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# MOLECULAR DYNAMICS STUDIES OF SIMPLE MODEL FLUIDS AND WATER CONFINED IN CARBON NANOTUBE

by

Jun Wang

## A DISSERTATION

Presented to the Faculty of

The Graduate College at the University of Nebraska

In Partial Fulfillment of Requirements

For the Degree of Doctor of Philosophy

Major: Chemistry

Under the Supervision of Professor Xiao Cheng Zeng

Lincoln, Nebraska August 2010

# MOLECULAR DYNAMICS STUDIES OF SIMPLE MODEL FLUIDS AND WATER CONFINED IN CARBON NANOTUBE

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University of Nebraska, 2010

Adviser: Xiao Cheng Zeng

Molecular Dynamics (MD) simulation is one of the most important computational techniques with broad applications in physics, chemistry, chemical engineering, materials design and biological science. Traditional computational chemistry refers to quantum calculations based on solving Schrodinger equations. Later developed Density Functional Theory (DFT) based on solving Kohn-Sham equations became the more popular *ab initio* calculation technique which could deal with ~1000 atoms by explicitly considering electron interactions. In contrast, MD simulation based on solving classical mechanics equations of motion is a totally different technique in the field of computational chemistry. Electron interactions were implicitly included in the empirical atom-based potential functions and the system size to be investigated can be extended to  $\sim 10^6$  atoms. The thermodynamic properties of model fluids are mainly determined by macroscopic quantities, like temperature, pressure, density. The quantum effects on thermodynamic properties like melting point, surface tension are not dominant. In this work, we mainly investigated the melting point, surface tension (liquid-vapor and liquid-solid) of model fluids including Lennard-Jones model, Stockmayer model and a couple of water models (TIP4P/Ew, TIP5P/Ew) by means of MD simulation. In addition, some new structures of water confined in carbon nanotube were discovered and transport behaviors of water and ions through nano-channels were also revealed.

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### **Chapter 1 Introduction**

#### **1.1 Preface**

The sustainable development of our society depends on the continuous emergence of new technologies. Interface technology (ie. design of super-hydrophobic surface) and nano-technology (ie. design of sea water desalination membrane) are two examples of many newly developed technologies. In these fields, it is not only essential to obtain accurate physical and thermodynamic data, but also necessary to understand the mechanisms underlying various complex phenomena.

With the development of new computation methods and high performance computing resources, computational chemistry has been branched out from traditional theoretical chemistry. Modern computational chemistry now is a virtual instrument for theoretical chemists to test their models and ideas by performing virtual experiments on the computers just like experimental chemists doing real experiments in their labs. The advantage of modern computational chemistry is to design, characterize and optimize the subjects under investigation before beginning expensive experimental processes of synthesis, characterization, assembly and testing. In some cases, simulations would predict results not accessible by current state-of-the-art experimental instruments.

Modern computational chemistry mainly includes two categories, quantum mechanics-based electronic structure methods (QM) and molecular mechanics-based methods (MM). QM is usually deployed to investigate structures of small atomic clusters, vibrational frequencies of small molecules, various molecular spectrums including

photon electron spectrum, magnetic properties, excited state properties, and calculation of reaction path based on transition state theory. MM is typically used to study various phase diagrams, structure factor of liquids, solvation structure of ions, various transport coefficients (diffusion, viscosity, thermal conductivity), ensemble-based free energy calculation, various thermodynamic properties (heat capacity, isothermal compressibility, coefficient), thermal expansion surface/interface properties (surface tension. hydrophobic/hydrophilic properties), distinct structure and transport mechanism of small molecules confined in nano-channels. MM methods can be further classified into two types, Monte Carlo (MC) simulations and Molecular Dynamics (MD) simulations. The first type was named as MC because of large amount of random numbers used in this method and is mainly used to obtain phase diagrams and optimize geometries of atomic clusters. The second type can be applied to obtain not only the static properties but also dynamic properties based on time correlation functions. Therefore, MD is a more general method to some extent.

In this thesis MD simulations were performed to investigate the melting point, surface tension of model fluids including Lennard-Jones model, Stockmayer model and two water models (TIP4P-Ew and TIP5P-Ew). In addition, some new structures of water confined in carbon nanotube were discovered and transport behaviors of water and ions through nano-channels were also revealed.

#### **1.2 Introduction of MD simulation**

#### 1.2.1 A short history of MD simulation

The basic idea of MD simulation is to solve the classical equations of motion (Newtonian mechanics) for a many-particle system. This was first implemented by Alder

and Wainwright in 1957 for a system of hard spheres<sup>[1]</sup>. Since the first successful simulation of Lennard-Jones (LJ) particles by Rahman in 1964<sup>[2]</sup>, the properties of LJ model have been comprehensively investigated. After the initial work on atomic system, MD simulation has been extended to investigate linear diatomic molecules<sup>[3]</sup>, non-linear molecules like water<sup>[4]</sup>, small rigid molecules like methane<sup>[5]</sup>, flexible hydrocarbon molecules like butane<sup>[6]</sup>, even large molecules such as polymers and proteins<sup>[7]</sup>. In 1980 Andersen proposed a method for constant pressure MD, which extended the available MD ensembles from the natural *NVE* (constant particle number, volume and energy) ensemble to *NPH* (constant particle number, pressure and enthalpy) ensemble<sup>[8]</sup>. In 1984, Nose introduced a thermal reservoir method to maintain constant temperature, which further supplemented MD ensembles with *NVT*<sup>[9]</sup> (constant particle number, volume and temperature) and *NPT*<sup>[10]</sup> (constant particle number, pressure and temperature) ensembles.

#### 1.2.2 Typical procedure of a MD simulation

A typical MD simulation consists of three stages: initialization, equilibration and production (Fig. 1-1). During the initialization stage, all particles are assigned with initial coordinates and velocities, and all simulation parameters (potential function parameters, cut-off distance, time-step, equilibration steps, production steps, etc.) are set. Then the simulation is carried out for a number of equilibration steps and a certain number of production steps. Each equilibration step and production step is basically the same except that properties of interest are only calculated in the production stage. One unique data generated by solving MD equations of motion is the trajectory recording the time evolution of coordinates, velocities and even forces of all particles. A large amount of useful information can be obtained from analysis of the trajectory after the simulation is

completed.



Fig. 1-1 Schematic illustration of a MD simulation

#### 1.2.3 Key issues of MD simulation

#### 1.2.3.1 Potential energy

Potential energy is the first of thumb issue in MD simulation. The accuracy of potential energy calculation directly determines how particles move with time and the reliability of simulation results. In principle, potential energy of a system can be accurately obtained from quantum mechanics-based calculations, which is also the basic idea of the so-called *ab initio* MD. However, the system size to be investigated in a classical MD simulation can be up to  $\sim 10^8$  particles, which is far beyond the limit of QM simulations. Since the potential energy and force calculation will be performed millions of times in a classical MD simulation, constructing a suitable potential function is the only way to make classical MD simulation feasible.

In general the potential energy of a molecular system includes three parts, intramolecular potential, intermolecular potential and external potential. Intramolecular potential mainly contains bond potential, valence angle potential and dihedral angle potential, which are used to describe bond vibration, bond bending and bond torsion interactions within a molecule, respectively.

Intermolecular potential depends on coordinates of atom pairs, triplets, etc.

$$V_{\text{inter}} = \sum_{i} \sum_{j>i} v_2(r_i, r_j) + \sum_{i} \sum_{i>j} \sum_{i>j>k} v_3(r_i, r_j, r_k) + \dots$$
(1-1)

The first term, also called the pair potential, depends only on inter-atomic distance and accounts for most of the total energy. The second term, also called three-body term, and the rest of the terms are non-additive contributing up to 10 per cent of the total energy<sup>[11]</sup>. The calculation of these non-additive terms is very time consuming. Usually the average effects of these non-additive terms can be implicitly included by defining an effective pair potential:

$$V_{\text{inter}} = \sum_{i} \sum_{j>i} v_2^{eff} \left( r_i, r_j \right)$$
(1-2)

However, the explicit calculation of three-body term is still necessary to maintain some special structures like tetrahedral structure for bulk silicon and carbon even if the effective pair potential is used.

External potential is used to describe the effect of external field on the system particles, which only depends on the coordinates of individual atoms:

$$V_{\text{extern}} = \sum_{i} v_1(r_i)$$
(1-3)

Common external fields are electric field, magnetic field, gravitational field and wall potentials.

#### 1.2.3.2 Periodic boundary condition (PBC)

In order to use relatively small number of molecules to simulate bulk properties, PBC should be introduced. Otherwise, molecules on the surface will experience different forces from molecules in the bulk. In PBC the simulation box is replicated throughout the space to form an infinite lattice. Minimum image convention states that as the molecule leaves the central box, one of its images will enter through the opposite face. Thus, the molecules at the boundary of the central box will experience the same local environment as they were in the center of the box. Use of PBC will suppress any density fluctuation with a wavelength greater than the box length<sup>[11]</sup>. Therefore, the simulation near the phase transition should be performed in a large box because the critical fluctuations usually occur at long wavelengths. Transitions known to be first order often exhibit the characteristics of higher order transitions when simulated in a small box<sup>[11]</sup>. PBC may also affect the nucleation rate when the system is rapidly cooled. If the external field is present, then either it has the same periodicity as the simulation box, or PBC must be abandoned in the respective direction<sup>[11]</sup>. Despite the above limitations, PBC has little effect on the equilibrium thermodynamic properties and structure of fluids away from phase transitions. Usually effects of PBC should be tested by increasing the system size.

#### 1.2.3.3 Solution of equations of motion

Many-particle equations of motion can be written as either a second order differential equation or a pair of first order differential equations. In principle, they can be solved by the usual finite difference methods like Runga-Kutta. However, these methods require several times of force calculation in each MD step, which is quite inefficient for MD simulation since force calculation is the most time-consuming step in MD simulation. Two main numerical algorithms were developed specially for MD simulation, Gear predictor-corrector method and Verlet method<sup>[11]</sup>. Usually Verlet method could allow relatively larger time step and use less arrays. However, the method should be modified to deal with non-Newton equations of motion. Gear method is more accurate in smaller time step and can be directly used to solve any form of equation of motion<sup>[11]</sup>.

There are two implementations of Gear predictor-corrector method, Adams-Gear implementation and Nordsieck-Gear implementation<sup>[12]</sup>. The former uses position, velocity, acceleration of current step and accelerations of previous steps as main variables to integrate equations of motion. The latter uses position and successive time derivatives of position as main variables and is more commonly seen in MD codes.

In Nordsieck-Gear implementation, the time-step scaled successive time derivatives of position  $\underline{r_0}$  (Note: all vectors will be represented with an underscore) are actually used, i.e. scaled velocity  $\underline{r_1} = \delta \cdot \underline{\dot{r_0}}$  (Note: one dot means the first derivative with respective to time), scaled acceleration  $\underline{r_2} = \frac{1}{2} \delta t^2 \cdot \underline{\ddot{r_0}}$  (Note: two dots designate the second derivative with respective to time), scaled third derivative  $\underline{r_3} = \frac{1}{6} \delta t^3 \cdot \underline{\ddot{r_0}}$ ,  $etc^{[11]}$ . Take the six-value Nordsieck-Gear method as an example, the predictor step takes the form:

The corresponding corrector step takes the form:

$$\frac{r_{0}}{r_{1}} = \frac{r_{0}}{r_{1}} + c_{0}\Delta \underline{r}$$

$$\frac{r_{1}}{r_{1}} = \frac{r_{1}}{r_{1}} + c_{1}\Delta \underline{r}$$

$$\frac{r_{2}}{r_{2}} = \frac{r_{2}}{r_{2}} + c_{2}\Delta \underline{r}$$

$$\frac{r_{3}}{r_{3}} = \frac{r_{3}}{r_{3}} + c_{3}\Delta \underline{r}$$

$$\frac{r_{4}}{r_{5}} = \frac{r_{4}}{r_{5}} + c_{5}\Delta \underline{r}$$
(1-5)

Both correction coefficients and  $\Delta \underline{r}$  depend on the order of the differential equation. For first order differential equation  $\underline{\dot{r}} = f(\underline{r})$ ,  $\Delta \underline{r} = r_1^{corrected} - r_1^{predicted}$ . For second order differential equation  $\underline{\ddot{r}} = f(\underline{r})$ ,  $\Delta \underline{r} = r_2^{corrected} - r_2^{predicted}$ . The corresponding correction coefficients can be found in the appendix of reference [11].

Another two integration methods often coded in MD programs are variants of Verlet algorithms, Leapfrog Verlet method and Velocity Verlet method.

Leapfrog Verlet method updates the velocities at half time-step. The velocities at current time-step can be obtained from the average<sup>[11]</sup>:

$$\underline{\underline{v}}\left(t + \frac{1}{2}\delta t\right) = \underline{\underline{v}}\left(t - \frac{1}{2}\delta t\right) + \delta t \underline{\underline{a}}(t)$$

$$\underline{\underline{r}}(t + \delta t) = \underline{\underline{r}}(t) + \delta t \underline{\underline{v}}\left(t + \frac{1}{2}\delta t\right)$$

$$\underline{\underline{v}}(t) = \frac{\underline{\underline{v}}\left(t + \frac{1}{2}\delta t\right) + \underline{\underline{v}}\left(t - \frac{1}{2}\delta t\right)}{2}$$
(1-6)

The Velocity Verlet method proceeds in two steps. First, it updates the velocities to the half time-step and updates the position to the full time-step. Second, it updates the velocities to the full time-step after the force calculation<sup>[11]</sup>.

$$\underline{\underline{v}}\left(t+\frac{1}{2}\delta t\right) = \underline{\underline{v}}(t) + \frac{1}{2}\delta t \underline{a}(t)$$

$$\underline{\underline{r}}(t+\delta t) = \underline{\underline{r}}(t) + \delta t \underline{\underline{v}}\left(t+\frac{1}{2}\delta t\right)$$

$$\underline{\underline{v}}(t+\delta t) = \underline{\underline{v}}\left(t+\frac{1}{2}\delta t\right) + \frac{1}{2}\delta t \underline{\underline{a}}(t+\delta t)$$
(1-7)

#### **1.2.3.4 Equations of motion for rigid molecules**

The motion of each atom within a rigid molecule is not independent, which is subjected to the shape of the molecule. Two main strategies have been developed to keep the molecular shape during MD simulation, constraint strategy and rigid body approximation. The former strategy proceeds in two steps. First, all molecules are decomposed into their constitution atoms and move independently as if the system only consists of a bunch of atoms without any constraints. Second, constraints are introduced to correct the coordinates of atoms so that relative positions of some atoms can be fixed to form molecules with a certain shape. The latter strategy ignores the internal motion of atoms within each molecule and each molecule is treated as a rigid body. Thus, the equations of motion include two parts, the translational motion of the center of mass for each molecule and the rotational motion of each molecule about its center of mass.

Three methods have been developed to implement the constraint strategy, matrix method, SHAKE method and RATTLE method<sup>[11]</sup>.

Matrix method directly constrains the distance between two atoms to be a predefined value by introducing an undetermined multiplier into each constraint equation. After tedious manipulation of these constraint equations, a set of linear equations about those undetermined multipliers will be obtained. The coefficients of undetermined multipliers formed a c×c matrix, where c is the number of constraints within the molecule. The key

step in this method is to inverse this matrix in order to solve undetermined multipliers. For large molecules with many constraints like proteins, this step could be very timeconsuming.

A special algorithm called SHAKE is developed to avoid inversion of large matrix in each MD step. The idea is to go through each constraint, cyclically, adjusting the coordinates so as to satisfy each in turn. Therefore, the SHAKE algorithm is implemented in iterations. Usually, 3-4 iterations are enough to satisfy all constraints. However, it is hard to converge when rigid triangulated units like water are involved. Therefore, water molecules are usually constrained by the matrix method.

The original SHAKE method can be only used with Verlet integration algorithm. The Velocity Verlet version of SHAKE is also developed and given the name RATTLE. The major difference of RATTLE from SHAKE is that besides the constraints applied to positions, constraint forces also correct velocities to ensure that the derivatives of constraint equations are also satisfied.

When molecules are treated as rigid bodies, the focus is turned to the rotational equations of motion since the translational part can be solved in the same way as an atomic system. The orientation of a molecule can be uniquely defined by three Euler angles  $(\theta, \phi, \psi)$ . In principle the rotational equations of motion should be expressed in terms of Euler angles. Singularity issue appears if expressed in this form. Therefore, the actual rotational equations of motion coded in MD programs are often expressed in terms of four quaternion numbers. The quaternions  $\underline{q} = (q_w, q_x, q_y, q_z)$  are defined in terms of Euler angles<sup>[11]</sup>:

$$q_{w} = \cos\frac{1}{2}\theta\cos\frac{1}{2}(\phi + \psi) \quad q_{x} = \sin\frac{1}{2}\theta\cos\frac{1}{2}(\phi - \psi)$$

$$q_{y} = \sin\frac{1}{2}\theta\sin\frac{1}{2}(\phi - \psi) \quad q_{z} = \cos\frac{1}{2}\theta\sin\frac{1}{2}(\phi + \psi)$$
(1-8)

with the restriction  $q_w^2 + q_x^2 + q_y^2 + q_z^2 = 1$ .

Two different coordinate systems, body-fixed frame and space fixed frame, are introduced to manipulate rotational equations. Any vector in body-fixed frame can be related to the corresponding one in space-fixed frame by  $\underline{e}^{b} = \underline{A} \cdot \underline{e}^{s}$  (Note: All matrix are expressed with two underscores),  $\underline{e}^{s} = \underline{A}^{-1} \cdot \underline{e}^{b} = \underline{A}^{T} \cdot \underline{e}^{b}$ , where  $\underline{A}$  is the rotation matrix defined in terms of quaternions<sup>[11]</sup>:

$$\underline{\underline{A}} = \begin{pmatrix} q_{w}^{2} + q_{x}^{2} - q_{y}^{2} - q_{z}^{2} & 2(q_{x}q_{y} + q_{w}q_{z}) & 2(q_{x}q_{z} - q_{w}q_{y}) \\ 2(q_{x}q_{y} - q_{w}q_{z}) & q_{w}^{2} - q_{x}^{2} + q_{y}^{2} - q_{z}^{2} & 2(q_{y}q_{z} + q_{w}q_{x}) \\ 2(q_{x}q_{z} + q_{w}q_{y}) & 2(q_{y}q_{z} - q_{w}q_{x}) & q_{w}^{2} - q_{x}^{2} - q_{y}^{2} + q_{z}^{2} \end{pmatrix}$$
(1-9)

Rotational equations are usually solved in body-fixed coordinate system with two sets of first order differential equations<sup>[11]</sup>:

$$\begin{pmatrix} \dot{\omega}_{x}^{b} \\ \dot{\omega}_{y}^{b} \\ \dot{\omega}_{z}^{b} \end{pmatrix} = \begin{pmatrix} \frac{\tau_{x}^{b}}{I_{xx}} + \frac{(I_{yy} - I_{zz})}{I_{xx}} \omega_{y}^{b} \omega_{z}^{b} \\ \frac{\tau_{y}^{b}}{I_{yy}} + \frac{(I_{zz} - I_{xx})}{I_{yy}} \omega_{x}^{b} \omega_{z}^{b} \\ \frac{\tau_{z}^{b}}{I_{zz}} + \frac{(I_{xx} - I_{yy})}{I_{zz}} \omega_{x}^{b} \omega_{y}^{b} \end{pmatrix}$$
(1-10)

$$\begin{pmatrix} \dot{q}_{w} \\ \dot{q}_{x} \\ \dot{q}_{y} \\ \dot{q}_{z} \end{pmatrix} = \begin{pmatrix} \frac{1}{2} \left( -q_{x} \omega_{x}^{b} - q_{y} \omega_{y}^{b} - q_{z} \omega_{z}^{b} \right) \\ \frac{1}{2} \left( q_{w} \omega_{x}^{b} - q_{z} \omega_{y}^{b} + q_{y} \omega_{z}^{b} \right) \\ \frac{1}{2} \left( q_{z} \omega_{x}^{b} + q_{w} \omega_{y}^{b} - q_{x} \omega_{z}^{b} \right) \\ \frac{1}{2} \left( -q_{y} \omega_{x}^{b} + q_{x} \omega_{y}^{b} + q_{w} \omega_{z}^{b} \right) \end{pmatrix}$$
(1-11)

, where  $\omega^{b}$  and  $\tau^{b}$  are angular velocity and torque in body-fixed frame, I is the moment of inertia for three principle axis and dot means the time derivative.

The torque is usually calculated in space-fixed frame. For non-linear rigid molecules  $\underline{\tau}_{\underline{i}} = \sum_{a} \left( \underline{r}_{\underline{i},a} - \underline{r}_{\underline{i}} \right) \times \underline{f}_{\underline{i},a} = \sum_{a} \underline{d}_{\underline{i},a} \times \underline{f}_{\underline{i},a}$ , which can be converted to body-fixed frame by  $\underline{\tau}_{\underline{i}}^{b} = \underline{A} \cdot \underline{\tau}_{\underline{i}}$ .

