 0.98$. These bond order parameters have higher values when the contact layer and second layers are exclusive, which means that the inner portion of the system has higher degree of order and closer to the FCC structure. In particular, the whole system does not show strong FCC behavior as show in the value of W_{446} , which is below the threshold of 0.0007 even at the density 1.15 , however when the contact layer is exclusive for calculation, W_{446} reaches 0.007 at the average density of $\rho \approx 1.07$ and even lower density when the second layer is also exclusive for calculation. The system shows strong FCC behavior in the inner portion of the system, which is agreed with what have been shown by the radial density profiles. The values of $\hat{W}_4$ and $\hat{W}_6$ are close to the value of FCC at -0.159 and -0.013 , respectively. The analysis suggests that the freezing process is accompanied with the structure transformed from the loose layering structure to the structure of FCC core surrounding with a spherical shell.

Figure 6.5. Bond order parameters Q_4 , Q_6 , $\hat{W}_4$, $\hat{W}_6$, and W_{446} for hard spheres confined in hard spherical pore of $R = 8.0$ as the function of average density. The square, circle and triangle symbols represent all particles, exclusive of the first layer, exclusive of first and second layers, respectively.

For local structure analysis, the local order parameter q_4 and q_6 are not useful, since both are non-zero for all the common crystalline structures, nor for the fluid structure. Other two local order parameters $\hat{w}_4$ and $\hat{w}_6$ can be used as instruction when crystallization happens by showing close values to the

corresponding crystalline structures but it is generally difficult to use these parameters to pinpoint local structures by comparing the values. The local bond order parameter w_{446} though, is very sensitive to the local structure. An identical FCC cluster has $w_{446} \approx 2.5 \times 10^{-3}$, while other structures have the values in a much smaller order of magnitude. Mitus *et al* .[70] used the threshold of $w_{446}^c = 0.7 \times 10^{-3}$ to distinguish the local FCC clusters from other local structures. We adopt the criterion $w_{446} > w_{446}^c$ to identify local FCC clusters in this study.

Figure 6.6. Distribution of local bond order parameter w_{446} for the hard spheres confined in hard spherical pore of $R = 8.0$ at the average densities $\rho = 0.90, 0.95, 1.00, 1.05$, and 1.10 .

Figure 6.6 shows the distribution of w_{446} for the system of $R = 8.0$. At the fluid branch $\rho = 0.90$ and 0.95 , the distribution of w_{446} is very tight and has the peak value around zero. The whole distribution curve is far below the threshold

of 0.7×10^{-3} . For $\rho = 1.00, 1.05$, and 1.10 the distribution curves have a two-peaked structure, which clearly distinguishes the local FCC structures in the inner portion of the system from none FCC structures near the spherical wall. The fraction of the FCC clusters counted by the criterion as the function of average density for the pores $R = 5.0, 6.0, 6.5, 7.0, 7.5$, and 8.0 are given in Figure 6.7. No local FCC structure is found for the fluid phase, as shown on Figure 6.7. The fraction of FCC quickly increases when freezing happens, and reaches to $\sim 50\%$ at the average density $\rho > 1.1$ for most of the pores studied except for $R = 5.0$, of which the fraction of local FCC is obviously lower than other pores. We speculate that the for the pores of $R \leq 5.0$ the particles near the wall and the effect of wall take dominance, which makes the system diverges to the bulk largely, as seen on the equation of state shown in Figure 6.2, where the pressure is much larger than that of other pore sizes and of the bulk at the same density.

Figure 6.7. Fraction of FCC clusters as function of average density for the hard spheres confined in hard spherical pores of radii $R = 5.0, 6.0, 6.5, 7.0, 7.5$, and 8.0 .

6.4 Conclusion

In this chapter, we considered the hard spheres confined in hard spherical pores of different radii. We have determined the equation of state of the aforementioned systems with wide range of pore sizes via the MD simulation method. The microstructure of the systems is studied by the radial density profiles, which show layering structure as other confined systems at the dense fluid phase. The layering structure will transformed to the FCC structure in the center surrounded by a spherical shell accompanied with freezing. Such transformation is also observed by the global bond order parameters, which

show that the inner portion of the system is more close to the bulk behavior, while the portion near the wall are affected by the wall and diverges to the bulk behavior. We have also shown the fraction of those particles with local FCC structure. It is found that the pore of radius $R = 5.0$ and those pores of radii smaller than 5.0 have considerable lower fraction of local FCC structure than other larger pores.

Chapter 7

Hard-Sphere Fluids Confined in Single-walled Carbon Nanotubes

7.1 Introduction

Single-walled carbon nanotubes (SWCNTs) have become one of the most attractive materials in fabrication of nano-fluidic devices, due not only to their unusual electrical and mechanical but also structural properties. SWCNTs are rolled up graphite into cylindrical shape providing a hollow interior that can be served as a vessel for filling of fluid molecules. To understand the behavior of confined fluids in SWCNTs, one can consider three dominant factors: interaction forces of carbon atoms-fluid molecules and fluid-fluid molecules, radius of SWCNTs, and surface chirality. Many studies have been conducted to investigate the behaviors of confined fluids in SWCNTs, yet the structure and phase behaviors are still little explored in terms of solidification of fluids. We aim to investigate the effects of those factors on confined fluid properties via molecular simulations. Simple fluids such as hard sphere fluids under different chiral structures of SWCNTs are to be explored to elucidate, in particular, the influencing degree of those factors on the vicinity of the coexisting region of fluid and solid.

7.2 Simulation Methodology, Models and Details

7.2.1 Structure of Carbon Nanotubes

A single-walled carbon nanotube is made of a single graphite layer rolled up into a hollow cylinder so that the structure is one dimensional with axial symmetry. To construct SWCNTs in simulation, we first construct a two-dimensional honeycomb lattice shown in Figure 7.1. The unrolled unit cell of the nanotube is specified by the vector $\overline{OA}$ and vector $\overline{OB}$. In SWCNTs, the graphite sheet is rolled up in such a way that the vector $\overline{OA}$ becomes the circumference of the tube, where point O and A coincide. The vectors $\overline{OA}$ and $\overline{OB}$ define the chiral vector $\mathbf{C}_h$ and translational vector $\mathbf{T}$, respectively. The chiral vector $\mathbf{C}_h$ is defined as:

$$\mathbf{C}_h = na_1 + ma_2 \equiv (n, m) \quad (7.1)$$

where n and m are integers that $0 \leq m \leq n$, and the pair of integers (n, m) is called chiral index that uniquely defines a particular nanotube. The two vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ are the unit vectors of the 2D graphite lattice defined as:

$$\mathbf{a}_1 = \left(\frac{\sqrt{3}}{2}a, \frac{1}{2}a \right), \mathbf{a}_2 = \left(\frac{\sqrt{3}}{2}a, -\frac{1}{2}a \right) \quad (7.2)$$

where $a = |\mathbf{a}_1| = |\mathbf{a}_2|$ is the lattice constant. Considering the value of chiral index (n, m) 's the nanotubes divided into three categories: a) armchair nanotubes correspond to the case of $n = m$, or $\mathbf{C}_h = (n, n)$; b) zigzag nanotubes correspond to the case of $m = 0$, or $\mathbf{C}_h = (n, 0)$; c) chiral nanotubes correspond

to all other (n, m) chiral indices.

Figure 7.1. The 2D honeycomb lattice of a nanotube. (ref. [123]).

The direction of the chiral vector is measured by the chiral angle θ , which is defined as the angle between the vectors $\mathbf{C}_h$ and $\mathbf{a}_1$. The chiral angle θ can be calculated from the inner product of the vectors:

$$\cos \theta = \frac{\mathbf{C}_h \cdot \mathbf{a}_1}{|\mathbf{C}_h| |\mathbf{a}_1|} = \frac{2n + m}{2\sqrt{n^2 + m^2 + nm}} \quad (7.3)$$

with the values of θ in the range $0 \leq |\theta| \leq \pi/6$. The zigzag and armchair

nanotubes have $\theta = 0$ and $\theta = \pi/6$, respectively.