Rotational equations (1-10) and (1-11) can be directly solved by Gear predictorcorrector algorithm using correction coefficients for first-order differential equations. If Leapfrog Verlet or Velocity Verlet method is used, some modifications must be made to the original algorithm.

For linear molecules special rotational equations are developed since equations (1-10) and (1-11) contain too much redundant information. The distance between atomic site and center of mass (COM) of a molecule  $\underline{d}_{i,a}^{s} = r_{i,a}^{s} - r_{i}^{s}$  can be simplified to be  $\underline{d}_{i,a}^{s} = d_{i,a} \underline{e}^{s}$ , where  $d_{i,a}$  is the one dimensional coordinate of each site along the molecular axis and  $\underline{e}^{s}$  is the unit vector along the molecular axis. In other words, we can completely determine the atomic coordinates from molecular COM coordinates and  $\underline{e}^{s}$  by  $r_{i,a}^{s} = r_{i}^{s} + \underline{d}_{i,a}^{s} = r_{i}^{s} + d_{i,a} \underline{e}_{i}^{s}$ . Therefore, rotational equations of motion for linear molecules must be expressed in terms of  $\underline{e}^{s}$ . A special vector  $\underline{g}^{s}$  can be defined by rewriting the torque for linear molecules<sup>[11]</sup>:

$$\underline{\tau_i^s} = \sum_a d_{i,a} \underline{e^s} \times \underline{f_{i,a}^s} = \sum_a \underline{e^s} \times d_{i,a} \underline{f_{i,a}^s} = \underline{e^s} \times \sum_a d_{i,a} \underline{f_{i,a}^s} = \underline{e^s} \times \underline{g^s}$$
(1-12)

Finally, the rotation equation in form of second order differential equation for use with leapfrog algorithm can be written as<sup>[11]</sup>:

$$\frac{\ddot{e}^{s}(t)}{I} = \frac{\underline{g^{s}(t)} - \left[\underline{g^{s}(t)} \cdot \underline{e^{s}(t)}\right] e^{s}(t)}{I} - \frac{2\left[\frac{\dot{e}^{s}\left(t - \frac{1}{2}\delta t\right)}{\delta t} \cdot \underline{e^{s}(t)}\right] e^{s}(t)}{\delta t}$$
(1-13)

In general constraint strategy is more realistic and flexible since large molecules like proteins and polymers cannot be simply approximated as rigid bodies. However, it is hard to apply constraints to mass-less sites like the charge site in TIP4P water model. In this case quaternions-based method would have a clear advantage. If any molecule can be reasonably approximated as a rigid body, quaternions-based method should be the preferred choice.

#### **1.2.3.5** Time-saving techniques in MD simulation

#### 1.2.3.5.1 Verlet neighbor list

In order to save time on the force calculation, we can construct a neighbor list  $(r < r_c + \delta r)$  for each particle at the beginning of simulation, where  $\delta r$  is a parameter representing the width of the neighbor lists and  $r_c$  is the original cutoff distance. The lists can be kept for a certain number of steps before necessary update. In each step, for each particle i, we only need to check the distance between i and all its neighbors within the list instead of scanning from i+1 to N. One way of constructing the neighbor lists is to put all lists into one big array LIST(N\*NMAX) and use another array POINT(N) to specify the beginning and ending position of each particle i ranges from LIST(POINT(I)) to LIST(POINT(I+1)-1). Usually the neighbor list is updated automatically. Once the list is constructed, we record the positions of each particle as  $r_{i.old}$ . If max $\left(r_i - r_{i.old}\right) > 0.5 \delta r$ , then the neighbor list will be updated.  $\delta r$  controls how often the list will be updated,

usually  $\delta r = 0.08 r_c$  in LJ units<sup>[11]</sup>.

#### 1.2.3.5.2 Cell-based linked list

For large system, Verlet list array LIST(N\*NMAX) becomes too large to store easily. method<sup>[11]</sup> is alternative An to divide the simulation box into  $\operatorname{int}(L_x/r_c) \times \operatorname{int}(L_y/r_c) \times \operatorname{int}(L_z/r_c)$  cells. The number of cells in each direction must be equal or large than 4 to make this method efficient. Then we sort all particles into their appropriate cells and construct a linked list array LIST(N). This process is fast and may be performed every step. The potential and force calculations are performed by looping over cells. For each cell, we only consider interaction from its nearest 26  $(3 \times 3 \times 3 - 1)$ neighbor cells (reduce to only 13 cells with Newton's third law). For a given cell, a particle also interacts with all particles in the same cell that are further down the list. During the sorting process an array HEAD(NCELLS) is also constructed to specify the first particle in each cell. The advantage of this method is that the particles in each cell formed a linked list. For example, the first particle in cell i is HEAD(i). The second particle in cell i is LIST(HEAD(i)), the third particle in cell i is LIST(LIST(HEAD(i))), and so on. The last element in cell i will be a virtual particle with index 0. Therefore, there are NCELLS zero in the array LIST(N) with each indicating the ending of each cell. The array HEAD was initially assigned with NCELLS zero. Once a certain particle i is sorted into a certain cell icell, we can assign LIST(I)=HEAD(ICELL) and HEAD(ICELL)=I. For example, if the first particle 1 is sorted into cell 5, then LIST(1)=0, HEAD(5)=1 and we have a two elements linked list in cell 5 as HEAD(5)=1->LIST(1)=0. If the third particle 3 is also sorted into cell 5, then LIST(3)=HEAD(5) and HEAD(5)=3and we have a three elements linked list in cell 5 as HEAD(5)=3->LIST(3)=1>LIST(1)=0.

Usually the above two techniques are combined together in MD codes<sup>[12]</sup>. The combination idea is to use cell based linked list to construct and update the Verlet neighbor list instead of the regular all-pair method. Whenever the Verlet neighbor list is to be constructed or updated, the simulation box will be divided into  $int(L_x/r_i) \times int(L_y/r_i) \times int(L_z/r_i)$  cells. Then we can find each cell's 27 neighbors including the central cell itself. After that each particle is sorted into cells. To find each particle's neighbor list, the first step is to check which cell the selected particle i is located in. Then we can find its all 27 neighbor cells. After that we check the distance between the particle i and its possible neighbor j from all 27 cells (make sure j>i or j<i to meet the Newton's third law). If the distance is less than  $r_i$ , then the particle j is counted as a neighbor of particle i. The current neighbor list is being used in potential energy and force calculations until the next neighbor list update.

#### 1.2.3.6 Calculation of long range Coulomb force

If the system under investigation involves charge-charge interaction, then the calculation of long range Coulomb force is inevitable. Special techniques should be employed since the simple spherical cut off cannot conserve total energy very well.

#### 1.2.3.6.1 Ewald Sum

Ewald Sum is a technique originally developed for calculation of electrostatic energy in ionic crystals<sup>[11]</sup>. It has been adapted and accepted as an accurate and general method to calculate any electrostatic interactions, including charge-charge, dipole-dipole, charge-dipole, etc.

It is necessary to introduce the concepts of real space lattice and reciprocal space

lattice since Ewald Sum includes contributions from both spaces.

The real space lattice (the simulation cell) is defined as  $(\underline{a}, \underline{b}, \underline{c})$ , where  $\underline{a}, \underline{b}, \underline{c}$  are three vectors defining three edges of the simulation box.

The volume of the simulation cell can be calculated as  $vol = |\underline{a} \cdot \underline{b} \times \underline{c}|$ .

Then the reciprocal space lattice<sup>[13]</sup> can be defined as  $(\underline{u}, \underline{v}, \underline{w})$ , where  $\underline{u} = 2\pi \frac{\underline{b} \times \underline{c}}{\underline{a} \cdot \underline{b} \times \underline{c}}$ ,

$$\underline{v} = 2\pi \frac{\underline{c} \times \underline{a}}{\underline{a} \cdot \underline{b} \times \underline{c}}, \underline{w} = 2\pi \frac{\underline{a} \times \underline{b}}{\underline{a} \cdot \underline{b} \times \underline{c}}$$

The reciprocal space lattice vector<sup>[13]</sup> can be expressed as  $\underline{k} = k_x \underline{u} + k_y \underline{v} + k_z \underline{w}$ , where  $k_x, k_y, k_z$  are three arbitrary integers.

Take a general rectangle box as an example:

Real space lattice = 
$$\begin{pmatrix} L_x & 0 & 0 \\ 0 & L_y & 0 \\ 0 & 0 & L_z \end{pmatrix}$$
; Reciprocal space lattice =  $\begin{pmatrix} \frac{2\pi}{L_x} & 0 & 0 \\ 0 & \frac{2\pi}{L_y} & 0 \\ 0 & 0 & \frac{2\pi}{L_z} \end{pmatrix}$ 

Reciprocal space lattice vector  $\underline{k} = 2\pi \left(\frac{k_x}{L_x}, \frac{k_y}{L_y}, \frac{k_z}{L_z}\right).$ 

In the following equations V represents potential energy,  $\varepsilon_s$  denotes dielectric constant of the surroundings, q means charge, r denotes position or distance, f means force, P represents pressure, vol means system volume and  $\mu$  means dipole moment.

For charge-charge interaction in the ionic system:

The contribution to potential energy can be calculated as<sup>[11,13]</sup>.

$$V(\varepsilon_s = 1) = V(\varepsilon_s = \infty) + \frac{2\pi}{3vol} \left| \sum_{i=1}^{N} q_i \underline{r_i} \right|^2$$
(1-14)

$$V(\varepsilon_s = \infty) = V_{real} + V_{recip} - V_{self}$$
(1-15)

$$V_{real} = \frac{1}{4\pi\varepsilon_0} \sum_{i} \sum_{j>i} \frac{q_i q_j}{r_{ij}} erfc(\alpha r_{ij})$$
(1-16)

, where erfc(x) is the complementary error function,  $erfc(x) = \frac{2}{\sqrt{\pi}} \int_x^{\infty} e^{-t^2} dt$ ,  $\alpha$  is

the parameter determining the width of additional charge distribution.

$$V_{recip} = \frac{1}{2vol\varepsilon_0} \sum_{\underline{k}\neq 0} \frac{e^{-k^2/4\alpha^2}}{k^2} \left| \sum_{j=1}^N q_j e^{-i\underline{k}\cdot r_j} \right|^2$$
(1-17)

, where  $k^2 = \underline{k} \cdot \underline{k}$ , the sum over  $\underline{k}$  is performed through three loops over three components  $k_x = (-k_x^{\max}, k_x^{\max})$ ,  $k_y = (-k_y^{\max}, k_y^{\max})$ ,  $k_z = (-k_z^{\max}, k_z^{\max})$  with the restriction  $\underline{k} \neq (0,0,0)$ . In principle,  $k_x^{\max} = k_y^{\max} = k_z^{\max} = \infty$ . However, the summation is converged quickly. The parameters  $k_x^{\max}, k_y^{\max}, k_z^{\max}$  depend on  $\alpha$  and the length of cell vectors  $|\underline{a}|, |\underline{b}|, |\underline{c}|$ .

$$V_{self} = \frac{\alpha}{4\pi\varepsilon_0 \sqrt{\pi}} \sum_{i}^{N} q_i^2$$
(1-18)

The contribution to forces for MD simulation can be expressed as<sup>[13]</sup>:

$$\underline{f_i} = \underline{f_i^{real}} + \underline{f_i^{recip}} \tag{1-19}$$

$$\underline{f_i^{real}} = \frac{q_i}{4\pi\varepsilon_0} \sum_{j\neq i}^N \frac{q_j}{r_{ij}^3} \left( erfc(\alpha r_{ij}) + \frac{2\alpha r_{ij}}{\sqrt{\pi}} e^{-\alpha^2 r_{ij}^2} \right) \underline{r_{ij}}$$
(1-20)

$$\underline{f_i^{recip}} = -\frac{q_i}{vol\varepsilon_0} \sum_{\underline{k}\neq 0} real\left(i \cdot e^{i\underline{k}\cdot \underline{r_i}} \sum_{j}^{N} q_j e^{-i\underline{k}\cdot \underline{r_j}}\right) \frac{e^{-k^2/4\alpha^2}}{k^2} \underline{k}$$
(1-21)

, where the function real(x) returns the real part of a complex number.

The contribution to the pressure tensor can be calculated as<sup>[13]</sup>:

$$\underline{\underline{P}} \cdot vol = \underline{\underline{P}}^{real} \cdot vol + \underline{\underline{P}}^{recip} \cdot vol$$
(1-22)

$$\underline{\underline{P}^{real}} \cdot vol = \frac{1}{4\pi\varepsilon_0} \sum_{i} \sum_{j>i} \frac{q_i q_j}{r_{ij}^3} \left( erfc(\alpha r_{ij}) + \frac{2\alpha r_{ij}}{\sqrt{\pi}} e^{-\alpha^2 r_{ij}^2} \right) \underline{\underline{R}_{ij}}$$
(1-23)

, where matrix element  $R_{ij}^{\alpha\beta} = r_{ij}^{\alpha} r_{ij}^{\beta}$ 

$$\underline{\underline{P^{recip}}} \cdot vol = \frac{1}{2vol\varepsilon_0} \sum_{k\neq 0} \frac{e^{-k^2/4\alpha^2}}{k^2} \left| \sum_{j=1}^{N} q_j e^{-i\underline{k}\cdot\underline{r_j}} \right|^2 \left( \frac{1}{2} - 2\left(\frac{1}{4\alpha^2} + \frac{1}{k^2}\right) \underline{\underline{K}} \right)$$
(1-24)

, where matrix element  $K^{\alpha\beta} = k_{\alpha}k_{\beta}$ ,  $k_{\alpha}$ ,  $k_{\beta}$  are components of the vector  $\underline{k}$ ,  $\underline{1}$  is the unit matrix.

In the case of a molecular system including partial charges<sup>[13]</sup>:

The contribution to potential energy also includes three terms<sup>[11,13]</sup>:

$$V_{real} = \frac{1}{4\pi\varepsilon_0} \sum_{i} \sum_{j>i} \sum_{a} \sum_{b} \frac{q_{i,a}q_{j,b}}{r_{ab}} erfc(\alpha r_{ab})$$
(1-25)

, where  $r_{ab}$  is the distance between site a in molecule i and site b in molecule j.

$$V_{recip} = \frac{1}{2vol\varepsilon_0} \sum_{\underline{k}\neq 0} \frac{e^{-k^2/4\alpha^2}}{k^2} \left| \sum_{i=1}^N \sum_a q_{i,a} e^{-i\underline{k}\cdot \underline{r}_a} \right|^2$$
(1-26)

$$V_{self} = \frac{1}{4\pi\varepsilon_0} \left( \sum_{i}^{N} \sum_{a} \frac{\alpha}{\sqrt{\pi}} q_{i,a}^2 + \sum_{i}^{N} \sum_{a} \sum_{b>a} \frac{q_{i,a}q_{i,b}}{r_{ab}} \operatorname{erf}(\alpha r_{ab}) \right)$$
(1-27)

, where erf(x) is the error function and  $r_{ab}$  is the distance between site a in molecule i and site b in the same molecule.

The contribution to forces can be expressed as<sup>[13]</sup>:

$$\underline{f_{i,a}} = \underline{f_{i,a}^{real}} + \underline{f_{i,a}^{recip}} - \underline{f_{i,a}^{self}}$$
(1-28)

$$\underline{f_{i,a}^{real}} = \frac{q_{i,a}}{4\pi\varepsilon_0} \sum_{j\neq i}^N \sum_b \frac{q_{j,b}}{r_{ab}^3} \left( erfc(\alpha r_{ab}) + \frac{2\alpha r_{ab}}{\sqrt{\pi}} e^{-\alpha^2 r_{ab}^2} \right) \underline{r_{ab}}$$
(1-29)

$$\underline{f_{i,a}^{recip}} = -\frac{q_{i,a}}{vol\varepsilon_0} \sum_{\underline{k}\neq 0} real \left( i \cdot e^{i\underline{k}\cdot\underline{r}_{i,a}} \sum_{j}^{N} \sum_{b} q_{j,b} e^{-i\underline{k}\cdot\underline{r}_{j,b}} \right) \frac{e^{-k^2/4\alpha^2}}{k^2} \underline{k}$$
(1-30)

$$\underline{f_{i,a}}^{self} = \frac{q_{i,a}}{4\pi\varepsilon_0} \sum_{b\neq a} \frac{q_{i,b}}{r_{ab}^3} \left( erf(\alpha r_{ab}) - \frac{2\alpha r_{ab}}{\sqrt{\pi}} e^{-\alpha^2 r_{ab}^2} \right) \underline{r_{ab}}$$
(1-31)

The contribution to the atomic pressure tensor can be calculated as<sup>[13]</sup>:

$$\underline{\underline{P}} \cdot vol = \underline{\underline{P}^{real}} \cdot vol + \underline{\underline{P}^{recip}} \cdot vol - \underline{\underline{P}^{self}} \cdot vol$$
(1-32)

$$\underline{\underline{P}^{real}} \cdot vol = \frac{1}{4\pi\varepsilon_0} \sum_{i} \sum_{j>i} \sum_{a} \sum_{b} \frac{q_{i,a}q_{j,b}}{r_{ab}^3} \left( erfc(\alpha r_{ab}) + \frac{2\alpha r_{ab}}{\sqrt{\pi}} e^{-\alpha^2 r_{ab}^2} \right) \underline{\underline{R}_{ab}}$$
(1-33)

, where matrix element  $R_{ab}^{\alpha\beta} = r_{ab}^{\alpha}r_{ab}^{\beta}$  and  $r_{ab}$  is the distance between site a in molecule i and site b in molecule j.

$$\underline{\underline{P}^{recip}} \cdot vol = \frac{1}{2vol\varepsilon_0} \sum_{k \neq 0} \frac{e^{-k^2/4\alpha^2}}{k^2} \left| \sum_{j}^{N} \sum_{b} q_{j,b} e^{-i\underline{k}\cdot\underline{r}_b} \right|^2 \left( \frac{1}{2} - 2\left(\frac{1}{4\alpha^2} + \frac{1}{k^2}\right) \underline{\underline{K}} \right)$$
(1-34)

$$\underline{\underline{P}^{self}} \cdot vol = \frac{1}{4\pi\varepsilon_0} \sum_{i}^{N} \sum_{a} \sum_{b>a} \frac{q_{i,a} q_{i,b}}{r_{ab}^3} \left( erf(\alpha r_{ab}) - \frac{2\alpha r_{ab}}{\sqrt{\pi}} e^{-\alpha^2 r_{ab}^2} \right) \underline{\underline{R}_{ab}}$$
(1-35)

, where matrix element  $R_{ab}^{\alpha\beta} = r_{ab}^{\alpha}r_{ab}^{\beta}$  and  $r_{ab}$  is the distance between site a in molecule i and site b in the same molecule.