The diameter of the nanotube d_t is given by the length of the chiral vector:

$$d_t = \frac{|\mathbf{C}_h|}{\pi} = \frac{a}{\pi} \sqrt{n^2 + m^2 + nm} \quad (7.4)$$

The smallest vector perpendicular to the chiral vector $\mathbf{C}_h$ defines the translational vector $\mathbf{T}$ along the tube axis. The translational vector shown as $\overline{OB}$ in Figure 7.1 can be expressed in terms of the basic vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ in the form of:

$$\mathbf{T} = t_1 \mathbf{a}_1 + t_2 \mathbf{a}_2 \equiv (t_1, t_2) \quad (7.5)$$

with t_1 and t_2 are integer given by:

$$t_1 = \frac{2m+n}{d_R}, t_2 = \frac{2n+m}{d_R} \quad (7.6)$$

where d_R is the greatest common divisor of $(2m+n)$ and $(2n+m)$. The length of the unit cell is thus given by:

$$T = |\mathbf{T}| = a \frac{\sqrt{3(n^2 + nm + m^2)}}{d_R} \quad (7.7)$$

The rectangle OAB'B defined by the vectors $\mathbf{C}_h$ and $\mathbf{T}$ is the unit cell of the SWCNT. The number of carbon atoms in the unit cell, N_c , can be calculated from the area of nanotube unit cell $|\mathbf{C}_h \times \mathbf{T}|$ and the area of a hexagon $|\mathbf{a}_1 \times \mathbf{a}_2|$.

The ratio of these two gives the number of hexagons in the nanotube unit cell:

$$N = \frac{|\mathbf{C}_h \times \mathbf{T}|}{|\mathbf{a}_1 \times \mathbf{a}_2|} = \frac{2(n^2 + nm + m^2)}{d_R} \quad (7.8)$$

Note that each hexagon contains two carbon atoms, there are

$$N_c = 2N = \frac{4(n^2 + nm + m^2)}{d_R} \quad (7.9)$$

carbon atoms in the unit cell of the carbon nanotube.

The carbon atom site vectors within the nanotube unit cell are denoted by $i\mathbf{R}$, where i is an integer ($i = 1 \dots N$) and $\mathbf{R}$ the symmetry vector. The symmetry vector $\mathbf{R}$ is used to generate the coordinates of the carbon atoms in the 2D honeycomb lattice. The 2D Cartesian coordinates of a carbon atom are calculated by the projections of $i\mathbf{R}$ on the orthogonal vectors $\mathbf{C}_h$ and $\mathbf{T}$ of the nanotube unit cell. When $i\mathbf{R}$ goes out of the unit cell, periodic boundary conditions will be applied so that $i\mathbf{R}$ is shifted to lie within the unit cell through translation by an integral number of the vectors $\mathbf{C}_h$ and $\mathbf{T}$. The symmetry vector $\mathbf{R}$ can also be denoted in term of the basic vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ in the form of

$$\mathbf{R} = p\mathbf{a}_1 + q\mathbf{a}_2 \equiv (p, q) \quad (7.10)$$

where p and q are integers that do not have a common divisor except for unity.

The integers p and q are calculated by solving the equations given by:

$$\begin{aligned} t_1 q - t_2 p &= 1 \\ 0 < mp - nq &\leq N \end{aligned} \quad (7.11)$$

Figure 7.2. Symmetry vector $\mathbf{R}$.

The structural parameters given above are summarized in Table 7.1. Now that we have defined the structural parameters to generalize the site vectors of each carbon atoms in the 2D honeycomb lattice, now we can roll the 2D sheet into cylindrical shape in the form that the projection of $i\mathbf{R}$ on the chiral vector $\mathbf{C}_h$ after periodic boundary conditions becomes $r\varphi$, where r is the radius of the nanotube and φ the azimuth. The projection of $i\mathbf{R}$ on the transitional vector $\mathbf{T}$ after periodic boundary condition becomes the axis z . The cylindrical coordinates can be transformed to Cartesian coordinates:

$$\begin{cases} x = r \cos \varphi \\ y = r \sin \varphi \\ z = z \end{cases} \quad (7.12)$$

Figure 7.3. Schematic illustration of the 2D nanotube unit cell rolled up to 3D cylindrical shape.

Table 7.1. Structural parameters of Carbon Nanotubes

symbol	name	formula
a	length of unit vector	$a = \mathbf{a}_1 = \mathbf{a}_2 $
$\mathbf{a}_1, \mathbf{a}_2$	unit vectors	$\mathbf{a}_1 = \left(\frac{\sqrt{3}}{2}a, \frac{1}{2}a \right), \mathbf{a}_2 = \left(\frac{\sqrt{3}}{2}a, -\frac{1}{2}a \right)$
$\mathbf{C}_h$	chiral vector	$\mathbf{C}_h = n\mathbf{a}_1 + m\mathbf{a}_2 \equiv (n, m)$
d_t	diameter of natotube	$d_t = \frac{ \mathbf{C}_h }{\pi} = \frac{a}{\pi} \sqrt{n^2 + m^2 + nm}$
θ	chiral angle	$\cos \theta = \frac{\mathbf{C}_h \cdot \mathbf{a}_1}{ \mathbf{C}_h \mathbf{a}_1 } = \frac{2n + m}{2\sqrt{n^2 + m^2 + nm}}$
$\mathbf{T}$	translational vector	$\mathbf{T} = t_1\mathbf{a}_1 + t_2\mathbf{a}_2 \equiv (t_1, t_2)$
T	length of $\mathbf{T}$, or length of unit cell	$T = \mathbf{T} = a \frac{\sqrt{3(n^2 + nm + m^2)}}{d_R}$
N	number of hexagons in the unit cell	$N = \frac{2(n^2 + nm + m^2)}{d_R}$
N_c	number of carbon atoms in unit cell	$N_c = 2N = \frac{4(n^2 + nm + m^2)}{d_R}$
$\mathbf{R}$	symmetry vector	$\mathbf{R} = p\mathbf{a}_1 + q\mathbf{a}_2 \equiv (p, q)$
		$t_1q - t_2p = 1, 0 < mp - nq \leq N$

7.2.2 Simulation Models

In this work we consider hard-sphere fluids confined in the structure walls that have the structures of SWCNTs, which can be a simplified model representing realistic fluids confined in the SWCNTs. The fluid-fluid interactions is represented as hard-sphere potential that has pure impulsive interaction,

$$u_{f-f} = \begin{cases} \infty, & r_{ij} < \sigma_f \\ 0, & r_{ij} \geq \sigma_f \end{cases} \quad (7.13)$$

where σ_f is the diameter of the fluid particle and r_{ij} the distance between a pair of fluid particles. The carbon atoms are set stationary and the interaction between the fluid particles and carbon atoms is also represented as hard sphere potential,

$$u_{f-w} = \begin{cases} \infty, & r_{ij} < 1/2(\sigma_f + \sigma_c) \\ 0, & r_{ij} \geq 1/2(\sigma_f + \sigma_c) \end{cases} \quad (7.14)$$

where σ_c is the diameter of the carbon atoms. In MD simulations, the kinetic of fluid particles follow the method discussed in Chapter 2. For fluid-wall collision, as the wall particles are stationary, the collision of fluid particles with wall occurs when the distance of the fluid particle and a wall particle equal to $(\sigma_f + \sigma_c)/2$, with the momentum component of the fluid particle that parallels to the vector joining the center of the fluid and wall particles reversed to its opposite with the same magnitude.

The fluid particles are first arranged inside of the nanotubes in cylindrical layer structures, of which the number of layers and the initial structure of each layer depend on the diameter of the nanotubes. We have improved the initial packing method of fluid particles discussed in Chapter 4 with the idea of rolling the hexagonal planes into cylindrical shape similar to that of the carbon nanotubes. The 2D structure of a nanotube is a honeycomb lattice, if we add an additional particle to the center of each hexagon, we will have the full hexagonal plane. The hexagonal plane can be rolled up into cylindrical shape with a specific chiral vector similar to nanotube. Thus the following procedure is applied: 1) Calculate the diameter d_t of the interested nanotube (n, m) and lattice parameter a . 2) Calculate the chiral vector (n', m') for the hexagonal plane formed by the fluid particles which can have the maximum diameter that less than $d_t - (\sigma_c + \sigma_f)$, pack the first layer of fluid particles into cylindrical shape with that chiral vector. The lattice parameter is chosen small enough (i.e. $1.7321\sigma_f$, slightly larger than the close-packed lattice parameter) to ensure large density of fluid particles while not overlap with each other. 3) Repeat step 2 but the diameter of nanotube is replaced with the diameter of outer layer, and σ_c is replaced by σ_f , until the inner most layer. 4) If the inner most layer cannot hold a rolled-up hexagonal plane, we'll pack the particles into axial layers of triangle or square, or linear zigzag structure, depend on the diameter of that layer. See Figure 7.4 as an example, where the yellow spheres and red spheres represent carbon atoms on the nanotube wall and fluid particles, respectively.