For dipole-dipole interaction in the dipolar system<sup>[11,12]</sup>:

The contribution to potential energy can be expressed as<sup>[11,12]</sup>:

$$V(\varepsilon_s = 1) = V(\varepsilon_s = \infty) + \sum_{i} \sum_{j>i} \frac{4\pi}{3vol} \left(\underline{\mu_i} \cdot \underline{\mu_j}\right)$$
(1-36)

$$V(\varepsilon_s = \infty) = V_{real} + V_{recip} - V_{self}$$
(1-37)

$$V_{real} = \frac{1}{4\pi\varepsilon_0} \sum_{i} \sum_{j>i} \left[ \left( \underline{\mu}_i \cdot \underline{\mu}_j \right) \left( \frac{erfc(\alpha r_{ij})}{r_{ij}^3} + \frac{2\alpha}{\sqrt{\pi}r_{ij}^2} e^{-\alpha^2 r_{ij}^2} \right) \right] - \frac{1}{4\pi\varepsilon_0} \sum_{i} \sum_{j>i} \left[ \left( \underline{\mu}_i \cdot \underline{r}_{ij} \right) \underline{\mu}_j \cdot \underline{r}_{ij} \left( \frac{3erfc(\alpha r_{ij})}{r_{ij}^5} + \frac{2\alpha}{\sqrt{\pi}r_{ij}^2} \left( 2\alpha^2 + \frac{3}{r_{ij}^2} \right) e^{-\alpha^2 r_{ij}^2} \right) \right]$$
(1-38)

$$V_{recip} = \frac{1}{2vol\varepsilon_0} \sum_{\underline{k}\neq 0} \frac{e^{-k^2/4\alpha^2}}{k^2} \left| \sum_{j=1}^N \left( \underline{\mu_j} \cdot \underline{k} \right) e^{-i\left(\underline{k} \cdot \underline{r_j}\right)} \right|^2$$
(1-39)

$$V_{self} = \frac{2\alpha^3}{3\sqrt{\pi}} \sum_{i=1}^{N} \left( \underline{\mu}_i \cdot \underline{\mu}_i \right)$$
(1-40)

The contribution to forces can be expressed as<sup>[12]</sup>:

$$\underline{f_i} = \underline{f_i^{real}} + \underline{f_i^{recip}} \tag{1-41}$$

$$\frac{f_{i}^{real}}{I_{i}} = \frac{1}{4\pi\varepsilon_{0}} \sum_{j\neq i}^{N} \left(\underline{\mu}_{i} \cdot \underline{\mu}_{j}\right) \left[\frac{3erfc(\alpha r_{ij})}{r_{ij}^{5}} + \frac{2\alpha}{\sqrt{\pi}r_{ij}^{2}}\left(2\alpha^{2} + \frac{3}{r_{ij}^{2}}\right)e^{-\alpha^{2}r_{ij}^{2}}\right] \frac{r_{ij}}{r_{ij}} \\
- \frac{1}{4\pi\varepsilon_{0}} \sum_{j\neq i}^{N} \left(\underline{\mu}_{i} \cdot \underline{r}_{ij}\right) \left(\underline{\mu}_{j} \cdot \underline{r}_{ij}\right) \left[\frac{15erfc(\alpha r_{ij})}{r_{ij}^{7}} + \frac{2\alpha}{\sqrt{\pi}r_{ij}^{2}}\left(4\alpha^{4} + \frac{10\alpha^{2}}{r_{ij}^{2}} + \frac{15}{r_{ij}^{4}}\right)e^{-\alpha^{2}r_{ij}^{2}}\right] \frac{r_{ij}}{r_{ij}} \quad (1-42)$$

$$+ \frac{1}{4\pi\varepsilon_{0}} \sum_{j\neq i}^{N} \left[\frac{3erfc(\alpha r_{ij})}{r_{ij}^{5}} + \frac{2\alpha}{\sqrt{\pi}r_{ij}^{2}}\left(2\alpha^{2} + \frac{3}{r_{ij}^{2}}\right)e^{-\alpha^{2}r_{ij}^{2}}\right] \left[\underline{\left(\underline{\mu}_{j} \cdot \underline{r}_{ij}\right)}\underline{\mu}_{i} + \left(\underline{\mu}_{i} \cdot \underline{r}_{ij}\right)\underline{\mu}_{j}}\right] \\
= \frac{f_{i}^{recip}}{r_{ij}} = -\frac{1}{vol\varepsilon_{0}} \sum_{\underline{k}\neq 0} real\left(i \cdot e^{i(\underline{k}\cdot\underline{r}_{i})}\sum_{j=1}^{N} \left(\underline{\mu}_{j} \cdot \underline{k}\right)e^{-i(\underline{k}\cdot\underline{r}_{j})}\right) \left(\underline{\mu}_{i} \cdot \underline{k}\right)\frac{e^{-k^{2}/4\alpha^{2}}}{k^{2}} \underbrace{k} \quad (1-43)$$

The special vector related to torque for linear molecule  $\underline{\tau} = \underline{\mu}^s \times \underline{g}$  can be calculated as<sup>[12]</sup>:

$$\underline{g_i} = \underline{g_i^{real}} + \underline{g_i^{recip}}$$
(1-44)

$$\frac{g_{i}^{real}}{g_{i}} = -\frac{1}{4\pi\varepsilon_{0}} \sum_{j\neq i}^{N} \left( \frac{erfc(\alpha r_{ij})}{r_{ij}^{3}} + \frac{2\alpha}{\sqrt{\pi}r_{ij}^{2}} e^{-\alpha^{2}r_{ij}^{2}} \right) \underline{\mu_{j}}$$

$$+ \frac{1}{4\pi\varepsilon_{0}} \sum_{j\neq i}^{N} \left[ \frac{3erfc(\alpha r_{ij})}{r_{ij}^{5}} + \frac{2\alpha}{\sqrt{\pi}r_{ij}^{2}} \left( 2\alpha^{2} + \frac{3}{r_{ij}^{2}} \right) e^{-\alpha^{2}r_{ij}^{2}} \right] \underline{(\mu_{j} \cdot r_{ij})} \underline{r_{ij}}$$

$$\frac{g_{i}^{recip}}{r_{ij}^{ecip}} = -\frac{1}{vol\varepsilon_{0}} \sum_{\underline{k}\neq 0} real \left( e^{i(\underline{k}\cdot r_{j})} \sum_{j=1}^{N} \left( \underline{k} \cdot \underline{\mu_{j}} \right) e^{-i(\underline{k}\cdot r_{j})} \right) \frac{e^{-k^{2}/4\alpha^{2}}}{k^{2}} \underline{k}$$

$$(1-46)$$

The contribution to the pressure tensor can be calculated as<sup>[14]</sup>:

$$\underline{\underline{P}} = \underline{\underline{P}^{real}} + \underline{\underline{P}^{recip}} \tag{1-47}$$

Define the real space pair force as

$$\frac{f_{ij}^{real}}{I_{ij}} = \frac{1}{4\pi\varepsilon_{0}} \left( \underline{\mu}_{i} \cdot \underline{\mu}_{j} \right) \left[ \frac{3erfc(\alpha r_{ij})}{r_{ij}^{5}} + \frac{2\alpha}{\sqrt{\pi}r_{ij}^{2}} \left( 2\alpha^{2} + \frac{3}{r_{ij}^{2}} \right) e^{-\alpha^{2}r_{ij}^{2}} \right] \underline{r_{ij}} \\
- \frac{1}{4\pi\varepsilon_{0}} \left( \underline{\mu}_{i} \cdot \underline{r}_{ij} \right) \left( \underline{\mu}_{j} \cdot \underline{r}_{ij} \right) \left[ \frac{15erfc(\alpha r_{ij})}{r_{ij}^{7}} + \frac{2\alpha}{\sqrt{\pi}r_{ij}^{2}} \left( 4\alpha^{4} + \frac{10\alpha^{2}}{r_{ij}^{2}} + \frac{15}{r_{ij}^{4}} \right) e^{-\alpha^{2}r_{ij}^{2}} \right] \underline{r_{ij}} \quad (1-48)$$

$$+ \frac{1}{4\pi\varepsilon_{0}} \left[ \frac{3erfc(\alpha r_{ij})}{r_{ij}^{5}} + \frac{2\alpha}{\sqrt{\pi}r_{ij}^{2}} \left( 2\alpha^{2} + \frac{3}{r_{ij}^{2}} \right) e^{-\alpha^{2}r_{ij}^{2}} \right] \left[ \underline{\left( \underline{\mu}_{j} \cdot \underline{r}_{ij} \right) \underline{\mu}_{i}} + \underline{\left( \underline{\mu}_{i} \cdot \underline{r}_{ij} \right) \underline{\mu}_{j}} \right]$$

Then

$$volP_{\alpha\beta}^{real} = \sum_{i} \sum_{j>i} r_{ij\alpha} f_{ij\beta}^{real}$$
(1-49)

$$volP_{\alpha\beta}^{recip} = \frac{1}{2vol\varepsilon_0} \sum_{\underline{k}\neq 0} \left\{ B_{1\alpha\beta} \left| \sum_{j=1}^N \left( \mu_j \cdot \underline{k} \right) e^{-i\left(\underline{k}\cdot\underline{r}_j\right)} \right|^2 + B_{2\alpha\beta} \right\} \frac{e^{-k^2/4\alpha^2}}{k^2}$$
(1-50)

where 
$$B_{1\alpha\beta} = \delta_{\alpha\beta} - \frac{2k_{\alpha}k_{\beta}}{k^2} - \frac{k_{\alpha}k_{\beta}}{2\alpha^2}$$
,  $B_{2\alpha\beta} = 2\sum_{i=1}^{N} \mu_{i\alpha}k_{\beta}real\left(e^{i\left(\underline{k}\cdot r_{i}\right)}\sum_{i=1}^{N}\left(\underline{\mu_{j}}\cdot\underline{k}\right)e^{i\left(\underline{k}\cdot r_{j}\right)}\right)$  and  $\delta_{\alpha\beta}$ 

is the kronecker-delta function<sup>[14]</sup>.

### 1.2.3.6.2 Switching function

Another simple technique is to use some form of switching function to smoothly turn

off interactions over a range of distance ( $r_{on} < r < r_{cut}$ ) so that the total energy can be well conserved with dramatically reduced computation cost. Actually switching function can be applied to short range interactions as well.

One example is the switching function used in Cerius<sup>2</sup> package<sup>[15]</sup>

$$S(r) = \begin{cases} 1.0 & r < r_{on} \\ \frac{(r_{cut} - r)^2 (r_{cut} + 2r - 3r_{on})}{(r_{cut} - r_{on})^3} & r_{on} < r < r_{cut} \\ 0.0 & r > r_{cut} \end{cases}$$
(1-51)

The total interaction energy now can be expressed as  $U(r) = U_0(r) \cdot S(r)$ , where  $U_0(r)$  is the original interaction energy without switching function.

The magnitude of force between a pair of particles

$$f(r) = -\frac{dU}{dr} = -\left(S(r)\frac{dU_0(r)}{dr} + U_0(r)\frac{dS(r)}{dr}\right) = S(r)f_0(r) - U_0(r)\frac{dS(r)}{dr}$$
(1-52)

, where  $f_0(r)$  is the original force without switching function.

The force vector  $\underline{f(r)} = f(r)\frac{\underline{r}}{r}$ 

In the case of the above switching function,

$$\frac{dS(r)}{dr} = \frac{6(r - r_{cut})(r - r_{on})}{(r_{cut} - r_{on})^3}$$
(1-53)

For a point dipole the special g vector should be modified accordingly:

$$\underline{g}^{s} = -\nabla_{\underline{e}^{s}} U_{0}(\underline{e^{s}}, r) S(r) = S(r) \left( -\nabla_{\underline{e^{s}}} U_{0}(\underline{e^{s}}, r) \right) = S(r) \underline{g}^{s}_{0}$$
(1-54)

, where  $\underline{g}_0^s$  is original g vector without switching function.

#### 1.2.3.7 Thermostat and barostat

#### 1.2.3.7.1 Temperature control in NVT ensemble

The first Hamiltonian-conserved method to control temperature in *NVT* ensemble is the one proposed by Nose<sup>[9]</sup>. A fictitious coordinate *s* is introduced as an extra degree of freedom to represent a thermal reservoir. Two time units are introduced, the real time *t*' and virtual time *t*, they are related by dt = s(t')dt',  $t = \int s(t')dt'$ <sup>[12]</sup>.

In terms of virtual time t, the dot is used to denote d/dt. The translation equations of motion for use with Gear method are<sup>[12]</sup>:

$$\underline{\ddot{r}_i} = \left(\underline{f_i} / m_i\right) / s^2 - 2\dot{s}\underline{\dot{r}_i} / s \tag{1-55}$$

$$Q_{s}\ddot{s} = \sum_{i} m_{i} \dot{r_{i}}^{2} s - (f+1)k_{B}T / s$$
(1-56)

The reservoir has a thermal inertia  $Q_s$  (fictitious mass). Real particle velocities are related to time derivative of positions by  $\underline{v}_i = s\dot{r}_i$ . Similarly,  $\underline{a}_i = s^2 \ddot{r}_i$ . The potential energy associated with s is  $V_s = (f+1)k_BT \ln s$ . f is the number of degree of freedom in the original system (f=3N if the system consists of N atoms). The kinetic energy associated with s is  $K_s = 0.5Q_s\dot{s}^2$ . The extended system Hamiltonian  $H_s = 0.5s^2\sum_i m_i \dot{r}_i^2 + K_s + V + V_s$  is conserved.

In terms of real time t', the dot is used to denote d/dt'. In this case  $\underline{v_i} = \underline{\dot{r}_i}$ ,  $\underline{a_i} = \underline{\ddot{r}_i}$ .

The translation equation of motions for use with Gear method are<sup>[12]</sup>:

$$\underline{\ddot{r}_i} = \underline{f_i} / m_i - \dot{s}\underline{\dot{r}_i} / s \tag{1-57}$$

$$Q_{s}\ddot{s} = \sum_{i} m_{i} \dot{\underline{r}_{i}}^{2} s - (f+1)k_{B}Ts + Q_{s}\dot{s}^{2} / s$$
(1-58)

 $K_s = 0.5Q_s \dot{s}^2 / s^2$ ,  $V_s = (f+1)k_B T \ln s$ . The extended system Hamiltonian

 $H_s = 0.5 \sum_i m_i \underline{\dot{r}_i}^2 + K_s + V + V_s \text{ is conserved.}$ 

Hoover<sup>[16,13]</sup> further improved Nose's method by removing the fictitious coordinate s: The equations of motion become

$$\underline{\dot{r}_i} = \underline{v_i} , \ \underline{\dot{v}_i} = \underline{f_i} / m_i - \chi \underline{v_i} , \ \dot{\chi} = (temp / T - 1) / \tau_T^2$$
(1-59)

, where *temp* is the instantaneous temperature,  $\chi$  is the friction coefficient and  $\tau_T$  is the time relaxation constant to control temperature.

The conserved quantity is  $H_{NVT} = H_{NVE} + fT \left( \tau_T^2 \chi^2 / 2 + \int_0^t \chi dt \right)$ , where *f* is the number of degree of freedom in the system.

#### 1.2.3.7.2 Pressure control in NPH ensemble

Andersen<sup>[8]</sup> proposed an effective method to control pressure in *NPH* ensemble using the similar extended system idea. Here the variable V is redefined as the system volume and is treated as a fictitious coordinate to represent a piston. The piston has a fictitious mass  $Q_v$  and is associated with a kinetic energy  $K_v = 0.5Q_v\dot{V}^2$  and a potential energy  $U_V = PV$ 

Scaled coordinates, velocities etc. are usually used.  $\underline{r_i} = \underline{r'_i} / V^{1/3}$ ,  $\underline{\dot{r_i}} = \underline{v_i} / V^{1/3}$ ,  $\underline{\ddot{r_i}} = \underline{a_i} / V^{1/3}$  so that  $U = U(V^{1/3} \underline{r_i})$ ,  $K = 0.5V^{2/3} \sum_i m_i \underline{\dot{r_i}}^2$ 

The translation equation of motions for use with Gear method are<sup>[11]</sup>:

$$\frac{\ddot{r}_{i}}{\dot{r}_{i}} = \frac{f_{i}}{f_{i}} / (m_{i} V^{1/3}) - (2/3) \dot{r}_{i} \dot{V} / V$$
(1-60)

$$\ddot{V} = (press - P)/Q_{\nu} = \left(\frac{V^{2/3}\sum_{i} m_{i} \dot{\underline{r}_{i}}^{2} + V^{1/3}\sum_{i} \sum_{j>i} r_{ij}}{3V} - P\right)/Q_{\nu}$$
(1-61)

, where *press* is the instantaneous pressure.

The extended system Hamiltonian  $H_V = K + K_V + U + U_V$  is conserved.

The above method changes the box size isotropically which only controls the total pressure to the preset value. The three diagonal components of pressure tensor may not be exactly equal to the preset value in the case of solid phase.

For anisotropic change of box size we can treat three edge lengths as extra degrees of freedom. This method allows three box lengths to change independently so that all three diagonal components of pressure tensor will be equal to the preset value. This method is particularly useful for solid simulations.

$$r_{i,x} = r'_{i,x} / L_x, r_{i,y} = r'_{i,y} / L_y, r_{i,z} = r'_{i,z} / L_z$$

$$\dot{r}_{i,x} = v_{i,x} / L_x, \dot{r}_{i,y} = v_{i,y} / L_y, \dot{r}_{i,z} = v_{i,z} / L_z$$

$$K_{vx} = 0.5Q_v \dot{L}_x^2, K_{vy} = 0.5Q_v \dot{L}_y^2, K_{vz} = 0.5Q_v \dot{L}_z^2$$

$$U_V = PV = PL_x L_y L_z, K = 0.5\sum_i m_i \left( L_x^2 \dot{r}_{i,x}^2 + L_y^2 \dot{r}_{i,y}^2 + L_z^2 \dot{r}_{i,z}^2 \right)$$
(1-62)

The equation (1-59) can be rewritten for x direction as:

$$\ddot{r}_{i,x} = f_{i,x} / (m_i L_x) - (2/3) \dot{r}_{i,x} \dot{V} / V$$
(1-63)

, where 
$$\dot{V}/V = \left[\frac{d}{dt}(L_x L_y L_z)\right]/(L_x L_y L_z) = \frac{\dot{L}_x}{L_x} + \frac{\dot{L}_y}{L_z} + \frac{\dot{L}_z}{L_z}$$
  
So,  $\ddot{r}_{i,x} = f_{i,x}/(m_i L_x) - 2\dot{r}_{i,x}\frac{1}{3}\left(\frac{\dot{L}_x}{L_x} + \frac{\dot{L}_y}{L_z} + \frac{\dot{L}_z}{L_z}\right) = f_{i,x}/(m_i L) - 2\dot{r}_{i,x}\frac{\dot{L}}{L}$  for cubic box.

Therefore, the equation (1-59) can be generalized to be:

$$\ddot{r}_{i,x} = f_{i,x} / (m_i L_x) - 2\dot{r}_{i,x} \dot{L}_x / L_x$$
  

$$\ddot{r}_{i,y} = f_{i,y} / (m_i L_y) - 2\dot{r}_{i,y} \dot{L}_y / L_y$$
  

$$\ddot{r}_{i,z} = f_{i,z} / (m_i L_z) - 2\dot{r}_{i,z} \dot{L}_z / L_z$$
(1-64)

If we consider the pressure acting on x direction, then  $P = F_x / (L_y L_z)$ ,  $F_x$  is the external

force acting on the area of  $L_y L_z$ , so  $F_x = PL_y L_z$ , the internal force  $f_x$  acting on the area of  $L_y L_z$  is  $f_x = press_x L_y L_z$ , where *press* is the instantaneous pressure. The equation (1-60) can be generalized to be:

$$\ddot{L}_{x} = \left( press_{x}L_{y}L_{z} - PL_{y}L_{z} \right) / Q_{y}$$
(1-65)
  
, where  $press_{x} = \frac{L_{x}^{2}\sum_{i}m_{i}\dot{r}_{i,x}^{2} + L_{x}\sum_{i}\sum_{j>i}r_{ij,x} \cdot f_{ij,x}}{L_{x}L_{x}L_{z}}$ 

Then we can derive the following equations:

$$\ddot{L}_{x} = \left(L_{x}\sum_{i}m_{i}\dot{r}_{i,x}^{2} + \frac{1}{L_{x}}\sum_{i}\sum_{j>i}r'_{ij,x}f_{ij,x} - L_{y}L_{z}P\right)/Q_{v}$$

$$\ddot{L}_{y} = \left(L_{y}\sum_{i}m_{i}\dot{r}_{i,y}^{2} + \frac{1}{L_{y}}\sum_{i}\sum_{j>i}r'_{ij,y}f_{ij,y} - L_{x}L_{z}P\right)/Q_{v}$$

$$\ddot{L}_{z} = \left(L_{z}\sum_{i}m_{i}\dot{r}_{i,z}^{2} + \frac{1}{L_{z}}\sum_{i}\sum_{j>i}r'_{ij,z}f_{ij,z} - L_{x}L_{y}P\right)/Q_{v}$$
(1-66)

The extended system Hamiltonian  $H_V = K + K_{vx} + K_{vy} + K_{vz} + U + U_V$  is conserved. It is straightforward to further extend the above case to control three main components of pressure to be three different values or only control one component of pressure to be a fixed value.

Hoover<sup>[16,13]</sup> further improved the above method by avoiding scaled coordinates:

$$\underline{\dot{r}_i} = \underline{v_i} + \eta \left( \underline{r_i} - \underline{R_0} \right), \ \underline{\dot{v}_i} = \underline{f_i} / m_i - \eta \underline{v_i}, \ \dot{\eta} = V \left( press - P \right) / \left( NT \tau_P^2 \right), \ \dot{V} = 3\eta V$$
(1-67)

, where  $\eta$  is the barostat friction coefficient,  $R_0$  is the system center of mass and  $\tau_p$  is the time relaxation constant to control pressure.

The conserved quantity is  $H_{NPH} = H_{NVE} + PV + 3NT\eta^2 \tau_P^2 / 2$ .

#### 1.2.3.7.3 Combined temperature and pressure control in NPT ensemble

It is straightforward to combine Nose's temperature control method<sup>[9]</sup> and Andersen's pressure control method<sup>[8]</sup> together to control both temperature and pressure in *NPT* ensemble<sup>[12]</sup>.

Scaled coordinates are introduced  $\underline{r_i} = \underline{r'_i} / V^{1/3}$ .