Periodic boundary conditions are applied on the axial direction of the nanotube, which is chosen to be the z direction. The volume of the nanotube is

defined as:

$$V = \pi r_t^2 L \quad (7.15)$$

where r_t is the radius of the nanotube (distance from the axis to the center of carbon atoms) and L is the length of the nanobue. Note that the actually accessible volume of the nanotube is slightly larger, nevertheless, the definition serves well for simplification purpose. The reduced density is thus defined as

$$\rho^* = \frac{N}{\pi r_t^2 L} \sigma_f^3 \quad (7.16)$$

where σ_f is the diameter of the fluid particles, and N the number of fluid particles. In the rest of this chapter, all length scales are in unit of σ_f , and other units, if not specified, are reduced units defined in Table 2.2 with the superscript * omitted.

Figure 7.4. Screenshots of: (left) a nanotube of chiral index (20, 3); (right) the same nanotube filled with fluid particles (red spheres) in three cylindrical

layers.

The pressure is calculated via Eqn. (2.36) with every collision of the fluid particles contributes an amount to Eqn. (2.36), while the fluid-wall collisions do not contribute to the overall pressure. The volume used for calculation pressure is the same as Eqn. (7.15).

The axial distribution of fluid particles is observed by the similar axial distribution function $g(z)$ discussed in Chapters 4 and 5, with the radius of the cross section set to nanotube radius r_t .

The radial distribution of fluid particles is monitored by the reduced radial density profiles $\rho(r)$. Calculation of $\rho(r)$ in the nanotubes is similar to that of the cylindrical pores, with the upper limit of the distance to the axis of the tube set to $r_t + 0.5\sigma_c$. The interior of the nanotubes is divided into 500 concentric cylindrical shells with same thickness $\Delta r = (r_t + 0.5\sigma_c)/500$. The local density at r is the sample average of number of particles in the shell at distance $r \pm \Delta r$ to the pore axis divided by the shell volume.

To observe the onset of the phase transition, we apply the 2D hexagonal order parameter Φ_6 for each layer of the fluid particles. To calculate Φ_6 , the cylindrical layers are unrolled into a flat plane. By denoting the distance of the center of a cylindrical layer to the axis of pore as r_0 , the cylindrical coordinate of a particle at that layer is (r, φ, z) . To unroll the cylindrical plane into a flat plane, the coordinates of all particles at the cylindrical plane are first projected to the cylindrical surface of radius r_0 , the arc length $r_0\varphi$ of the projection

becomes the x coordinate and the z coordinate becomes the y coordinate on the $2D$ flat plane after unrolling, which gives:

$$\begin{cases} x = r_0 \varphi \\ y = z \end{cases} \quad (7.17)$$

Periodic boundary conditions are applied in both x and y directions when the $2D$ hexagonal order parameter is calculated. Note that r_0 is accurately chosen by the position of the peaks at the radial density profiles for each cylindrical layer.

7.2.3 Simulation Details

The diameters of carbon atoms and fluid particles are set to 0.5 and 1.0, respectively, and the lattice parameter a is set to 0.875 for the nanotubes. We choose these parameters to ensure that the fluid particles do escape from the hollow portion of the hexagon formed by carbon atoms on the nanotube. The MD simulations are first performed in the canonical ensemble with the number of fluid particles N , volume of the nanotube V and temperature T unchanged during simulation. The number of fluid particles is determined by the target density and number of unit cells with the equation $N = \rho V = \frac{1}{2} n \rho \pi r_t^2 |\mathbf{T}|$, where n is the number of unit cells and $|\mathbf{T}|$ the length of a unit cell, respectively. All length scales are in unit of the fluid particle σ_f . Other reduced properties are defined in Table 2.2 with the length scale of σ_f . The reduced time step Δt is fixed at 0.05 with every meter updated and the momenta of all particles rescaled to meet the target temperature at the end of each time step.

The equilibrium time step is set to 10^5 and afterwards the system is switched to the microcanonical ensemble for another 2×10^5 steps to collect data.

7.3 Results and Discussion

7.3.1 Narrow SWCNTs

In this section we discuss those nanotubes that can only hold one cylindrical layer of fluid particles. The previous chapters have discussed hard cylindrical pores that have the same range of diameters and we found that the fluid-solid coexistence can be clearly seen by the constant pressure regime on the equation of state. We will extend the same idea to SWCNTs. The chiral indices are chosen to be (6, 5), (7, 4), and (9,1), which can hold the triangular packing of fluid particles, and (8, 4), (9, 3), and (10, 1), which can hold the square packing of fluid particles. The parameters for these nanotubes are listed in Table 7.2.

Table 7.2. Structure parameters for the narrow SWCNTs

Chiral Index	Diameter	Number of Carbon Atoms in Unit Cell	Length of Unit Cell	Number of Unit Cell	Length of Nanotube	Number of Carbon Atoms
(6, 5)	2.6569	364	14.4573	3	43.3719	1092
(7, 4)	2.6859	124	4.87179	10	48.7197	1240
(9, 1)	2.6569	364	14.4573	3	43.3719	1091
(8, 4)	2.9475	112	4.0097	12	48.1164	1344
(9, 3)	3.0126	156	5.4643	8	43.7144	1248
(10, 1)	2.9344	148	5.3224	8	42.5792	1184

The equations of state for the hard spheres confined in these nanotubes are shown in Figure 7.5. From the equations of state we can clearly observe that they are divided into three branches for all the indices of interest. For the indices (6, 5), (7, 4) and (9, 1), the equations of state are close to each other at the fluid and solid phases, and have little but observable variation on pressure at fluid-solid coexistence. The coexistence pressure of (9, 1) is a little larger than other two indices, even the cases of (9, 1) and (6, 5) have exactly same diameter and length of unit cell. This implies that the different wall structures have significant impact on the freezing of the fluid confined in the nanotubes. Larger deviation on the fluid-solid coexistence is found in chiral indices (8, 4), (9, 3) and (10, 1). The nanotubes of these chiral indices have little difference in diameter. The coexistence pressures shift in the order of (9, 3), (8, 4), and (10, 1), and the freezing densities shift in the same order. The coexistence pressure

of (10, 1), which is around 11, is much larger than that of other two indices with close diameters.

Figure 7.5. The equation of state of hard spheres confined in SWCNTs of the chiral indices: top (6, 5), (7, 4) and (9, 1); bottom (8, 4), (9, 3) and (10, 1).

The normalized radial density profiles ($\rho(r)/\rho$) of the hard spheres confined in the nanotube (6, 5) at different average densities are shown in Figure 7.6. All profiles show that the maximum local density appears near the

CNT wall at the distance $r = r_t - 0.5(\sigma_c + \sigma_f)$. The minimum values are found in the axis of the nanotubes and the values increase with r until the maximum value at $r_t - 0.5(\sigma_c + \sigma_f)$. The local densities then decrease as the reason that the regime $r > r_t - 0.5(\sigma_c + \sigma_f)$ becomes less accessible. The maximum normalized local density near the inner wall of nanotubes increases with the average density, however the normalized local density near the axis decreases significantly with the increase of the average density. For $\rho = 0.0998$, the normalized local density at $r = 0$ has the value of 3.69167, which decreases to 1.53333 when the average density increases to $\rho = 0.1996$, and further decrease to 0.00612 for $\rho = 0.4075$. The normalized local densities are zero at the pore axis for the average density larger than 0.4366. This behavior is similar to that of hard spheres confined in structureless cylindrical hard wall of the same diameter.

Figure 7.6. Normalized radial density profiles for the hard spheres confined in SWCNT of chiral index (6, 5) at different average densities.