In terms of virtual time t, the dot is used to denote d/dt. The combined equations of motion for use with Gear method are<sup>[12]</sup>:

$$\frac{\ddot{r}_{i}}{Q_{s}\ddot{s}} = \frac{(f_{i} / m_{i})}{(s^{2}V^{1/3})} - (2\dot{s} / s + 2\dot{V} / 3V)\dot{\underline{r}_{i}}}{Q_{s}\ddot{s}} = V^{2/3}s\sum_{i}m_{i}\dot{\underline{r}_{i}}^{2} - (f + 1)k_{B}T / s$$

$$Q_{v}\ddot{V} = press - P = \frac{s^{2}}{3V^{1/3}}\sum_{i}m_{i}\dot{\underline{r}_{i}}^{2} + \frac{1}{3V^{2/3}}\sum_{i}\sum_{j>i}r_{ij} \cdot \underline{f_{ij}} - P$$
(1-68)

The extended system Hamiltonian:

$$H_{NPT} = 0.5V^{2/3}s^{2}\sum_{i}m_{i}\frac{\dot{r_{i}}^{2}}{M_{i}} + K_{V} + U(\underline{r'}) + U_{V} + K_{s} + U_{s} \text{ is conserved, where}$$
$$K_{V} = 0.5Q_{v}\dot{V}^{2}, U_{V} = PV, K_{s} = 0.5Q\dot{s}^{2}, U_{s} = (f+1)k_{B}T\ln s$$

In terms of real time t', the dot is used to denote d/dt'. The combined equations of motion for use with Gear method are<sup>[12]</sup>:

$$\frac{\ddot{r}_{i}}{\dot{r}_{i}} = \left(\underline{f}_{i} / m_{i}\right) / (V^{1/3}) - \left(\dot{s} / s + 2\dot{V} / 3V\right) \underline{\dot{r}_{i}}$$

$$Q_{s} \ddot{s} = Q_{s} \dot{s}^{2} / s + \left(V^{2/3} \sum_{i} m_{i} \frac{\dot{r}_{i}^{2}}{s} - (f + 1)k_{B}T\right) s \qquad (1-69)$$

$$Q_{v} \ddot{V} = \frac{Q_{v} \dot{s} \dot{V}}{s} + \left(V^{2/3} \sum_{i} m_{i} \frac{\dot{r}_{i}^{2}}{s} + V^{1/3} \sum_{i} \sum_{j>i} r_{ij} \cdot \underline{f}_{ij} - 3PV\right) s^{2} / 3V$$

The extended system Hamiltonian:

$$H_{NPT} = 0.5V^{2/3} \sum_{i} m_{i} \frac{\dot{r_{i}}^{2}}{s} + K_{V} + U(\underline{r'}) + U_{V} + K_{s} + U_{s} \quad \text{is conserved, where}$$
$$K_{V} = 0.5Q_{v} \dot{V}^{2} / s^{2}, \ U_{V} = PV, \ K_{s} = 0.5Q\dot{s}^{2} / s^{2}, \ U_{s} = (f+1)k_{B}T \ln s.$$

Hoover<sup>[16,13]</sup> improved the above method by removing fictitious coordinate s and avoiding scaled coordinates:

$$\frac{\dot{r}_i}{\dot{\eta}} = \frac{v_i}{V(press - P)} + \eta \left( \frac{r_i}{r_i} - \frac{R_0}{P} \right), \\ \dot{v}_i = \frac{f_i}{V(press - P)} / \left( \frac{NT\tau_P^2}{P} \right), \\ \dot{V} = 3\eta V$$
(1-70)

, where <u>R<sub>0</sub></u> is the center of mass of the system,  $\eta$  is the barostat friction coefficient to adjust velocities, forces and volume.  $\tau_P$  is the barostat relaxation time constant. *press* is the instantaneous pressure while P is the expected pressure. The conserved quantity is  $H_{NPT} = H_{NVT} + PV + 3NT\eta^2 \tau_P^2/2$ .

For anisotropic change of box size, we can treat three edge lengths as extra degrees of freedom.

$$\begin{aligned} r_{i,x} &= r'_{i,x} / L_x, r_{i,y} = r'_{i,y} / L_y, r_{i,z} = r'_{i,z} / L_z \\ \dot{r}_{i,x} &= v_{i,x} / L_x, \dot{r}_{i,y} = v_{i,y} / L_y, \dot{r}_{i,z} = v_{i,z} / L_z \\ K_{vx} &= 0.5Q_v \dot{L}_x^2 / s^2, K_{vy} = 0.5Q_v \dot{L}_y^2 / s^2, K_{vz} = 0.5Q_v \dot{L}_z^2 / s^2 \\ U_V &= PV = PL_x L_y L_z, K = 0.5\sum_i m_i \left( L_x^2 \dot{r}_{i,x}^2 + L_y^2 \dot{r}_{i,y}^2 + L_z^2 \dot{r}_{i,z}^2 \right) \end{aligned}$$
(1-71)

$$Q_{s}\ddot{s} = Q_{s}\dot{s}^{2} / s + \left(\sum_{i} m_{i} \left(L_{x}^{2} \dot{r}_{i,x}^{2} + L_{y}^{2} \dot{r}_{i,y}^{2} + L_{z}^{2} \dot{r}_{i,z}^{2}\right) - (f+1)k_{B}T\right)s$$
(1-72)

$$\ddot{r}_{i,x} = f_{i,x} / (m_i L_x) - (\dot{s} / s + 2\dot{L}_x / L_x) \dot{r}_{i,x} 
 \ddot{r}_{i,y} = f_{i,y} / (m_i L_y) - (\dot{s} / s + 2\dot{L}_y / L_t) \dot{r}_{i,y} 
 \ddot{r}_{i,z} = f_{i,z} / (m_i L_z) - (\dot{s} / s + 2\dot{L}_z / L_z) \dot{r}_{i,z}$$
(1-73)

$$\ddot{L}_{x} = \dot{L}_{x}\dot{s}/s + \left(L_{x}\sum_{i}m_{i}\dot{r}_{i,x}^{2} + \frac{1}{L_{x}}\sum_{i}\sum_{j>i}r'_{ij,x}f_{ij,x} - L_{y}L_{z}P\right)s^{2}/Q_{v}$$

$$\ddot{L}_{y} = \dot{L}_{y}\dot{s}/s + \left(L_{y}\sum_{i}m_{i}\dot{r}_{i,y}^{2} + \frac{1}{L_{y}}\sum_{i}\sum_{j>i}r'_{ij,y}f_{ij,y} - L_{x}L_{z}P\right)s^{2}/Q_{v}$$

$$\ddot{L}_{z} = \dot{L}_{z}\dot{s}/s + \left(L_{z}\sum_{i}m_{i}\dot{r}_{i,z}^{2} + \frac{1}{L_{z}}\sum_{i}\sum_{j>i}r'_{ij,z}f_{ij,z} - L_{x}L_{y}P\right)s^{2}/Q_{v}$$
(1-74)
The extended system Hamiltonian

$$H_{NPT} = K + K_{vx} + K_{vy} + K_{vz} + U(\underline{r'}) + U_v + K_s + U_s \quad \text{is conserved, where}$$
$$K_s = 0.5Q\dot{s}^2 / s^2, \quad U_s = (f+1)k_BT \ln s.$$

Hoover<sup>[16,13]</sup> improved the above method by removing fictitious coordinate s and avoiding scaled coordinates:

$$\dot{r}_{i,x} = v_{i,x} + \eta_x (r_{i,x} - R_{0,x}), \\ \dot{r}_{i,y} = v_{i,y} + \eta_y (r_{i,y} - R_{0,y}), \\ \dot{r}_{i,z} = v_{i,z} + \eta (r_{i,z} - R_{0,z}) \\ \dot{v}_{i,x} = f_{i,x} / m_i - (\chi + \eta_x) v_{i,x}, \\ \dot{v}_{i,y} = f_{i,y} / m_i - (\chi + \eta_y) v_{i,y}, \\ \dot{v}_{i,z} = f_{i,z} / m_i - (\chi + \eta) v_{i,z} \\ \dot{\chi} = (temp / T - 1) / \tau_T^2, \\ \dot{L}_x = \eta_x L_x, \\ \dot{L}_y = \eta_y L_y, \\ \dot{L}_z = \eta_z L_z$$
(1-75)  
$$\dot{\eta}_x = V (press_x - P_x) / (NT\tau_P^2), \\ \dot{\eta}_y = V (press_y - P_y) / (NT\tau_P^2), \\ \dot{\eta}_z = V (press_z - P_z) / (NT\tau_P^2) \\ \dot{\eta}_y = V (press_y - P_y) / (NT\tau_P^2), \\ \dot{\eta}_z = V (press_z - P_z) / (NT\tau_P^2), \\ \dot{\eta}_y = V (press_y - P_y) / (NT\tau_P^2), \\ \dot{\eta}_z = V (press_y - P_z) / (NT\tau_P^2) + ($$

$$H_{NP_{x}P_{y}P_{z}T} = H_{NVT} + (P_{x} + P_{y} + P_{z})V/3 + NT(\eta_{x}^{2} + \eta_{y}^{2} + \eta_{z}^{2})\tau_{P}^{2}/2.$$

#### 1.2.3.8 Analysis of MD simulation results

The methods to analyze MD simulation results highly depend on personal preference and what specific quantity one wants to measure based on the simulation trajectory. However, general methods have been developed to obtain commonly interested information from MD simulation.

#### 1.2.3.8.1 RMS fluctuation and fluctuation-based analysis

The RMS (root mean square) fluctuation can be defined by<sup>[11]</sup>

$$\sigma(A)^{2} = \left\langle \delta A^{2} \right\rangle_{ensemble} = \left\langle A^{2} \right\rangle_{ensemble} - \left\langle A \right\rangle_{ensemble}^{2}$$
(1-76)

, where  $\delta(A) = A - \langle A \rangle_{ensemble}$ .

The fluctuation can be used to calculate not only the error bar of a measured quantity but also several commonly used thermodynamic quantities, such as constant volume heat capacity  $C_{\nu}$ , constant pressure heat capacity  $C_{p}$ , thermal pressure coefficient  $\gamma_{\nu}$ , isothermal compressibility  $\beta_T$ , thermal expansion coefficient  $\alpha_P$ .

For example,  $C_V$  can be determined from the fluctuation of potential energy under *NVT* ensemble<sup>[11]</sup>:

$$C_{V} = \frac{3}{2}Nk_{B} + \frac{\left\langle \delta V^{2} \right\rangle_{NVT}}{k_{B}T^{2}}$$
(1-77)

 $C_P$  can be obtained from the fluctuation of enthalpy under NPT ensemble<sup>[11]</sup>:

$$C_P = \left\langle \delta (K + V + press \cdot vol)^2 \right\rangle_{NPT} / k_B T^2$$
(1-78)

#### 1.2.3.8.2 Pair distribution function and structure factor

Pair distribution function is one of the most important quantities revealing how atoms are organized in a system, which is defined as<sup>[11]</sup>:

$$g(r) = \frac{vol}{N^2} \left\langle \sum_{i} \sum_{j>i} 2\delta(r - r_{ij}) \right\rangle = \frac{1}{N} \left\langle \sum_{i} \frac{\sum_{j>i} 2\delta(r < r_{ij} < r + dr)}{\rho \frac{4}{3} \pi ((r + dr)^3 - r^3)} \right\rangle$$
(1-79)

, where  $\delta(r < r_{ij} < r + dr) = \begin{cases} 1, & r < r_{ij} < r + dr \\ 0, & \text{otherwise} \end{cases}$ ,  $\rho = \frac{N}{vol}$ .

Basically it tells one the probability of finding a pair of atoms with a separation of r. In addition, it can be used to calculate the static structure factor:

$$S(k) = 1 + 4\pi\rho \int_0^\infty r^2 \frac{\sin kr}{kr} g(r) dr$$
 (1-80)

, where  $k = |\underline{k}|$  and  $\underline{k}$  means a reciprocal space lattice vector. S(k) can be also obtained from X-ray diffraction experiment. Therefore, calculation of g(r) allows one to directly compare the simulation result with the experiment result.

#### 1.2.3.8.3 Time correlation function-based analysis

By considering A and B to be evaluated at two different times, the time correlation function is defined:

$$c_{AB}(t) = \frac{\langle A(t)B(0)\rangle}{\langle A(t)B(t)\rangle}$$
(1-81)

If A and B represent the same quantity, then auto-correlation function is defined as:

$$c_{AA}(t) = \frac{\langle A(t)A(0) \rangle}{\langle A(t)^2 \rangle}$$
(1-82)

The general transport coefficient  $\gamma$  based on Green-Kubo relation is defined as:

$$\gamma = \int_0^\infty dt \left\langle \dot{A}(t) \dot{A}(0) \right\rangle \tag{1-83}$$

The general transport coefficient  $\gamma$  based on Einstein relation is defined as:

$$\gamma = \frac{\left\langle \left(A(t) - A(0)\right)^2\right\rangle}{2t} \tag{1-84}$$

Several commonly seen transport coefficients can be calculated based on time correlation function.

The average diffusion coefficient in three dimensions is defined through velocity autocorrelation by<sup>[11]</sup>:

$$D = \frac{1}{3} \int_0^\infty dt \left\langle \underline{v_i(t)} \cdot \underline{v_i(0)} \right\rangle \tag{1-85}$$

The x component of diffusion coefficient is defined by  $D_x = \int_0^\infty dt \langle v_{i,x}(t)v_{i,x}(0) \rangle$  with similar expression for y and z component. Therefore,  $D = \frac{1}{3} (D_x + D_y + D_z)$ 

The average diffusion coefficient in three dimensions based on Einstein relation is<sup>[11]</sup>:

$$D = \frac{\left\langle \left( \underline{r_i(t)} - \underline{r_i(0)} \right)^2 \right\rangle}{6t}$$
(1-86)

The x component of diffusion coefficient is defined by  $D_x = \frac{\langle (r_{i,x}(t) - r_{i,x}(0))^2 \rangle}{2t}$  with

similar expression for y and z component. Therefore,  $D = \frac{1}{3} (D_x + D_y + D_z)$ 

In practice, the above ensemble average should be calculated for each of N particles, the results are added together and divided by N.

So, 
$$D = \frac{1}{3} \int_0^\infty dt \frac{\sum_{i=1}^N \left\langle \underline{v_i(t)} \cdot \underline{v_i(0)} \right\rangle}{N}$$
 or  $D = \frac{\sum_{i=1}^N \left\langle \left( \underline{r_i(t)} - \underline{r_i(0)} \right)^2 \right\rangle}{6tN}$ 

In order to improve the statistics, the above mentioned correlation functions are actually calculated using a multiple time origins rule<sup>[11]</sup>. Say we have  $\tau_{run}$  frames of velocity numbered as  $(0, \tau_{run} - 1)$ saved during the simulation.

Then velocity autocorrelation function at  $t = \tau \partial t$  is

$$\left\langle \underline{v_i(t)} \cdot \underline{v_i(0)} \right\rangle = \left\langle \underline{v_i(\tau)} \cdot \underline{v_i(0)} \right\rangle = \frac{1}{\tau_{run} - \tau} \sum_{\tau_0 = 0}^{\tau_{run} - 1 - \tau} \underbrace{v_i(\tau_0)}_{\tau_0 = 0} \cdot \underline{v_i(\tau_0 + \tau)}$$
(1-87)

The statistics for long-time correlation function will be poor due to the decrease of the number of terms  $\tau_{run} - \tau$  in the summation. However, the correlation function should decay to zero in a time which is short compared with the complete run time. In practice, not every successive data point is used as a time origin. Instead, the summation will be over every fifth or tenth point as time origin. Of course, the number of terms in the average will not be  $\tau_{run} - \tau$  any more.

## **1.3 Lennard-Jones model**

The most famous effective pair potential in MD simulation is probably the Lennard-Jones (LJ) 12-6 potential<sup>[17]</sup>:

$$v^{LJ}(r) = 4\varepsilon \left[ (\sigma / r)^{12} - (\sigma / r)^{6} \right]$$
(1-88)

, where  $\varepsilon$  and  $\sigma$  are energy parameter and length parameter, respectively. The LJ potential shows the typical features of intermolecular interactions. There is a steeply rising repulsive wall at short distance  $(0 < r < 2^{1/6} \sigma)$  due to overlap between electron clouds. The potential equals to zero when  $r = \sigma$  and reaches its minimum value  $-\varepsilon$  when  $r = 2^{1/6} \sigma$ . After that, the potential will gradually increase and asymptotically approach zero, generating an attractive tail at large r. The LJ potential can be used to describe atom-atom interactions for various atom types with appropriate chosen  $\varepsilon$  and  $\sigma$ . Usually the initial guess of  $\varepsilon$  and  $\sigma$  would be based on the polarizability and vdW radius of the selected atom type, respectively. Further adjustment of  $\varepsilon$  and  $\sigma$  would be fitted to reproduce experimental data of the interested molecules. Therefore,  $\varepsilon$  and  $\sigma$  are not only dependent on the atom type but also affected by the local environment where atom resides. For example, the carbon atom in graphite may have a different  $\varepsilon$  and  $\sigma$  from that in diamond. If we use  $\varepsilon$  and  $\sigma$  as the basic energy unit and length unit in our system, then the difference between various atom types disappears and all correspond to the same so-called LJ particle:

$$v^{LJ}(r) = 4\left((1/r)^{12} - (1/r)^{6}\right)$$
(1-89)

Use of LJ reduced units is very useful for investigating general properties of liquids, solids, etc, which is why LJ potential is the most thoroughly investigated model in all MD simulations. So far various data including complete phase diagrams, liquid structure, interface properties, various transport coefficients and thermodynamic properties have

been reported in MD simulations of LJ model. Most importantly, any newly developed MD simulation method will be usually tested using LJ potential.

## **1.4 Stockmayer model**

Although the attractive tail of LJ potential could account for correlation between the electron clouds surrounding the atoms (vdW interaction or London dispersion), it is not enough to represent interactions between charged species or neutral molecules with dipole. During his PhD (1937-1940) at MIT, Stockmayer introduced a potential which describes the interaction energy between two dipoles<sup>[18]</sup>:

$$v^{DD}\left(\underline{r_{ji}},\underline{\mu_{i}},\underline{\mu_{j}}\right) = \frac{1}{r_{ji}^{3}} \left[\underline{\mu_{i}} \cdot \underline{\mu_{j}} - \frac{3}{r_{ji}^{2}} \left(\underline{\mu_{i}} \cdot \underline{r_{ji}}\right) \left(\underline{\mu_{j}} \cdot \underline{r_{ji}}\right)\right]$$
(1-90)

, where  $v^{DD}$  means the potential energy between two dipoles  $\underline{\mu_i}$  and  $\underline{\mu_j}$ .

The complete Stockmayer potential also includes the LJ potential part:

$$v^{SM}\left(\underline{r_{ji}},\underline{\mu_{i}},\underline{\mu_{j}}\right) = v^{LJ}\left(\underline{r_{ji}}\right) + v^{DD}\left(\underline{r_{ji}},\underline{\mu_{i}},\underline{\mu_{j}}\right)$$
(1-91)

Thus a Stockmayer particle can be constructed by putting a point dipole on the center of a LJ particle. In principle any polar molecule (especially linear geometry) can be modeled using Stockmayer potential. Similar to LJ model, Stockmayer model can be used to investigate general properties of polar molecules. So far Stockmayer model is mainly used as polar solvent in the study of ion solvation dynamics. It was also involved in the study of mixture of polar and non-polar fluids. As far as its own properties concerned, the main properties investigated include the dielectric properties, phase diagrams (mostly liquid-vapor equilibrium) and interface properties.

## **1.5 Common water models**

Despite the fact that sometimes Stockmayer model has been used to simulate certain properties of water, it is seldom employed in MD simulation of water because of strong hydrogen bonding interfaction among water molecules. Also, water is a non-linear molecule consisting of three atoms and it can be too rough to use a point dipole to represent a reasonable model of water. So far at least 46 different water models have been developed. Based on their geometry definitions four categories can be classified as shown in Fig. 1-2.



Fig. 1-2 Four geometries of water models

Among them, only a few were commonly employed in MD simulations of water, such as SPC<sup>[19]</sup>, SPC/E<sup>[20]</sup>, TIP3P<sup>[21]</sup>, TIP4P<sup>[22]</sup>, TIP4P-Ew<sup>[23]</sup>, TIP5P<sup>[24]</sup> and TIP5P-Ew<sup>[25]</sup>. The common form of potential function for various water models includes LJ interaction between oxygen atoms and electrostatic interaction between charged species.

$$v^{water} = \sum_{A \in i} \sum_{B \in j} \frac{q_A q_B}{r_{AB}} + 4\varepsilon \left[ \left( \frac{\sigma}{r_{OO}} \right)^{12} - \left( \frac{\sigma}{r_{OO}} \right)^6 \right]$$
(1-92)

For type A geometry, charged species are same as atoms with oxygen carrying negative charge and hydrogen carrying positive charge. For type B and C geometry, the negative charge is not located on oxygen atom but on a massless charge site instead. For type D geometry, the negative charge is further split in half and distributed evenly on two massless charge sites, respectively. The potential parameters for various water models are shown in Table 1-1.