The axial distribution functions for the hard-sphere fluids confined in the nanotube of chiral index (6, 5) is shown in Figure 7.7. At low densities 0.1996, 0.2994 and 0.4075 we observe similar axial distribution with the hard cylindrical pores of the same diameter. The axial distribution functions have the peak value at $z = 1.0$ and a smaller peak at $z = 2.0$ for the average density 0.1996, which moves to smaller distance as the average density increases. The axial distribution functions decay to 1.0 at the axial distance $z > 3.0$. The fluids at these average densities do not have long range order. For larger densities (0.4574, 0.5073, and 0.5364), two distant peaks at the axial distribution functions are found at the two side of the peak at $z = 1.0$ corresponding to the possible short range order at the axial distance $z < 3.0$, though the system is still in the fluid phase. The fluid particles form tetrahedral clusters in the nanotube. The systems still have no long range order as shown in Figure 7.7 that axial distribution functions decay to 1.0 at long distance. For larger densities (i.e. 0.5697, 0.5780, 0.5863, 0.5988, and 0.6071), strong orders are observed. The axial distribution functions show regular peaks at periodic distance. The peaks become sharper as the average density increases. Note that for average densities 0.5697 and 0.5780 the value of $g(z)$ at the distance between the sharp peaks are not zero, which indicates that the fluid and solid phases can coexist in the nanotube at these densities, as also shown in Figure 7.5 that the pressures at these two densities are almost the same.

The bond order parameter Q_6 and the 2D hexagonal order parameter Φ_6 as the function of density is shown in Figure 7.8 for the same nanotube. Both the parameters increase slightly with average density at the fluid branch indicating slight increase of short range order in the system. The two parameters increase

sharply when freezing happen at $\rho \approx 0.5489$ until the melting density at $\rho \approx 0.5863$. The two order parameters almost do not change above melting density.

Figure 7.7. Axial distribution function $g(z)$ of the hard spheres confined in

SWCNT of chiral index (6,5) at different densities from fluid to solid.

Figure 7.8. The bond order parameter Q_6 and 2D hexagonal order parameter Φ_6 as the function of density for the hard spheres confined in SWCNT of index (6, 5).

7.3.2 Large SWCNTs

In this section the nanotubes that can hold multi-layers of fluid particles are studied. The parameters are listed in Table 7.3.

Table 7.3. Structure parameters for the large SWCNTs

Chiral Index	Diameter	Number of Carbon Atoms in Unit Cell	Length of Unit Cell	Number of Unit Cell	Length of Nanotube	Number of Carbon Atoms
(24, 0)	6.6845	96	1.5155	20	30.310888	1920
(14, 14)	6.7537	56	0.875	25	21.875	1400
(26, 2)	7.5355	488	6.8339	3	20.5019	1464
(16, 16)	7.7186	64	0.875	25	21.875	1600
(28, 0)	7.7985	112	1.5155	20	30.310888	2240
(20, 12)	7.7985	784	10.6088	2	21.2176	1568

The equations of state for these nanotubes are shown in Figure 7.9 . At the fluid branch we can clearly observe that the pressure is higher for those nanotubes of smaller diameter at the same density, highest pressure is found in the nanotube (24, 0) of diameter 6.6845, and lowest pressure is found in the nanotubes (28, 0) and (20, 12), which have the same diameter of 7.7985. The equations at the fluid branch almost overlap for those nanotubes of close diameters. The entire equations of (28, 0) and (20, 12) are overlapped indicating that the chiral difference of the nanotubes of large diameters has no significant

impact on the equations of state of the confined hard sphere fluids, compared to the small nanotubes of chiral indices (6,5) and (9,1), which have identical diameters yet the coexistence pressure of (9,1) is larger than that of (6,5).

Figure 7.9. The equations of state for the hard spheres confined in SWCNTs of different chiral indices.

The 2D hexagonal order parameter Φ_6 for the first and second layers of fluid particles for these nanotubes is shown in Figure 7.10. The first and second layers of fluid particles are transformed from disordered structure to ordered hexagonal planes in terms of sharp change of the value from near zero to around 0.8. Such sharp change is associated with the fluid-solid phase transition of the particles confined in the nanotubes. From Figure 7.10 we can also observe that the first and second layers almost freeze at the same average density. The freezing density of SWCNT (14, 14) is found to be smallest of all nanotubes of interest, followed by the SWCNT (24, 0) that has slightly larger freezing density. The freezing densities found in SWCNTs (16, 16), (28, 0) and (20, 12) are much larger than those found in SWCNTs (24, 0) and (14,14), and fluids confined in SWCNT (26, 2) show freezing density between those freezing densities for fluids in the other two groups. Both difference of diameter and surface chirality have impact on the freezing density. In general, the SWCNTs with larger diameter shows larger freezing density of the confined fluids. The effect of different chirality must be taken into account, though such effect is not so obvious as those small SWCNTs discussed in the previous section, as seen on the almost overlap of Φ_6 within the same group in Figure 7.10.

Figure 7.10. The 2D hexagonal order parameter Φ_6 for the first and second layers of fluid particle confined in SWCNTs of different chiral indices as the function of average density.

7.4 Conclusion

In this chapter we consider the hard-sphere fluids confined in SWCNTs of different chiralities. Both fluid-fluid and fluid-carbon interactions are simplified as perfect elastic collision and the carbon atoms are maintained stationary. The

fluid particles can be self-assembled into layered structures because of entropic effects. The chiral indices of the carbon nanotubes are chosen that the interior of the nanotubes can hold single or multiple layers of fluid particles. The EOS's of fluids confined in these nanotubes are precisely calculated, which show similar fluid branch, fluid-solid coexistence and solid branch on the EOS's as discussed in the previous chapters, where structureless wall are studied. We find that in the small nanotubes, the difference in chiral structure has significant impact on the coexistence pressure while in large nanotubes the impact is less pronounced. The reason is the structural wall modifies the distribution of the contact layer. For those CNTs that contain only one layer of fluid particles, such impact is essential, whereas for the CNTs that contains multi-layer of fluid particle, the impact on the contact layer does not have significant contribution to the overall properties.

Chapter 8

Conclusions

Molecular simulation techniques were applied to understand the fluid-solid phase behavior and structure of simple fluids confined in various geometries and artificial CNT structures. The collision-based MD method was used to determine the equation of state precisely. We have also performed simulations using NPT MC. The MD and NPT MC results on fluid and solid branches are in good agreement. However we found NPT MC method to be inefficient to determine the equation of state in the vicinity of fluid-solid phase transition, while the MD method is more precise and efficient at that regime. In most cases, when our results show a constant pressure versus density regime, the onset of fluid-solid phase transition and fluid-solid coexistence is obtained.

We systematically investigated the effect of the pore size, pore geometries, potential parameters, and temperature to the fluid-solid phase transition. In agreement with others, we found that the hard-sphere fluids do not have phase transition within hard cylindrical pores of diameter less than a threshold value. Freezing and melting densities and the coexistence pressure had complex crossover relations as a function of the pore sizes. Even for the fluid phase, the pressures at the same average density do not have monotonous dependence on the pore sizes, while in general the behavior tends to become more similar to that of bulk fluids in larger pores. Such non-monotonic behavior can be found in both cylindrical and spherical pore confinements. With square-well potential, there is a threshold of the potential well range,

below which the fluid-solid coexistence pressure times inversed temperature does not change much with temperature, while above which the fluid-solid coexistence pressure dramatically decreases with the decrease of temperature. The solid phase of square-well fluids under narrow cylindrical hard pores has similar behavior with that of hard-sphere fluids, due to wall effects and entropic dominance. For the hard-sphere fluids confined in carbon nanotubes, we found that the surface chirality pronouncedly affects the fluid-solid behavior in small nanotubes that can hold one cylindrical layer of fluid particles. For large nanotubes that can hold multi-layers of fluid particles such effect is not strongly pronounced.

We have also investigated the structure of the bulk and confined fluids at a broad range of average densities. The structural change during fluid-solid phase transition was emphasized in these studies, using the density profiles, pair correlation functions, structure factor, global and local bond order parameters, 2D hexagonal order parameters. No structural rearrangement was found in the cylindrical pores of diameter less than 2.0. For cylindrical pores of diameter 2.2 and 2.5, there is a partial ordered phase found prior to freezing. The large cylindrical pores have cylindrical hexagonal layers of particles in solid phases, though the most stable and close-packed structure is still to be determined in near future. In all pore sizes and geometries, the freezing is accompanied with the structure transformed from disordered or partial ordered phase to strongly ordered phase. We have elucidated subtle effects of those parameters on the phase transitions of simple fluids under confinement (i.e. cylindrical, spherical, and SWCNT).

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4. S.K. Kwak, **H.C. Huang** and J.K. Singh, "Structure, Fluid-Solid Coexistence and Phase Transition of Model Fluids in Cylindrical Pore", AIChE Annual Meeting, 2008, Philadelphia, USA
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