Model	Geom	$\sigma(\text{\AA})$	Е	$l_1(\text{\AA})$	$l_2(\text{\AA})$	<i>q</i> <sub>1</sub> (e)	<i>q</i> <sub>2</sub> (e)	$ heta(^{\circ})$	φ(°)
	-etry		(kcal/mol)						
$\operatorname{SPC}^{[19]}$	а	3.166	0.155354	1.0		0.410	-0.820	109.5	
SPC/E <sup>[20]</sup>	а	3.166	0.155354	1.0		0.424	-0.848	109.5	
TIP3P <sup>[21]</sup>	а	3.151	0.152103	0.957		0.417	-0.834	104.5	
TIP4P <sup>[22]</sup>	с	3.154	0.154876	0.957	0.15	0.520	-1.04	104.5	52.3
TIP4P-Ew <sup>[23]</sup>	с	3.164	0.162750	0.957	0.125	0.524	-1.048	104.5	52.3
TIP5P <sup>[24]</sup>	d	3.120	0.159990	0.957	0.70	0.241	-0.241	104.5	109.5
TIP5P-Ew <sup>[25]</sup>	d	3.097	0.178011	0.957	0.70	0.241	-0.241	104.5	109.5

Table 1-1 potential parameters for common water models

## **1.6 Two popular Silicon models**

Even if  $\varepsilon$  and  $\sigma$  of LJ model can be adjusted to reproduce experimental data of various single-atom molecules, not all of them can be modeled using LJ potential. Although LJ potential is an effective pair potential which implicitly includes the threebody interaction, it is not sufficient to stabilize the tetragonal structures present in semiconductors like Si and Ge. Two non-additive potentials have been proposed for this purpose.

The first one is called Stillinger-Weber (SW) potential<sup>[26]</sup>. It consists of a pair

potential term and a three-body term:

$$v^{SW} = v_2(r_{ij}) + v_3(\underline{r_i}, \underline{r_j}, \underline{r_k}) = \mathcal{F}_2(r_{ij} / \sigma) + \mathcal{F}_3(\underline{r_i} / \sigma, \underline{r_j} / \sigma, \underline{r_k} / \sigma)$$
(1-93)

, where  $\varepsilon$  and  $\sigma$  are energy parameter and length parameter for SW potential.

In terms of reduced units the pair potential term can be written as:

$$f_2(r) = \begin{cases} A (Br^{-p} - r^{-q}) \exp[(r-a)^{-1}], & r < a \\ 0, & r \ge a \end{cases}$$
(1-94)

In terms of reduced units the three-body potential term includes three cyclic terms.

$$f_3(\underline{r_i}, \underline{r_j}, \underline{r_k}) = h_i(r_{ij}, r_{ik}, \theta_{jik}) + h_j(r_{ji}, r_{jk}, \theta_{ijk}) + h_k(r_{ki}, r_{kj}, \theta_{ikj})$$
(1-95)

The form of each cyclic term is equivalent except the permutation of the triplet. Take  $h_i(r_{ij}, r_{ik}, \theta_{jik})$  as an example, it has the following form:

$$h_i(r_{ij}, r_{ik}, \theta_{jik}) = \begin{cases} \lambda \exp[\gamma(r_{ij} - a)^{-1} + \gamma(r_{ik} - a)^{-1}] (\cos \theta_{jik} + 1/3)^2, & r_{ij} < a \text{ and } r_{ik} < a \\ 0, & \text{otherwise} \end{cases}$$
(1-96)

Seven function parameters are A = 7.049556277, B = 0.6022245584, p = 4, $q = 0, a = 1.80, \lambda = 21, \gamma = 1.20$ 

Two reduced unit parameters for Silicon are  $\varepsilon = 50$  kcal/moland  $\sigma = 0.20951$  nm.

The second one is called Tersoff potential<sup>[27]</sup>. The potential is modeled as a sum of pair-wise interactions. However, the coefficient of the attractive term depends on the local environment, resulting in a many-body effect:

$$\begin{aligned} v^{\text{Tersoff}} &= \sum_{j>i} v_{ij}, \ v_{ij} = f_C(r_{ij}) [f_R(r_{ij}) + b_{ij} f_A(r_{ij})] \\ f_R(r_{ij}) &= A \exp(-\lambda r_{ij}), \ f_A(r_{ij}) = -B \exp(-\mu r_{ij}) \\ f_C(r_{ij}) &= \begin{cases} 1, \ r_{ij} < R \\ 0.5 + 0.5 \cos[\pi (r_{ij} - R) / (S - R)], \ R < r_{ij} < S \\ 0, \ r_{ij} > S \end{cases}$$
(1-97)  
$$b_{ij} &= (1 + \beta^n \zeta_{ij}^n)^{-1/2n}, \ \zeta_{ij} &= \sum_{k \neq i,j} f_C(r_{ik}) g(\theta_{jik}), \ g(\theta_{jik}) = 1 + c^2 / d^2 - c^2 / [d^2 + (h - \cos \theta_{jik})^2] \end{aligned}$$

The eleven parameters for Silicon are:

 $A = 1.8308 \times 10^{3} \text{ ev}, B = 4.7118 \times 10^{2} \text{ ev}, \lambda = 24.799 \text{ nm}^{-1}, \mu = 17.322 \text{ nm}^{-1}, \beta = 1.1 \times 10^{-6},$   $n = 7.8734 \times 10^{-1}, c = 1.0039 \times 10^{5}, d = 16.217, h = -5.9825 \times 10^{-1}, R = 0.27 \text{ nm}, S = 3.0 \text{ nm}$ **1.7 Introduction of carbon nanotube** 

In 1991 Iijima<sup>[28]</sup> discovered a new allotrope of carbon, carbon nanotube (CNT), which initiated a wave of research on CNTs and related carbon nanostructures. CNT can be classified into single-wall CNT (SWCNT) and multi-walls CNT (MWCNT). As far as SWCNT is concerned, its diameter and chirality can be determined by defining a chiral vector  $\underline{R} = ma_1 + na_2$  ( $m \ge n$  and m, n are non-negative integers) as shown in Fig. 1-3.



Fig. 1-3 Chiral vector R and chiral angle  $\theta$  of 2D graphite sheets

 $\underline{a_1}, \underline{a_2}$  are two unit vectors of hexagonal cells in graphite. Chiral angle  $\theta$  is the angle between  $\underline{a_1}$  and  $\underline{R}$ . Usually SWCNT is described by a pair of integers (m, n), whose structure can be obtained by rolling up a graphene nanoribbon layer along the chiral

vector  $\underline{R}$ . When m = n > 0, it is called armchair CNT. If m > n = 0, it is called zigzag CNT. Both armchair CNT and zigzag CNT are achiral. The rest CNTs with m > n > 0 are all called chiral CNT. Typical structures of armchair, zigzag and chiral CNT are shown in Fig. 1-4.



Fig. 1-4 Structure of (a) armchair (b) zigzag (c) chiral SWCNTs with similar diameters Finally the diameter and chiral angle of (m, n) CNT can be determined as<sup>[29]</sup>:

$$d = \frac{a_{c-c}\sqrt{3(m^2 + mn + n^2)}}{\pi}$$
(1-98)

$$\theta = \arctan(\frac{\sqrt{3}n}{2m+n}) \tag{1-99}$$

, where  $a_{c-c}$  is the carbon-carbon bond length in a graphite sheet, approximately 0.142 nm.

The driven power of so many CNT-based research is of course coming from CNT's extraordinary properties for various applications. For example, CNT can be used to make complex materials<sup>[30]</sup>, gas storage materials<sup>[31]</sup> and nanowires for conducting electricity<sup>[32]</sup>. One property concerned in this thesis is its hydrophobic 1-D nano-channel which can serve as a simplified model of ion-channels for mimicing their critical features

(hydrophobic inner surfaces, high selectivity and fast flow rates).

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## Chapter 2 Calculation of melting point for Stockmayer

model and four water models

## **2.1 Introduction**

Melting point is one of the most important thermodynamic data for a given substance. Determination of melting point at different pressure is indispensable for constructing a complete phase diagram. Since melting point is the temperature for liquid and solid coexisting at equilibrium, it is therefore the prerequisite of many surface/interface properties involving liquid-solid equilibrium, such as surface roughness, anisotropic crystal growth, surface tension/interface free energy. Although it is quite simple to directly measure the melting point at moderate pressure by performing real experiments, it is usually very difficult to obtain experimental data of surface/interface properties even with current state-of-the-art instruments. Therefore, scientists have to resort to modern computational chemistry methods, particularly MD simulation. However, MD simulation is a model-based method. The investigated subjects in MD simulation are not real substances but models representing real substances. Although models are constructed to resemble the real substances as much as possible, so far no model can reproduce all experimental data of a certain substance. For example, it is known to all that the melting point of real water at atmospheric pressure is 273.15K. However, the calculated melting points of many water models have different values from this experimental data. Therefore, in order to investigate properties of liquid-solid interface we have to obtain accurate melting point of the investigated molecular model in the first step.

## **2.2 Computational Methods**

Many different approaches have been developed to calculate melting points from classical force-field-based simulations. Free energy method<sup>[1,2]</sup> is the first one proposed to calculate melting point. Later a direct two-phase coexistence approach was also developed<sup>[3,4]</sup>. A special void creation method<sup>[5]</sup> was proposed to overcome the overestimated melting point obtained from incremental heating a single solid phase. A phase switch technique<sup>[6]</sup> designed for Monte Carlo simulations was also created. More recently a superheating-undercooling method<sup>[7]</sup> was developed to estimate the melting point from maximums of superheating and undercooling.

However, the study of melting point by MD simulation has been based on two main approaches, namely the free-energy approach and the coexistence approach. The first approach locates the melting point by requiring equality of free energies for solid and liquid phases<sup>[8]</sup>, where free energies are usually calculated by the thermodynamic integration method<sup>[1]</sup>. The second approach simulates a system containing solid and liquid in coexistence under different ensembles. For example, constant volume and energy ensemble (*NVE*) will directly give a point (T, P) on the melting curve<sup>[4]</sup>. Constant pressure and enthalpy ensemble (*NPH*) generates the melting temperature at a certain pressure<sup>[9]</sup>. If the system initially containing coexisting solid and liquid is simulated at constant pressure and temperature ensemble (*NPT*), the system will finally become pure solid or liquid, which defines upper or lower limit of melting point<sup>[10]</sup>. Therefore, a series of simulations is required to find the melting point. Although the melting point could also be estimated using the simple superheating-undercooling method<sup>[7]</sup>, generally this method is believed to be less accurate than previous two methods.

In this work, the coexistence approach is deployed to locate the melting point. One difficulty of employing the coexistence approach in MD simulation is due to the limitations of applying periodic boundary condition (PBC). As mentioned in Chapter 1, use of PBC will suppress any density fluctuation with a wavelength greater than the box length. However, critical fluctuations of coexisting liquid-solid usually occur at long wavelengths. Therefore, a relative large system size is required to obtain stable coexisting liquid-solid. Another difficulty of calculating melting point by coexisting method is that it takes a long time to allow the simulation system to reach the final equilibrium temperature under *NVE/NPH* ensemble or form single phase near melting point under *NPT* ensemble. These two difficulties made this work tougher and more important.

Two different protocols are used to search the melting points for Stockmayer model and water models. For Stockmayer model which does not have any information about its melting point at the investigated dipole moment  $\mu^*$ , a tedious protocol is adopted. First, a superheating-undercooling scan<sup>[7,11]</sup> is performed to get a rough range of melting point for each  $\mu^*$ . Then the coexistence approach under *NPT* ensemble is deployed to obtain more accurate estimated interval of melting point for each  $\mu^*$ . Finally, the coexistence approach under *NPH* ensemble is employed to determine a specific value of melting point.

For water models with melting points estimated from previous simulations by free energy method<sup>[8,12-15]</sup>, a relative simple protocol can be used. Two initial temperatures are chosen, guided by free energy method, to start two independent simulations under *NPH* ensemble which can directly give the final equilibrium temperature, melting point.

## **2.3 Simulation details**

#### 2.3.1 Stockmayer model

Reduced units are used throughout this study. The LJ part of Stockmayer model is modified as below to be consistent with the definition in the later mentioned cleaving wall method<sup>[16]</sup> for interfacial free energy calculation.

$$u_{LJ}(r) = \begin{cases} 4\left[\left(\frac{1}{r}\right)^{12} - \left(\frac{1}{r}\right)^{6}\right] + C_{1}, & r \le 2.3\\ C_{2}\left(\frac{1}{r}\right)^{12} + C_{3}\left(\frac{1}{r}\right)^{6} + C_{4}\left(\frac{1}{r}\right)^{2} + C_{5}, & 2.3 < r < 2.5\\ 0, & 2.5 < r \end{cases}$$
(2-1)

, where  $C_1 = 0.016132$ ,  $C_2 = 3136.6$ ,  $C_3 = -68.069$ ,  $C_4 = -0.083312$ ,  $C_5 = 0.74689$ .

Due to the appearance of long range dipole-dipole interaction, simple spherical cut off can not assure the total Hamiltonian is well conserved. Standard Ewald sum with "tinfoil" boundary conditions (external region has a dielectric constant of infinity) is used to deal with the long range dipole-dipole interaction. The details of using Ewald sum technique in the dipolar system can be found in section 1.2.3.6.1 of Chapter 1.

For the present study, we choose to calculate melting point at P=0 with reduced dipole moments  $\mu^* = 1$ ,  $\sqrt{2}$ ,  $\sqrt{3}$ . The (111) interface is chosen to merge the liquid phase and solid phase together. The cell linked list and the Verlet neighbor list<sup>[17,18]</sup> are used to save time on force calculation. The equations of motion are integrated using Leapfrog Verlet algorithm[17] with a time step dt = 0.001. The moment of inertia *I* is set to 0.025. The Ewald convergence parameter  $\alpha = 1.23$  is chosen large enough to assure that the real space contribution to the dipole-dipole energy can be safely cut off at 2.6. Due to the use of Ewald sum we select a relative small system consisting of 1584 solid particles. The rectangular box size is  $L_x = 12.582$ ,  $L_y = 11.887$ ,  $L_z = 11.207$  depending on the initial density. The maximum reciprocal lattice vector  $k_x = 12$ ,  $k_y = 12$ ,  $k_z = 12$  is chosen large enough to converge the dipole-dipole energy.

The superheating-undercooling scan is started with an ideal crystal configuration under *NPT* ensemble. The temperature is gradually increased until the solid is melted. After that the melted structure is cooled down step by step until the system crystallized again. The temperature is increased or decreased by 0.025 reduced units every 50000 MD steps, corresponding to a heating/cooling rate 0.0005 or 0.0125K/ps (1K/ps~0.04 LJ unit<sup>[7]</sup>).

The coexistence approach under *NPT* ensemble is performed in the following way. (1) The initial solid configuration resulting from previous superheating process is relaxed under *NPT* ensemble to get well equilibrated solid system for each test temperature. In order to be consistent with the later applied cleaving wall method<sup>[16]</sup>, a special protocol is used to prepare the liquid system. (2) We first melt 1584 solid particles at high temperature (usually 4.00 in reduced unit) under *NVT* ensemble and cool the system down to the test temperature. The system is further relaxed under *NPT* ensemble to find actual liquid density at the test temperature. (3) Next, we randomly remove a certain number of particles from the prepared solid system in (1) to reduce the density to the liquid density obtained in (2). We then melt and re-cool the system to reach the test temperature in the *NVT* ensemble. (4) We merge the solid obtained in (1) with the liquid obtained in (3) and relax the combined system in the constant *z*-component of pressure and constant-temperature ensemble (*NP<sub>z</sub>T*) which allows the box length in *z* direction to change. This can lead to a seamless merge of solid and liquid system in *z* direction. An initial interface width of 0.25 is added to prevent overlap of solid and liquid particles during the merge of solid and liquid systems in (4). At each step of the above protocol an equilibration run of 20000 steps is followed by 30000 steps. (5) Finally the merged system is relaxed under *NPT* ensemble at the test temperature. At each test temperature the system continues to evolve until obvious crystallization/melting is observed or solidliquid equilibrium is maintained all the time (usually 150000 production steps after 50000 equilibration steps). Note, the maximum reciprocal lattice vector  $k_z$  should be doubled after the merge of solid and liquid system. Nose-Hoover thermostat<sup>[19]</sup> with both themostat and barostat time constant of 0.5 is used to retain a constant value of temperature and pressure.

The coexistence approach under *NPH* ensemble is performed in a similar way, but the final merged solid-liquid system is relaxed under *NPH* in stead of *NPT*.

#### 2.3.2 Water models

Four different water models are investigated in this work, TIP4P, TIP5P, TIP4P-Ew and TIP5P-Ew. The latter two models are just two variants of previous two models which are supposed to give better results for use with Ewald-sum technique. Melting points for four water models are all determined at P=1 bar. The initial configuration of proton-disordered ice is constructed to meet the Bernal-Fowler rule so that the entire ice has zero total dipole moment<sup>[20]</sup>.

Two different protocols are used to prepare equilibrated coexisting solid and liquid systems. For TIP4P and TIP5P models, the initial solid structure is equilibrated under *NPT* ensemble. Then the liquid phase is obtained by melting the solid phase at a high temperature under *NVT* ensemble followed by cooling the liquid to the original

temperature under *NVT* ensemble and equilibrating the liquid under  $NP_zT$  ensemble. Next, the well-equilibrated solid and liquid phases are brought into contact at the (001) interface of ice with a gap of 1Å to prevent overlap of solid and liquid. Then the entire two-phase system will undergo another brief  $NP_zT$  equilibration prior to the final production run under *NPH* ensemble.

For TIP4P-Ew and TIP5P-Ew models, the initial solid structure is first duplicated along the direction normal to the merging interface to generate two solid phases. Then one of them is melted at a high temperature and cooled to the initial temperature under *NVT* ensemble while immobilizing the other. The resulted two-phase system will be equilibrated under *NPT* ensemble for a while before the final production run under *NPH* ensemble.

The total number of water molecules in the two phase system is 12288. The dimension of the system is about 53.9×62.3×115.6Å<sup>3</sup>. A combined cell linked list and Verlet neighbor list technique<sup>[18]</sup> is used to save time on force calculations with a neighbor list width of 1Å. The quaternion technique is employed to solve the rotational equations for rigid bodies. The equations of motion are solved with a time step of 1 fs by Gear predictor-corrector algorithm in the case of TIP4P and TIP5P and Leapfrog Verlet algorithm in the case of TIP4P-Ew and TIP5P-Ew. For TIP4P and TIP5P models temperature and pressure are controlled by Nose-Andersen method<sup>[18]</sup> while those for TIP4P-Ew and TIP5P-Ew are adjusted by Nose-Hoover method<sup>[19]</sup>. The LJ part of water-water interaction is truncated at 9Å. Two different techniques are deployed to calculate long range electrostatic interactions. For TIP4P and TIP5P models a simple switching function is used to smoothly shift the Coulomb potential function to zero from 7Å to 9Å.

For TIP4P-Ew and TIP5P-Ew the electrostatic interactions are calculated by the smoothed-particle-mesh-Ewald (SPME) technique which is implemented in the parallel version of DL POLY2 MD program<sup>[21]</sup>.

## 2.4 Results and Discussion

#### 2.4.1 Stockmayer model

In the case of  $\mu^* = 1$  a superheating-undercooling process is started at T=0.617 (See Fig. 2-1). From the sudden jump of potential energy, the maximum of undercooling  $T_{-}$  and maximum of superheating  $T_{+}$  are found to be 0.400 and 0.800, respectively. Our calculated  $T_{+}$  0.800 is already lower than the triple point 0.964 from the DFT calculation<sup>[22]</sup>. It seems that DFT calculation overestimates the melting point of Stockmayer fluid. However, the pressure at the triple point from the DFT calculation<sup>[22]</sup> should not be zero because at P=0 vapor must be thermodynamically more favorable than either liquid or solid phase. Next, a number of test temperatures within 0.4 - 0.8 are selected for the coexistence solid-liquid simulation in the NPT ensemble. From Fig. 2-2, we can clearly see a step-by-step crystallization process occurred at T=0.617 since the potential energy is supposed to decrease after crystallization. Complete melting takes place at a higher temperature (T=0.675). At T=0.656, no obvious melting or crystallization is observed during the entire simulation period and the system maintains solid-liquid equilibrium. Partial crystallization and melting is observed just slightly below (T=0.655) and above (T=0.657) the equilibrium temperature, respectively. Our data indicated that 0.655-0.657 is the best interval in which the true melting point should be located. In fact, T = 0.656 is likely the best estimated freezing temperature at  $\mu^* = 1$ . Finally, two independent NPH searches are started at T=0.645 and T=0.665, respectively.

As shown in Fig. 2-3, both simulations end up with the same melting point  $T_m=0.656\pm0.001$ , consistent with the prediction from the *NPT* simulation. Compared to the melting point of LJ (T=0.617) at the similar condition (P=-0.02)<sup>[16]</sup>, the increased melting point seems entirely due to the added long-range dipole-dipole interaction.

Following the same procedure we found  $T_-$  and  $T_+$  to be 0.475 and 0.875 (See Fig. 2-4) in the case of  $\mu^* = \sqrt{2}$  while  $T_-$  and  $T_+$  for  $\mu^* = \sqrt{3}$  are 0.600 and 0.950 (See Fig. 2-7), respectively. Further *NPT* coexistence search narrows down the possible range of melting point to be 0.725-0.727 (See Fig. 2-5) in the case of  $\mu^* = \sqrt{2}$  and 0.834-0.836 (See Fig. 2-8) in the case of  $\mu^* = \sqrt{3}$ . Finally, *NPH* coexistence searches found the melting point  $T_m=0.726\pm0.002$  (See Fig. 2-6) for  $\mu^* = \sqrt{2}$  and  $T_m=0.835\pm0.005$  (See Fig. 2-9) for  $\mu^* = \sqrt{3}$ .

In general, the melting point increases with the dipolar strength, which is in accordance with the DFT calculation. Different methods of melting point calculation have their pros and cons. A simple superheating-undercooling scan may give a rough but accurate estimate of upper and lower limit of melting point. A series of *NPT* coexistence search can narrow down the melting point into a small interval, but a large amount of uncertainty may exist within this interval. A stable equilibrated solid-liquid system can be generated under *NPH* ensemble. However, too large deviation of initial temperature from the true melting point can also lead to complete crystallization or melting.





#### 2.4.2 Water models

For TIP4P and TIP5P models, we run two independent simulations with different initial temperatures. Two initial temperatures T=225K and T=235K are chosen for TIP4P model while T=265K and T=275K are chosen for TIP5P model. Fig. 2-10 (a) and Fig. 2-10 (b) showed the instantaneous kinetic temperature T versus the MD time t for the TIP4P and TIP5P systems, respectively. One can see that the kinetic temperature of the two systems gradually converges to nearly the same value at t~3500ps. We then used the next 500ps to compute  $T_m$ . For TIP4P model, the calculated  $T_m=229.3\pm1.0K$ , while for

TIP5P model,  $T_m=272.2\pm0.6K$ . These values of  $T_m$  are in very good agreement with  $T_m=229\pm9K$  and  $T_m=268\pm6K$  calculated based on the free energy method for the TIP4P and TIP5P models, respectively<sup>[8]</sup>. Interestingly, these values are also very close to  $T_m=232\pm5K$  and  $T_m=273.9K$  calculated based on a different free energy method using Ewald technique for long range interactions<sup>[15]</sup>. These results suggest that  $T_m$  of TIP4P and TIP5P models are not very sensitive to the inclusion of Ewald summation.

To calculate T<sub>m</sub> with the improved TIP4P-Ew and TIP5P-Ew models, we used identical system size and the similar simulation procedure as for TIP4P and TIP5P models. Since we had no priori information on their values of T<sub>m</sub>, except the location of the density of maximum (close to 274K), we first examined five initial temperatures within 240-280K with 10 K interval, for each model. We monitored the evolution of the system temperature, typically for about 200ps for the five independent simulations, from which we determined that the proper temperature range to locate T<sub>m</sub> is from 250K to 260K, for both models. In Fig. 2-11 (a), we plot the instantaneous kinetic temperature versus MD time for the two independent TIP4P-Ew systems, one with 250K and the other with 260K as the initial temperature. Once the temperatures of the two independent systems converge to nearly the same value, we view that both systems reach the full equilibration. Then we used the next 50ps to evaluate the melting temperature, which is  $T_m=257.0\pm1.1$ K. This value is much closer to the measured value (273K) than the original TIP4P model, namely, another major improvement over the TIP4P model. However, this equilibration at T=257K is only metastable for short 350ps simulation time since further 1ns long time simulations under NPT ensemble showed that solid and liquid phases can only exist at T=244K (See Fig. 2-12). This result is in good agreement with a

recent free energy calculation T=245.5K<sup>[15]</sup> and a two-phase *NPT* coexistence calculation upon a small system T=242K<sup>[23]</sup>. In Fig. 2-11 (b) we plot the temperature versus MD time for two independent TIP5P-Ew systems. Again, once the two systems reach equilibration, we used additional 50ps run to calculate the melting temperature, which is  $T_m$ =253.9±1.1K. This value, however, deviates from the measured value by 20K. Clearly some reparametrization to the TIP5P-Ew model is needed in order to reproduce the measured  $T_m$ . Further 1ns NPT coexistence simulation confirmed that the solid and liquid TIP5P-Ew model can stably coexist at T=254K even for a long time (See Fig. 2-13). This result is about 16K lower than the recent two-phase *NPT* coexistence calculation upon a small system T=270K<sup>[23]</sup>. We believe this discrepancy is due to the difference in system size (12288 molecules vs. 870 molecules). As we emphasized before, a large system size is required for phase coexistence simulation due to the limitation of using PBC.







## **2.5 Conclusions**

## 2.5.1 Stockmayer model

To the best of our knowledge the melting points ( $T_m = 0.656, 0.726, 0.835$ ) of Stockmayer fluids corresponding to three different dipole moments ( $\mu^* = 1, \sqrt{2}, \sqrt{3}$ ) at zero pressure were obtained from coexisting-phase MD simulations for the first time. As expected melting point increases with dipolar strength, which is due to the fact that dipole-dipole interaction energy increases with dipolar strength and melting a polar solid needs to overcome the dipole-dipole interaction energy between lattice sites. The melting data obtained in this work laid down a good foundation for further investigation of liquidsolid interface properties of Stockmayer model.

#### 2.5.2 Water models

Melting points ( $T_m = 229$ K, 272K, 244K, 254K) of four water models (TIP4P, TIP5P, TIP4P-Ew, TIP5P-Ew) at P=1 bar were obtained from coexistence-phase MD simulations for very large systems (12288 water molecules). Large system size ensured that solid and liquid can exist stably since it allows the density at the interface to fluctuate with long wave length which is important for measuring many interfacial properties. The obtained melting points are in good agreement with those obtained from the free energy method but with smaller error bars. Apparently TIP5P model is the best model to reproduce the experimental value of melting point. However, it may not be the best one to reproduce other properties of water. For example, the normal ice  $I_h$  phase for TIP5P model is not thermodynamically stable at 1 bar and the actual equilibrium solid phase of TIP5P model is ice II<sup>[24]</sup>. The latest *ab initio* MD simulation<sup>[25]</sup> even obtained a much higher melting point of water (>410K) which is quite different from the experimental value 273.15K.

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# Chapter 3 Calculation of liquid-solid interfacial free energy for Stockmayer model, SW/Tersoff silicon models and TIP4P-Ew/TIP5P-Ew water models by means of superheating-undercooling method

## **3.1 Introduction**

The free energy of the interface ( $\gamma$ ) at a given pressure is one of the fundamental thermodynamic properties of interfacial systems. For example, the liquid-vapor surface tension is relevant to capillary rise, and the solid-liquid interfacial free energy plays an important role in understanding the mechanism of nucleation and crystal growth. Despite its key role in interfacial systems,  $\gamma$  is difficult to measure experimentally. In most cases  $\gamma$  can be measured either indirectly from measurements of crystal nucleation rates or directly by contact angle measurements<sup>[1]</sup>. The former one is limited by the fact that nucleation primarily occurs heterogeneously while the latter method has been used to study only a few materials to date due to the difficulty of such experiments.

Theoretically, density-functional theory has been a primary choice to evaluate  $\gamma$ . However, previous studies have been primarily focused on simple model systems (hard-sphere and Lennard-Jones models) and calculations of solid-liquid interfacial free energies are not fully consistent in the literature<sup>[2-4]</sup>. Accurate  $\gamma$  can be also obtained through atomistic simulations such as using molecular dynamics (MD). To calculate liquid-vapor surface tension, four types of MD simulation techniques can be selected,

including the Kirkwood-Buff mechanical relation, thermodynamic free energy difference, finite-size scaling, and thermodynamic free-energy perturbation<sup>[5]</sup>. In the case of solidliquid interface, however, the mechanical relation method only gives the excess surface stress, rather than the interfacial free energy  $\gamma$ . Two simulation methods have been developed to compute solid-liquid interfacial free energy  $\gamma$ , namely the fluctuation method and the cleaving potential technique. The fluctuation method<sup>[6-9]</sup> examines the fluctuations in the height of the interface and performs a Fourier transform to compute the interfacial stiffness which can be fitted to obtain  $\gamma$ . The fluctuation method is able to distinguish the weak anisotropy of a system since the anisotropy of the stiffness is an order of magnitude larger than that of the free energy, but less accurate in determining  $\gamma$ due to the fitting process involved. The method cannot be used to resolve facetted interfaces because the fluctuation of interface height is too small. Broughton and Gilmer<sup>[10]</sup> proposed the cleaving potential technique which consists of four reversible steps: cleaving solid phase, cleaving liquid phase, merging solid and liquid interfaces and removing the fictitious cleaving potential. The total work obtained through thermodynamic integration in the four steps is directly related to  $\gamma$ . Davidchack and Laird<sup>[11-12]</sup> later proposed to use cleaving walls instead of cleaving potential which resulted in accuracy sufficient to resolve the anisotropies of interfacial free energy. More recently, Mu and Song<sup>[13]</sup> further improved the efficiency of the cleaving potential technique with a multistep thermodynamic perturbation method.

Although both the fluctuation and cleaving potential methods can yield accurate values of solid-liquid interfacial free energy, the simulations are computational expensive even for simple fluid systems such as hard sphere and Lennard-Jones. An efficient

simulation approach to obtain orientation averaged value of solid-liquid interfacial free energy is the superheating-undercooling hysteresis method developed by Luo *et al.*<sup>[14]</sup>. These authors demonstrated that this simulation method can give fair estimation of the solid-liquid interfacial free energy for the Lennard-Jones (LJ) system<sup>[15]</sup>. They also estimated the interfacial free energy of liquid water/ice system based on experimental undercooling data<sup>[16]</sup>. Moreover, a direct comparison of solid-liquid interfacial free energy for LJ system resulting from the hysteresis method and the fluctuation method or the cleaving potential technique was also made<sup>[16]</sup>. The excellent agreement demonstrated the accuracy of the hysteresis method. Here, we employed such a superheating-undercooling hysteresis method to estimate the orientation averaged solid-liquid interfacial free energy of Stockmayer model, two silicon models and two water models.

## **3.2 Computational Methods**

The principle of superheating and undercooling method is based on classical nucleation theory<sup>[14]</sup> where the highest temperature achieved by superheating a solid  $(T_+)$  or the lowest temperature obtained by undercooling a liquid  $(T_-)$  depends on a dimensionless nucleation barrier parameter  $(\beta)$  and the heating rate (Q).  $\beta$  can be calculated by the equation<sup>[14]</sup>,

$$\beta = (A_0 - b \log_{10} Q) \theta_c (1 - \theta_c)^2$$
(3-1)

, where  $A_0$  and b were fitted to be 59.4 and 2.33, respectively, for a number of elements and compounds. The heating/cooling rate Q is normalized by 1 K/s. In principle, the dimensionless temperature  $\theta_c$  can be obtained either as  $\theta_c^+ = T_+ / T_m$  or  $\theta_c^- = T_- / T_m$ , where  $T_m$  is the melting temperature. However,  $T_-$  is usually much more difficult to determine due to the possible formation of amorphous solid under the fast cooling rate in MD simulations. Hence, we calculate  $\beta$  by using only the superheating temperature  $T_+$  and the melting point  $T_m$  of respective models. Once  $\beta$  is obtained, solid-liquid interface free energy ( $\gamma_{sl}$ ) can be calculated by<sup>[14]</sup>,

$$\gamma_{sl} = \left(\frac{3}{16\pi}\beta k_B T_m \Delta H_{m,v}^2\right)^{1/3}$$
(3-2)

, where  $k_B$  is the Boltzmann constant and  $\Delta H_{m,v}$  is the enthalpy change per unit volume between the solid and liquid phase at the melting point. In practice  $\Delta H_{m,v}$  is normalized to the average volume of solid and liquid at the melting temperature.

## **3.3 Simulation details**

#### 3.3.1 Stockmayer model

Three different dipolar strengths ( $\mu^* = 1, \sqrt{2}, \sqrt{3}$ ) are considered in this work. The superheating-undercooling scan is started with an ideal (111) crystal (reduced size 12.4×11.7×11.0) consisting of 1584 (11×12×12 unit cells) Stockmayer particles at P=0 under *NPT* ensemble. The temperature is gradually increased until the solid is melted. After that the melted structure is cooled down step by step until the system crystallized again. The temperature is increased or decreased by 0.025 every 50000 MD steps with a reduced time step *dt* = 0.001, corresponding to a heating/cooling rate 0.0005 or 0.0125K/ps (1K/ps~0.04 LJ unit<sup>[15]</sup>). Standard Ewald sum technique is used to calculate long range dipole-dipole interactions. Other simulation details can be found in section 2.3.1 of Chapter 2.

#### 3.3.2 Silicon models

We deployed both Stillinger-Weber (SW)<sup>[17]</sup> and Tersoff-89<sup>[18]</sup> models to compute  $\gamma_{sl}$ 

of silicon. The reduced units of energy ( $\varepsilon$ ) and length ( $\sigma$ ) for SW model are  $\varepsilon$  =  $3.4739 \times 10^{-19}$  J and  $\sigma = 0.20951$  nm while for the Tersoff-89 model they are  $\varepsilon =$  $1.6022 \times 10^{-19}$  J and  $\sigma = 0.1$  nm. Each MD time step corresponds to 0.5 fs. The simulations started with crystalline silicon structures of  $5 \times 5 \times 5$  cell units, which contain 1,000 atoms, and a temperature of 1,000K for SW model and 2,000K for Tersoff-89. Two heating rates are applied to the structure. The heating rate of  $1 \times 10^{11}$  K/s increases the temperature of the system by 12.5 K every 50,000 steps while that of  $5 \times 10^{11}$  K/s increases the temperature by 12.5 K every 250,000 steps. The first 5,000 steps after the heating are used for equilibration, and thermodynamic data is measured during the remaining steps until the next temperature increase. The cooling process is performed when the temperature of the system reaches 3,000K for SW and 4,000K for Tersoff-89 model. The structure is then cooled down to 500K (1,500K for Tersoff-89) using the same rate as the heating. Potential energy and volume are recorded during the process in order to observe the superheating/undercooling temperature. The systems are run in isobaric-isothermal (NPT) ensemble by using the Nose-Andersen method. Pressure of the systems is set at zero for all simulations.

#### 3.3.3 Water models

We adopted a procedure similar to that reported in the original paper<sup>[14]</sup> to determine the highest temperature  $T_{+}$  achievable in a superheated solid, and the lowest temperature  $T_{-}$  achievable in an undercooled liquid, before a phase transformation occurs. First, a proton-disordered hexagonal ice  $I_{h}$  is equilibrated at an initial temperature (153.6K for TIP4P-Ew<sup>[19]</sup> and 150.5K for TIP5P-Ew<sup>[20]</sup>) in the MD simulation with the isobaric-isothermal (*NPT*) ensemble. The temperature and pressure (1

bar) are controlled by using Nose-Hoover<sup>[21]</sup> technique. Standard periodic boundary conditions are applied in all directions of the orthorhombic box containing 768 water molecules. Both TIP4P-Ew and TIP5P-Ew water molecules are treated as rigid bodies in the MD simulations, and the corresponding rotation equations are solved by using Quaternion algorithm with a time step of 1.0 fs and 0.5 fs, respectively. Next, the solid (ice) phase is subjected to incremental heating until it melts. Thereafter, the melt (liquid water) is subjected to incremental cooling. Thermodynamic properties are calculated within every 50 ps heating/cooling step after another 50 ps system equilibration. At the end of each heating/cooling step the temperature is increased or decreased by 3.8 K, corresponding to a heating/cooling rate of 0.076 K/ps. All MD simulations are performed using DL\_POLY2 package<sup>[22]</sup>. The long-range charge-charge interactions are treated with the smooth-particle-mesh-Ewald (SPME) technique.

## **3.4 Results and Discussion**

#### 3.4.1 Stockmayer model

As shown in Fig. 2-1, Fig. 2-4 and Fig. 2-7 in Chapter 2, the maximum of superheating  $T_+$  can be clearly determined to be 0.800, 0.875 and 0.950 for  $\mu^* = 1, \sqrt{2}, \sqrt{3}$ , respectively from the sudden increase of potential energy. In order to obtain  $\Delta H_{m,v}$  another independent MD simulation is performed at exactly the melting point (determined from previous two-phase coexistence simulations) during both heating and cooling process for  $\mu^* = 1, \sqrt{2}, \sqrt{3}$ , respectively. The obtained  $\Delta H_{m,v}$  and orientation averaged  $\gamma_{sl}$  are shown in Table 3-1. In general,  $\gamma_{sl}$  does not show a simple increase or decrease trend with the dipolar strength. Although both  $\Delta H_{m,v}$  and  $T_m$  increase

with  $\mu^*$ , the nucleation barrier  $\beta$  decreases with  $\mu^*$  instead, which leads to the complex behavior of  $\gamma_{sl}$  with respect to  $\mu^*$ .

	$T_+$	$T_m$	$ heta_c^{\scriptscriptstyle +}$	β	$V_s$	$V_l$	$\Delta H_{m,v}$	$\gamma_{sl}$	$\mathcal{Q}$
	$(\mathcal{E}/K_B)$	$(\mathcal{E}/K_B)$			$(\sigma)$	$(\sigma)$	$(\varepsilon/\sigma')$	$(\varepsilon/\sigma^2)$	(K/ps)
$\mu^* = 1$	0.80(3)	0.656(1)	1.22(4)	2.1(3)	1.03(2)	1.16(2)	1.11(3)	0.47(2)	0.0125
$\mu^* = \sqrt{2}$	0.88(3)	0.726(2)	1.21(3)	1.8(2)	0.994(2)	1.13(3)	1.36(4)	0.53(2)	0.0125
$\mu^* = \sqrt{3}$	0.95(3)	0.835(5)	1.14(4)	0.78(4)	0.965(3)	1.09(3)	1.49(4)	0.44(3)	0.0125
3.4.2 Silicon models									

Table 3-1 Physical properties of Stockmayer model in the superheating process

Silicon crystal undergoes superheating during the heating process and the structure melts at a temperature higher than the melting points (Table 3-2). The melting points of the structure are determined by the coexisting solid-liquid phase method<sup>[23]</sup>. The melting point of Tersoff-89 model is 2567K, which is higher than both experimental value and the SW model. A potential energy of the system versus temperature curve shows the system undergoes a phase transition at the superheating temperature  $(T^{\dagger})$  (Fig. 3-1). The ratio of superheating temperature to melting temperature is quite high due to the strong covalent bond in silicon crystal. During the cooling process, the potential energy and volume of silicon do not show a sudden change as observed in superheating due to the use of rapid cooling rates. The volume of the system with increasing temperature is shown in Fig. 3-2. Similar to potential energy curves, a sudden drop of volume is observed when the crystalline structure of silicon breaks down. However, in the cooling process, the volume increases gradually with decreasing temperature during the transition. A larger fluctuation is observed with the Tersoff model (Fig. 3-2 b), likely due to the much higher starting temperature used than the SW model [note that the melting temperature of Tersoff model is about 900 K higher than that of the SW model (Table 3-2)].

Once we calculated the nucleation barrier parameter ( $\beta$ ), we can determine the solidliquid surface tension ( $\gamma_{sl}$ ) by Eq. (3-2). Since the simulation is carried out at zero pressure, the enthalpy change at melting point is equal to the change of internal energy of the system. We calculate the difference of enthalpy between the solid and liquid state at the melting point. We then divide the values by the average molar volume of the solid and liquid to obtain the enthalpy change per unit volume at melting point. The average  $\gamma_{sl} \sim$ 0.413 J/m<sup>2</sup> (Table 3-2), which is in good agreement with measured results, ranging from 0.34 – 0.4 J/m<sup>2</sup>. Moreover, the two silicon models give very close values of  $\gamma_{sl}$ , even though the two models give dramatically different melting point. This suggests that the value of  $\gamma_{sl}$  is less sensitive to the model. Using a different heating rate also does not affect the final result of  $\gamma_{sl}$ , as shown in Table 3-2. Finally, we note that the  $\gamma_{sl}$  of SW silicon is about half the value of the liquid-vapor surface tension ( $\sim 0.8 \text{ J/m}^2$ )<sup>[24]</sup>.

**Table 3-2.** Physical properties of silicon in the superheating process. Heating rate (Q), superheating melting point ( $T^+$ ), melting point ( $T_m$ ), ratio of superheating melting point to melting point ( $\theta_c$ ), nucleation barrier parameter ( $\beta$ ), average volume per atom (V), enthalpy change per unit volume between solid and liquid state at melting point ( $\Delta H_m$ ) and solid-liquid surface tension ( $\gamma_{sl}$ ) are displayed. The first two rows are results of Stillinger-Weber model and the last two rows are those of Tersoff-89 model.

	Q	$T^{+}$	$T_m$	_	β	$V \qquad \Delta H_m$		γsl
	(×10 <sup>11</sup> K/s)	(K)	(K)	$ heta_c$		(nm <sup>3</sup> )	$(\times 10^9 \text{ Jm}^{-3})$	(J/m <sup>2</sup> )
SW	1.00	2338	1678	1.39	7.28	0.0196	2.64	0.412
	5.00	2388	1678	1.42	8.18	0.0196	2.64	0.429
Tersoff	1.00	3260	2567	1.27	3.13	0.0206	3.31	0.417
	5.00	3220	2567	1.25	2.60	0.0206	3.31	0.392


#### 3.4.3 Water models

Although homogeneous nucleation has been demonstrated in undercooling experiments, accurate superheating data for ice is rarely reported because heterogeneous melting renders measuring the correct superheating limit  $T_+$  difficult. Conversely, homogeneous crystallization of liquid water is rarely reported in MD simulations except one work<sup>[25]</sup>. This is because ice nucleus formation is a rare event in the MD simulation of undercooled water. Similarly, Zheng *et al.*<sup>[26]</sup> reported that recrystallization of complex molecules by cooling the liquid is very difficult to achieve in MD simulations. Although it is challenging to determine the limiting value of  $T_-$  from MD simulation,  $\beta$  and  $\gamma_{sl}$  can still be deduced from  $T_+$  for a given  $T_m$ . The equilibrium melting temperature  $T_m$  for TIP4P-Ew and TIP5P-Ew water models have been determined using the two-phase coexistence approach reported previously<sup>[27-28]</sup>.  $\Delta H_m$  can be calculated from the enthalpy

difference between the solid and liquid at  $T_m$ , while  $\Delta H_{m,v}$  is normalized to the average volume of solid and liquid at the melting temperature.

As expected, upon superheating, the volume of solid ice gradually increases with increasing the temperature before a sudden reduction of the volume (due to the collapse of ice structure) (Fig. 3-3). This behavior is unique in heating tetrahedral structure materials<sup>[29]</sup>. Near the superheating limit, there is an obvious potential energy jump (Fig. 3-4) as well as one order-of-magnitude increase of diffusion coefficient (Fig. 3-5). These observations confirmed that melting occurs at 321K for TIP4P-Ew and 314K for TIP5P-Ew. Moreover, additional constant stress-constant temperature (NST) simulation and a NPT simulation with 2592 water molecules are also performed to demonstrate that the superheating limit is not sensitive to system size, box shape (Fig. 3-7 and Fig. 3-8). Although the diffusion coefficient of liquid water can decrease to the same magnitude as that of  $I_h$  ice below 210K upon undercooling (Fig. 3-5), no ordered structure was observed from the analysis of configuration snapshots at the low temperatures. A stiffer undercooling curve of volume change is obtained for TIP5P-Ew (Fig. 3-3), but still not sufficient to locate  $T_{\rm due}$  to the continuous decrease of potential energy (Fig. 3-4). The volume of liquid water eventually fluctuates near a constant after a slow increase from 280K to 230K (Fig. 3-3). Based on the temperature dependence of radial distribution function (Fig. 3-6) the liquid water may undergo a continuous transformation toward an amorphous ice upon undercooling.

The calculated interfacial free energies  $\gamma_{sl}$  with two different heat/cooling rates for two water models are shown in Table 3-3. It appears that the heating/cooling rate has little effect on the calculated  $\gamma_{sl}$ . Overall, the calculated  $\gamma_{sl}$  are consistent with a previous MD simulation result<sup>[30]</sup> (39 mJ m<sup>-2</sup>), as well as within the range of measured values<sup>[16]</sup> (25~44 mJ m<sup>-2</sup>). Conversely, both TIP4P-Ew and TIP5P-Ew models give rise to higher  $\gamma_{sl}$  compared to the result (28.0 mJ m<sup>-2</sup>)<sup>[16]</sup> and the accurate direct measurement<sup>[31]</sup> (29.1 mJ m<sup>-2</sup>). The discrepancy is probably due to the empirical TIP4P-Ew and TIP5P-Ew models of water employed in this work. For example, both models underestimate the melting temperatures of water, which renders the material dependent parameter  $\beta$  larger by a factor of four (two for TIP5P-Ew) compared to the reported value<sup>[16]</sup> (1.0).

Table 3-3

	$T_{+}$	$T_m$	$A^+$	ß	$V_s$	$V_l$	$\Delta H_{m,v}$	$\gamma_{sl}$	Q
	(K)	(K)	$v_c$	$\rho$	(Å <sup>3</sup> )	(Å <sup>3</sup> )	$(\times 10^{8} \text{J/m}^{3})$	$(mJ/m^2)$	(K/ps)
TIP4P -Ew	321(6)	244(1)	1.32(3)	4.5(9)	32.0(1)	30.2(2)	2.40(5)	37(3)	0.0762
TIP4P -Ew	317(7)	244(1)	1.30(4)	4.1(9)	32.0(1)	30.2(2)	2.40(5)	36(3)	0.0200
TIP5P -Ew	314(6)	254(1)	1.24(3)	2.4(7)	31.4(1)	29.9(3)	3.90(7)	42(4)	0.0762
TIP5P -Ew	314(6)	254(1)	1.24(3)	2.5(7)	31.4(1)	29.9(3)	3.90(7)	42(4)	0.0200

Extensive quantities are presented per molecule. Numbers in parentheses indicate the estimated error on the last digit(s) shown.



Fig. 3-3





(c) Volume vs. temperature (TIP5P-Ew)(d) Potential energy vs. temperature(TIP5P-Ew)Fig. 3-7 Superheating under *NST* ensemble with the Berendsen barostat to allow the change of both size and shape of the box.



Fig. 3-8 Superheating process performed on a large system including 2592 molecules

## **3.5 Conclusions**

#### 3.5.1 Stockmayer model

Orientation averaged  $\gamma_{sl}$  for Stockmayer model at zero pressure are found to be 0.47, 0.53 and 0.44, respectively, for  $\mu^* = 1, \sqrt{2}, \sqrt{3}$  based on superheatingundercooling MD simulations. In contrast with melting point,  $\gamma_{sl}$  does not simply increase with  $\mu^*$ . The much smaller nucleation barrier  $\beta$  for  $\mu^* = \sqrt{3}$  offsets the effect due to larger melting point and  $\Delta H_{m,v}$  and reduces its  $\gamma_{sl}$  significantly. However, this trend is not observed in the more reliable calculations by the cleaving-wall method and the fluctuation method as shown in Chapter 4.

#### 3.5.2 Silicon models

In this work, we have deployed the superheating method of Luo *et al.*<sup>[14]</sup> to compute the solid-liquid interfacial tension of silicon. Since there is no other computer simulation report on  $\gamma_{sl}$  of silicon, we hope this piece of data can provide a useful benchmark on the interfacial properties of the two models of silicon. The obtained  $\gamma_{sl}$ 

(0.41-0.43J/m<sup>2</sup>) is consistent with a recent obtained value 0.37 J/m<sup>2</sup> by means of timeconsuming cleaving wall method, although the latter is able to distinguish  $\gamma_{sl}$  between different interface orientations.

#### 3.5.3 Water models

We employed the Luo *et al.*'s method<sup>[14]</sup> and superheating/undercooling data directly from MD simulations to estimate the solid-liquid interfacial free energy  $\gamma_{sl}$  of liquid water/ice interface with two water models. With the melting temperature  $T_m$  obtained from independent simulations<sup>[27-28]</sup>, the calculated  $\gamma_{sl}$  are consistent with a previous direct MD simulation<sup>[30]</sup>, but appreciably higher than the results obtained based on experimental undercooling data<sup>[16]</sup>. More accurate values of the liquid water/ice interfacial free energy for the two model systems can be computed by using either the fluctuation or cleaving potential method. A recent study<sup>[32]</sup> using the cleaving wall technique has investigated the  $\gamma_{sl}$  of TIP4P model and obtained values around 24 mJ/m<sup>2</sup>, which is closer to the accurate experimental value 29.1 mJ/m<sup>2[31]</sup>. However, they did not employ Ewald sum technique to deal with the long range electrostatic interactions.

## **3.6 References**

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# Chapter 4 Calculation of liquid-solid interfacial free energy for Stockmayer model using cleaving wall method and fluctuation method

## **4.1 Introduction**

Although the superheating method is able to estimate a rough orientation averaged liquid-solid interfacial free energy  $\gamma_{sl}$ , it can not tell the difference of  $\gamma_{sl}$ between different interface orientations (anisotropy) which determines the stability of dendrite growth. According the classical nucleation theory, interfacial free energy creates the barrier to form a nucleus. As shown in Eqn. 3-2 in chapter 3 a higher interfacial free energy means a higher nucleation barrier if the anisotropy of melting temperature and  $\Delta H_{m,v}$  are negligible (usually this is true). Therefore, the interface orientation with the lowest  $\gamma_{sl}$  will have the lowest nucleation barrier and the crystal would like to grow in that specific direction.

Two simulation methods have been developed to compute solid-liquid interfacial free energy  $\gamma$  with enough accuracy to show the difference between various orientations, namely the fluctuation method and the cleaving potential technique. The fluctuation method<sup>[1-4]</sup> examines the fluctuations in the height of the interface and performs a Fourier transform to compute the interfacial stiffness which can be fitted to obtain  $\gamma$ . The fluctuation method is able to distinguish the weak anisotropy of a system since the anisotropy of the stiffness is an order of magnitude larger than that of the free energy, but less accurate in

determining  $\gamma$  due to the fitting process involved. The method cannot be used to resolve facetted interfaces because the fluctuation of interface height is too small. Broughton and Gilmer<sup>[5]</sup> proposed the cleaving potential technique which consists of four reversible steps: cleaving solid phase, cleaving liquid phase, merging solid and liquid interfaces and removing the fictitious cleaving potential. The total work obtained through thermodynamic integration in the four steps is directly related to  $\gamma$ . Davidchack and Laird<sup>[6-7]</sup> later proposed to use cleaving walls instead of cleaving potential which resulted in accuracy sufficient to resolve the anisotropies of interfacial free energy. More recently, Mu and Song<sup>[8]</sup> further improved the efficiency of the cleaving potential technique with a multistep thermodynamic perturbation method.

The Stockmayer (SM) fluid with its long range dipolar interaction is particularly interesting because it is a reasonable model to represent molecular fluids with particles carrying a permanent dipole moment, such as water. Previous studies of the SM fluids can be briefly summarized. First, the SM fluids can be used to study ion solvation dynamics in polar solvents<sup>[9-16]</sup>. Second, dielectric properties of the SM fluids have been reported<sup>[17-21]</sup>. Third, SM/LJ binary fluids can be used to study mixtures of polar and nonpolar fluids<sup>[22-24]</sup>. Fourth, SM clusters can be used to study effect of dipole strength on structures of polar clusters<sup>[7,25-26]</sup>. As for the thermodynamic properties of the SM fluids such as phase equilibria and surface tensions, most previous studies have focused on the liquid-vapor equilibria<sup>[27-32]</sup> while only a few studies have considered solid-liquid phase equilibria<sup>[33-34]</sup>. The only systematic study of the liquid-solid phase equilibria of SM fluids was based on the classical density functional theory (DFT)<sup>[35]</sup>. As for computer simulation of the liquid-vapor interfacial tension of SM fluids, we are aware of only two

reports<sup>[16,30]</sup>, but none for the solid-liquid interfaces.

In this work both cleaving method and fluctuation method are deployed to calculate  $\gamma_{sl}$  for Stockmayer model with three different orientations and three different dipolar strengths.

## **4.2 Computational Methods**

#### 4.2.1 Cleaving wall method

In this work the cleaving wall method developed by Davidchack and Laird<sup>[7]</sup> is deployed to calculate  $\gamma$ . The method consists of four reversible steps: cleaving solid phase, cleaving liquid phase, merging solid and liquid phases, and removing the fictitious cleaving potential. The total work required in the four steps divided by the area of the interface is  $\gamma$ .

The same cleaving potential used to cleave LJ system<sup>[7]</sup> is retained in this work.

$$\phi(r) = \begin{cases} 4 \left[ \left(\frac{1}{r}\right)^{12} - \left(\frac{1}{r}\right)^{6} \right] + 1, \ r < r_{w} = 2^{1/6} \\ 0, \ r_{w} \le r \end{cases}$$
(4-1)

We designated the planes at the periodic boundary and normal to the *z* axis as the cleaving planes. For each cleaving plane, two cleaving walls (One left, one right) are constructed to "sandwich" the cleaving plane in the middle. In order to assure that the system on one side of the cleaving plane interacts only with the cleaving wall on the other side, the cleaving potential is defined as the minimum of the two wall potentials<sup>[7]</sup>.

$$\phi_i(r) = \min(\phi_{i,1}, \phi_{i,2}) \tag{4-2}$$

$$\phi_{i,1}(r) = \sum_{j} \phi(r_{i} - r_{j,wall1})$$
(4-3)

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$$\phi_{i,2}(r) = \sum_{j} \phi(r_{i} - r_{j,wall\,2})$$
(4-4)

$$\min(x, y) = \begin{cases} x, & x \le y - \delta(x+y) \\ y, & x \ge y + \delta(x+y) \\ p(x, y), & \text{otherwise} \end{cases}$$
(4-5)

$$p(x,y) = \frac{x+y}{4}(2-\delta) - \frac{(x-y)^2}{4\delta(x+y)}$$
(4-6)

, where index i means particles in the system while index j represents particles on the wall. The function p(x, y) is introduced to remove discontinuity of the gradient of  $\phi_i(r)$  at the points where  $\phi_{i,1} = \phi_{i,2}$ . The parameter  $\delta$  is still set to be 2.5 in this work.

The reversible work in steps 1, 2, and 4 is calculated via the following integral<sup>[7]</sup>:

$$w_{1,2,4} = -\int_{z_i}^{z_f} \left\langle \frac{\partial \phi}{\partial z} \right\rangle dz \tag{4-7}$$

The integrand  $-\left\langle \frac{\partial \phi}{\partial z} \right\rangle$  is actually the z component of the force between the system particle and wall particle.  $z_i, z_f$  are initial and final positions of the cleaving wall, respectively.

In step 3, the boundary conditions are gradually rearranged with three systems, namely liquid-liquid (LL) system, solid-solid system (SS) and liquid-solid (LS) system. The total interaction energy in step 3 is given by<sup>[7]</sup>

$$U(\lambda) = (1 - \lambda) \sum_{i < j, LL, SS} u(r_{ij}) + \lambda \sum_{i < j, LS} u(r_{ij}) + \sum_{i} \phi(r_i, z_f)$$
(4-8)

, where  $\lambda$  is a coupling parameter gradually varied from 0 to 1. The work done in step 3 can be calculated from the integral<sup>[7]</sup>

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$$w_3 = \int_0^1 \left\langle \frac{\partial U}{\partial \lambda} \right\rangle d\lambda \tag{4-9}$$

$$\frac{\partial U}{\partial \lambda} = \sum_{i < j, LS} u(r_{ij}) - \sum_{i < j, LL, SS} u(r_{ij})$$
(4-10)

When  $\lambda = 0$  the main contribution to total energy comes from a purely liquid-liquid system + solid-solid system while it comes from a purely liquid-solid system when  $\lambda = 1$ . In between all three systems will partially contribute to the total energy.

Finally the interfacial free energy can be calculated as

$$\gamma = \frac{w_1 + w_2 + w_3 + w_4}{2A} \tag{4-11}$$

, where A is the area of one interface (while two interfaces are created).

#### 4.2.2 Fluctuation method

The unique feature of fluctuation method is to directly measure the so-called interfacial stiffness  $\tilde{\gamma}$  instead of interfacial free energy  $\gamma$  for a certain interface orientation. The advantage of this feature is due to the fact that the anisotropy of the stiffness is an order of magnitude larger than that of the free energy, which makes it easier to distinguish the difference between orientations.

The interfacial stiffness  $\tilde{\gamma}(\theta)$  is related to interfacial free energy  $\gamma(\theta)$  by<sup>[4]</sup>

$$\widetilde{\gamma}(\theta) = \gamma(\theta) + \frac{d^2 \gamma(\theta)}{d\theta^2}$$
(4-12)

, where  $\theta$  is defined as the angle between a chosen short direction axis (i.e. [001]) and the direction normal to the interface. To the lowest order  $\gamma(\theta)$  can be approximated as<sup>[2]</sup>

$$\gamma(\theta) = \gamma_0 (1 + \varepsilon \cos 4\theta) \tag{4-13}$$

, where  $\varepsilon$  is the anisotropic parameter and  $\gamma_0$  is the orientation averaged free energy.

Then the corresponding  $\widetilde{\gamma}(\theta)$  can be derived as<sup>[2]</sup>

$$\widetilde{\gamma}(\theta) = \gamma_0 (1 - 15\varepsilon \cos 4\theta) \tag{4-14}$$

Therefore, the interface stiffness  $\tilde{\gamma}(\theta)$  anisotropy is an order of magnitude larger than that of interface free energy  $\gamma(\theta)$  and is much easier to compute accurately by MD simulations.

Another way to represent anisotropy of  $\gamma$  is to express it as a function of the normal direction unit vector  $\underline{n} = n_1(1,0,0) + n_2(0,1,0) + n_3(0,0,1)$ , where  $\{n_1,n_2,n_3\}$  are Cartesian components of the unit vector  $\underline{n}$  normal to the interface plane. For example, to the second order  $\gamma(\underline{n})$  may be expanded as<sup>[4]</sup>

$$\gamma(\underline{n}) = \gamma_0 \left( 1 + \varepsilon_1 \left( \sum_i n_i^4 - \frac{3}{5} \right) + \varepsilon_2 \left( 3 \sum_i n_i^4 + 66n_1^2 n_2^2 n_3^2 - \frac{17}{7} \right) \right)$$
(4-15)

, where  $\varepsilon_1$  and  $\varepsilon_2$  are two anisotropic parameters and  $\gamma_0$  is the orientation averaged free energy.

In the case of (100) interface with  $(n_1 = 1, n_2 = 0, n_3 = 0)$ , we have

$$\gamma(100) = \gamma_0 \left( 1 + \frac{2}{5}\varepsilon_1 + \frac{4}{7}\varepsilon_2 \right)$$
(4-16)

In the case of (110) interface with  $(n_1 = 1/\sqrt{2}, n_2 = 1/\sqrt{2}, n_3 = 0)$ , we have

$$\gamma(110) = \gamma_0 \left( 1 - \frac{1}{10} \varepsilon_1 - \frac{13}{14} \varepsilon_2 \right)$$
(4-17)

In the case of (111) interface with  $(n_1 = 1/\sqrt{3}, n_2 = 1/\sqrt{3}, n_3 = 1/\sqrt{3})$ , we have

$$\gamma(111) = \gamma_0 \left( 1 - \frac{4}{15} \varepsilon_1 + \frac{64}{63} \varepsilon_2 \right)$$
(4-18)

If  $\underline{n}$  is measured around [001] axis such as interface (100) in this work, then  $\underline{n} = (\cos\theta, \sin\theta, 0)$ . By substituting  $(n_1 = \cos\theta, n_2 = \sin\theta, n_3 = 0)$  into Eqn. (4-15) we can express  $\gamma$  as a function of  $\theta$ :

$$\gamma(\theta) = \gamma_0 \left( 1 + \varepsilon_1 \left( \cos^4 \theta + \sin^4 \theta - \frac{3}{5} \right) + \varepsilon_2 \left( 3 \left( \cos^4 \theta + \sin^4 \theta \right) - \frac{17}{7} \right) \right)$$
(4-19)

Using Eqn. (4-12) we can also derive  $\tilde{\gamma}$  as a function of  $\theta$ :

$$\widetilde{\gamma}(\theta) = \gamma_0 \left( 1 - 3(\varepsilon_1 + 3\varepsilon_2) \left( \cos^4 \theta - 8\cos^2 \theta \sin^2 \theta + \sin^4 \theta \right) - \frac{3}{5}\varepsilon_1 - \frac{17}{7}\varepsilon_2 \right) \quad (4-20)$$

Or we can express  $\tilde{\gamma}$  as a function of <u>n</u>:

$$\widetilde{\gamma}(\underline{n}) = \gamma_0 \left( 1 - 3(\varepsilon_1 + 3\varepsilon_2) \left( \sum_i n_i^4 - 8n_1^2 n_2^2 \right) - \frac{3}{5} \varepsilon_1 - \frac{17}{7} \varepsilon_2 \right)$$
(4-21)

In the case of (100) interface with  $(n_1 = 1, n_2 = 0, n_3 = 0)$  measured around short direction [001], we have

$$\widetilde{\gamma}(100) = \gamma_0 \left( 1 - \frac{18}{5} \varepsilon_1 - \frac{80}{7} \varepsilon_2 \right)$$
(4-22)

For  $\underline{n}$  measured around [1-10] axis such as interface (110) and (111) in this work,

$$\underline{n} = \left(\frac{\cos\theta}{\sqrt{2}}, \frac{\cos\theta}{\sqrt{2}}, \sin\theta\right). \text{ By substituting } \left(n_1 = \frac{\cos\theta}{\sqrt{2}}, n_2 = \frac{\cos\theta}{\sqrt{2}}, n_3 = \sin\theta\right) \text{ into Eqn.}$$

(4-15) we can express  $\gamma$  as a function of  $\theta$ :

$$\gamma(\theta) = \gamma_0 \left( 1 + \left(\varepsilon_1 + 3\varepsilon_2\right) \left(\frac{1}{2}\cos^4\theta + \sin^4\theta\right) - \frac{3}{5}\varepsilon_1 + \varepsilon_2 \left(\frac{33}{2}\cos^4\theta\sin^2\theta - \frac{17}{7}\right) \right)$$
(4-23)

Using Eqn. (4-12) we can also derive  $\tilde{\gamma}$  as a function of  $\theta$ :

$$\widetilde{\gamma}(\theta) = \gamma_0 \begin{pmatrix} 1 + (\varepsilon_1 + 3\varepsilon_2) \left( -\frac{3}{2} \cos^4 \theta + 18 \cos^2 \theta \sin^2 \theta - 3 \sin^4 \theta \right) - \frac{3}{5} \varepsilon_1 \\ + \frac{33}{2} \varepsilon_2 \left( 2 \cos^6 \theta - 21 \cos^4 \theta \sin^2 \theta + 12 \cos^2 \theta \sin^4 \theta \right) - \frac{17}{7} \varepsilon_2 \end{pmatrix}$$
(4-24)

In the case of (110) interface with  $(n_1 = 1/\sqrt{2}, n_2 = 1/\sqrt{2}, n_3 = 0)$  or  $(\sin \theta = 0, \cos \theta = 1)$ measured around short direction [1-10], we have

$$\widetilde{\gamma}(110) = \gamma_0 \left( 1 - \frac{21}{10} \varepsilon_1 + \frac{365}{14} \varepsilon_2 \right)$$
(4-25)

In the case of (111) interface with  $(n_1 = 1/\sqrt{3}, n_2 = 1/\sqrt{3}, n_3 = 1/\sqrt{3})$  or  $(\sin \theta = 1/\sqrt{3}, \cos \theta = \sqrt{2}/\sqrt{3},)$  measured around short direction [1-10], we have

$$\widetilde{\gamma}(111) = \gamma_0 \left( 1 + \frac{12}{5}\varepsilon_1 - \frac{1280}{63}\varepsilon_2 \right)$$
(4-26)

Summary of  $\tilde{\gamma}$  and  $\gamma$  expressed in terms of  $\gamma_0$ ,  $\varepsilon_1$  and  $\varepsilon_2$  is shown in Table 4-1.

Interface	Short direction	Interfacial free energy	Interfacial stiffness
100	001	$\gamma_0 \left( 1 + \frac{2}{5} \varepsilon_1 + \frac{4}{7} \varepsilon_2 \right)$	$\gamma_0 \left( 1 - \frac{18}{5} \varepsilon_1 - \frac{80}{7} \varepsilon_2 \right)$
110	1-10	$\gamma_0 \left( 1 - \frac{1}{10} \varepsilon_1 - \frac{13}{14} \varepsilon_2 \right)$	$\gamma_0 \left( 1 - \frac{21}{10} \varepsilon_1 + \frac{365}{14} \varepsilon_2 \right)$
111	1-10	$\gamma_0 \left( 1 - \frac{4}{15} \varepsilon_1 + \frac{64}{63} \varepsilon_2 \right)$	$\gamma_0 \left( 1 + \frac{12}{5} \varepsilon_1 - \frac{1280}{63} \varepsilon_2 \right)$

Table 4-1 Summary of interfaces simulated including the short direction

The number of independent stiffness measurements to determine  $\gamma$  depends on the order of the expansion. For the lowest order, two orientation stiffness measurements are enough to obtain the two parameters  $\gamma_0$  and  $\varepsilon$ . Usually  $\gamma$  is expanded up to the second order. In this case at least three orientation stiffness measurements are required to get the three parameters  $\gamma_0$ ,  $\varepsilon_1$ , and  $\varepsilon_2$ . However, four or more orientation stiffness

measurements are recommended to get a better fit of  $\gamma_0$ ,  $\varepsilon_1$ , and  $\varepsilon_2$ .

Now the question we have is how to calculate the interfacial stiffness  $\tilde{\gamma}$  for a certain interface orientation, which is the key issue of fluctuation method. The answer is implicated in the name of this method, fluctuation. The fluctuation of interface height can be used to determine  $\tilde{\gamma}$ .

The success of this method depends on the fact that the solid-liquid interface at the melting point is usually rough instead of faceted. Note that the fluctuation method can not be applied if the interface obtained is faceted.

In order to obtain a rough interface in MD simulation, special shape of the simulation box is required. We need to set the cross section of the interface as a special rectangle (one very long direction and one very short direction) in the fluctuation method in order to generate rough ribbon-like interfaces with large fluctuations of the interface height

because the mean square height of the interface scales proportionally to the length of long direction L if the cross section of the interface is a rectangle while it only scales as  $\ln L$  if the cross section of the interface is a square<sup>[1]</sup>. A typical simulation box for use with fluctuation method is a rectangular box with an extremely long y axis with length  $L_y$  and an extremely short x axis (short direction) with length  $L_x$ . The xy plane is parallel to the investigated interface. The z axis with length  $L_z$  which is normal to the interface should also be chosen long enough ( $L_z=1\sim 2L_y$ ) to avoid entropic interactions between two interfaces generated due to PBC. Usually  $L_x$  is chosen not much more than twice the major interaction range of the potential function.  $L_y \approx 10L_x$ ,  $L_z \approx 2L_y$ . This requirement usually means the system size of MD simulation will be very large for use with the fluctuation method.

In order to calculate interface height, we need to determine which atoms are liquid atoms, solid atoms or interface atoms. To do so, we need to calculate a local order parameter for each atom. For this, we choose a set of  $N_k$  wave vectors (reciprocal space vectors)  $\underline{k_i}$  such that  $\exp(i\underline{k_i} \cdot \underline{r_i}) = 1$  for any real space vector  $\underline{r_i}$  connecting nearest neighbors in a perfect fcc lattice. For fcc lattice each atom has 12 nearest neighbors. We omit one of each pair of antiparallel wave vectors such that  $N_k = 6$ . Then the local order parameter  $\psi_i$  for an atom *i* can be defined as<sup>[2]</sup>:

$$\psi_{i} = \left| \frac{1}{N_{k}} \frac{1}{Z} \sum_{j=1}^{Z} \sum_{m=1}^{N_{k}} \exp\left(i\underline{k}_{m} \cdot \underline{r}_{j}\right)^{2} = \left| \frac{1}{6} \frac{1}{Z} \sum_{j=1}^{Z} \sum_{m=1}^{6} \exp\left(i\underline{k}_{m} \cdot \underline{r}_{j}\right)^{2} \right|$$
(4-27)

, where the sum on  $r_j$  runs over each of Z neighbors found within a distance  $r_c$  of atom *i*.  $r_c$  is chosen to be between the first- and second-neighbor shells in the perfect fcc lattice. Usually an average local order parameter is used to determine interface atoms<sup>[2]</sup>.

$$\overline{\psi_i} = \frac{1}{Z+1} \left( \psi_i + \sum_{j=1}^Z \psi_j \right)$$
(4-28)

Under this definition, the typical order parameter for a solid atom is >0.1(1 for perfect lattice atom), the typical order parameter for a liquid atom is <0.05, and the typical order parameter for an interface atom is in the range  $0.05\sim0.1$ .

For a macroscopically flat interface, the interface height can be defined as the deviation of z coordinate of each interface atom from the average z coordinate of all interface atoms. The interface plane (xy plane) can be divided into grids with grid points separated by  $\Delta x$  and  $\Delta y$ . Each interface atom can be sorted into a certain grid (i,j) with

height  $h_{ii}$ .

,

Then Fourier Transform of  $h_{ij}$  can be defined as<sup>[2]</sup>:

$$h(\underline{k}) = \frac{\Delta x \Delta y}{\sqrt{L_x L_y}} \sum_{ij} h_{ij} \exp\left(i\underline{k} \cdot \underline{r_{ij}}\right)$$
(4-29)

where 
$$\underline{k} = 2\pi \left(\frac{k_x}{L_x}, \frac{k_y}{L_y}\right), \quad k_x, k_y = 0, \pm 1, \pm 2, \dots$$
 for a rectangular plane.

 $\underline{r_{ij}} = i\Delta x \cdot \underline{x} + j\Delta y \cdot \underline{y}$ ,  $\underline{x}$  and  $\underline{y}$  are unit vectors along x and y axis, respectively. If  $L_y >> L_x$ , then we have

$$\left\langle \left| h(\underline{k}) \right|^2 \right\rangle = \frac{k_B T}{\tilde{\gamma} k^2}$$
 (4-30)

, where 
$$k = |\underline{k}|, |h(\underline{k})|^2 = h(\underline{k})h(-\underline{k}), \ h(-\underline{k}) = \frac{\Delta x \Delta y}{\sqrt{L_x L_y}} \sum_{ij} h_{ij} \exp\left(-i\underline{k} \cdot \underline{r_{ij}}\right)$$

If we plot  $\ln \langle |h(\underline{k})|^2 \rangle$  against  $\ln k$ , we can obtain a straight line with the slope -2 and the intercept  $\ln \frac{k_B T}{\widetilde{\gamma}}$ , hence the interface stiffness  $\widetilde{\gamma}$ .

## 4.3 Simulation details

#### 4.3.1 Cleaving wall method

Ewald sum is used to deal with long range dipole-dipole interactions for use with cleaving wall method. The detailed implementation of Ewald sum can be found in section 1.2.3.6 of Chapter 1.

Given the freezing temperature and solid-liquid equilibrium densities for  $\mu^* = 1, \sqrt{2}, \sqrt{3}$  at P = 0 from the coexistence solid-liquid approach in Chapter 2, we

state point for  $\mu^* = 1$  $T = 0.656 \ \rho_s = 0.980 \ \rho_l = 0.869$  as the selected point for  $\mu^* = \sqrt{2}$  $T = 0.726 \ \rho_s = 1.009 \ \rho_l = 0.887$  as the state  $T = 0.835 \ \rho_s = 1.039 \ \rho_l = 0.923$  as the state point for  $\mu^* = \sqrt{3}$ . The cleaving wall method is performed in the NVT ensemble. The remaining simulation parameters are the same as those used in the coexistence solid-liquid simulations in Chapter 2. To prepare the liquid system for step 2, we removed a certain number of particles at random from solid system obtained at the end of step 1 to reduce density from  $\rho_c$  to  $\rho_1$  and melt them at a high temperature (T=4.00). The resulting liquid system was cooled down to  $T_m$ . For step 3 and 4, the maximum reciprocal lattice vector  $k_z$  is doubled after the merge of solid and liquid system because the same Ewald-sum convergence parameter  $\alpha$  was used in all four steps. The cleaving wall is constructed using the same strategy used for a LJ system<sup>[7]</sup>. The initial position of cleaving wall  $z_i$  is always set to 1.2 for all three interface orientations while the final position of cleaving wall  $z_f$  is chosen to be 0.62, 0.50 and 0.56 for (111), (110) and (100), respectively, to assure that no particles will cross the cleaving plane at the end of cleaving process. In step 1 and 2 the cleaving wall position zis varied from the initial  $z_i$  to final  $z_f$  with a typical increment of 0.02. In step 3 the parameter  $\lambda$  is varied from 0 to 1 with different length of increments. In step 4 z is increased from  $z_f$  to  $z_i$  with a typical increment of 0.01. At each z or  $\lambda$  an equilibration run of 20000 steps was followed by 30000 steps used to calculate average  $\partial \phi / \partial z$  or  $\partial U / \partial \lambda$ . The thermodynamic integrations Eqn. (4-7) and Eqn. (4-9) are calculated using the trapezoidal rule. All error bars are calculated using the block average technique<sup>[36]</sup>.

#### 4.3.2 Fluctuation method

The melting points were computed again with the switching function being used to treat the long-range dipole-dipole interaction since the system size is very large. The detailed implementation of switching function can be found in section 1.2.3.6 of Chapter 1. We followed the same procedure used in Morris and Song's work<sup>[4]</sup> to generate MD trajectories required for the fluctuation method. To create a rough interface, one direction of the simulation box is made extremely short. Three interfaces (100), (110) and (111) with respective short directions [001], [1-10] and [1-10] are investigated. For each interface three different dipolar strengths  $\mu^* = 1, \sqrt{2}, \sqrt{3}$  are considered. Therefore, nine independent simulations were performed. Here, the x axis was set as the short direction, yaxis was the corresponding long direction, and z axis was the direction normal to the interface. The corresponding geometries are summarized in Table 4-2. The initial solid structure was created based on the respective ideal crystal lattice with the initial density determined from previous melting point calculations. Then the solid structure was relaxed under NPT ensemble for 50000 MD steps to prepare the pure solid phase at P=0. Next, the prepared solid was melted at a high temperature and cooled to reach the freezing temperature in the NVT ensemble for 50000 MD steps. Subsequently, the liquid was relaxed in the  $NP_zT$  ensemble for another 50000 MD steps to obtain the pure liquid at  $P_z$ = 0. In this way the prepared pure solid phase and pure liquid phase contain the same number of particles with identical cross sections. Thereafter, the solid and liquid was joined together to create two solid-liquid interfaces, each with an initial gap of 0.5 to prevent overlap of solid and liquid particles. Then the merged system was briefly equilibrated under  $NP_zT$  ensemble for another 50000 MD steps to relax the system at the melting point and  $P_z=0$ . Finally the merged system was again equilibrated for 600000

MD steps under *NVE* ensemble, after which the production run was continued for two million MD steps for data collection. During the production runs, coordinates of all particles were stored every 1000 steps. In order to remove the high frequency interface height fluctuation, the coordinates were averaged every 200 steps to smooth the trajectory, which is important for accurate calculation of interfacial stiffness<sup>[4]</sup>. Additional analysis was undertaken in the 9 trajectory files. First, the local order parameter was calculated for each particle in order to find interface particles. To do so six wave vectors are selected

$$\underline{k_1} = \left(\frac{\sqrt{2}}{2}, \frac{\sqrt{2}}{2}, 0\right) , \quad \underline{k_2} = \left(\frac{\sqrt{2}}{2}, 0, \frac{\sqrt{2}}{2}\right) , \quad \underline{k_3} = \left(\frac{\sqrt{2}}{2}, -\frac{\sqrt{2}}{2}, 0\right) , \quad \underline{k_4} = \left(\frac{\sqrt{2}}{2}, 0, -\frac{\sqrt{2}}{2}\right) ,$$
$$\underline{k_5} = \left(0, -\frac{\sqrt{2}}{2}, -\frac{\sqrt{2}}{2}\right), \\ \underline{k_6} = \left(0, \frac{\sqrt{2}}{2}, -\frac{\sqrt{2}}{2}\right), \text{ for (100) interface. The cutoff distance } r_c \text{ to }$$

find neighbors of a particle is chosen to be 0.825  $a_0$  within  $\frac{\sqrt{2}}{2}a_0 \sim a_0$ . The interfacial particles have intermediate values (0.05~0.1) of the local order parameter and can be utilized to calculate the interface height. The interface plane (xy plane) is divided into 1×16 grids. For each frame of the trajectory we can calculate  $|h(\underline{k})|^2 = h(\underline{k})h(-\underline{k})$  as a function of k. The ensemble average  $\langle |h(\underline{k})|^2 \rangle$  can be obtained by averaging all frames of the trajectory. The interface stiffness  $\tilde{\gamma}$  can be obtained from the intercept  $\ln \frac{k_B T}{\tilde{\gamma}}$  in the plot  $\ln \langle |h(\underline{k})|^2 \rangle$  vs.  $\ln k$ .

Interface	Short direction	Geometry	Number of particles
100	001	6.419×51.349×68.875	20480
110	1-10	6.811×38.527×87.685	20736
111	1-10	6.810×58.976×59.642	21600
	1.5.1		

Table 4-2 Summary of simulation geometry

#### **4.4 Results and Discussion**

#### 4.4.1 Cleaving wall method

Using the cleaving-wall method together with the Ewald sum technique, we computed  $\gamma$  of (111), (110) and (100) interfaces for  $\mu^* = 1$ ,  $\sqrt{2}$ ,  $\sqrt{3}$ , respectively (See Table 4-3). Take (100) interface as an example, typical integrands for thermodynamic integration in steps 1, 2, 3 and 4 are shown in Fig. 4-1. Orientation averaged  $\gamma$  for  $\mu^* = 1$ ,  $\sqrt{2}$ ,  $\sqrt{3}$  are estimated to be  $0.348\pm0.002$ ,  $0.412\pm0.003$  and  $0.476\pm0.005$ , respectively. Similar to the trend of melting point, the interfacial free energy  $\gamma$  also increases with the dipolar strength. Except  $\mu^* = 1$ , an obvious anisotropy in  $\gamma$  can be seen, that is,  $\gamma_{100} > \gamma_{110} > \gamma_{111}$ . This anisotropy becomes stronger with the increase of dipolar strength. It is interesting to compare the relative strong anisotropy for the SM fluids to the weak anisotropy for the nonpolar LJ fluid<sup>[7]</sup>.

In Fig. 4, some hysteresis in step 2 and 4 can be observed. This may be due to our particular choice of the cleaving potential as used to cleave LJ system<sup>[7]</sup>. Here, the particles on the wall were treated as LJ particles without adding any dipole moment. Although this simple cleaving potential was strong enough to prevent particles from crossing the cleaving plane at the end of step 1 and step 2, it may be more sensible to have the cleaving wall constructed out of the same type of particles as in the system<sup>[7]</sup>. Further investigation is necessary to resolve this hysteresis issue.

Table 4-3



#### 4.4.2 Fluctuation method

Due to the large system size required by the fluctuation method, the long range dipole-dipole interaction was treated with a simple switching function. With this change the newly obtained melting points are 0.665(2), 0.734(3) and 0.842(3), respectively, for  $\mu^* = 1, \sqrt{2}, \sqrt{3}$ . After nine independent trajectories were generated, further post-simulation analysis was performed. Plots of  $\ln \langle |h(\underline{k})|^2 \rangle$  vs.  $\ln k$  for  $\mu^* = 1, \sqrt{2}, \sqrt{3}$  are shown in Fig. 4-2 (a-c), respectively. By linear regression the obtained interface stiffness and fitted interfacial free energy for  $\mu^* = 1, \sqrt{2}, \sqrt{3}$  are shown in Table 4-4, Table 4-5 and Table 4-6, respectively. The fitting process was based on the relation between  $\tilde{\gamma}$  and  $\gamma$  as shown in Table 4-1. Compared to the results obtained from cleaving wall method, a major difference is that the interfacial fluctuation method suggests a smaller anisotropic effect on different interface orientations, particularly for larger dipole moment. Nevertheless, the trend of anisotropy is the same as that predicted from the cleaving-wall method, i.e.  $\gamma_{100} > \gamma_{110} > \gamma_{111}$ , except for  $\mu^* = \sqrt{3}$  with which  $\gamma_{100} \sim \gamma_{110}$  was predicted from the interfacial fluctuation method. In general, the interfacial free energy  $\gamma$  also increases with the dipolar strength. Overall, the fitted orientation averaged interfacial free energy  $\gamma_0$  is comparable to (or slightly smaller than) that from the cleaving-wall method.

Moreover, Turnbull<sup>[37]</sup> suggested that the interfacial free energy scale with the latent heat [specifically,  $\gamma = C_T L_h \rho_s^{-1/3}$ <sup>[2]</sup>, where  $C_T$  = Turnbull coefficient,  $L_h$  = latent heat/volume, and  $\rho_s$  = solid phase density (atoms/volume)]. The latent heat  $L_h$  can be obtained from the enthalpy change between the solid and liquid phase at the freezing point during our superheating-undercooling scan in Chapter 3, which are 1.11±0.03, 1.36±0.03 and 1.49±0.04, respectively, for  $\mu^* = 1$ ,  $\sqrt{2}$ ,  $\sqrt{3}$ . The increased latent heat with dipole strength also supports our conclusion that melting point increases with dipole strength: as  $\mu^*$  increases, the enthalpy difference between the solid and liquid phases increases. Assuming the corresponding entropy change due to the change in  $\mu^*$  is small, a higher melting temperature will be required to compensate for the additional change in enthalpy. Based on the equilibrium solid phase density and the orientation averaged  $\gamma$  obtained from the cleaving-wall method and the fluctuation method, the effective Turnbull coefficient can be estimated as  $0.31\pm0.01$  from the cleaving-wall method and  $0.29\pm0.02$  from the fluctuation method, which are very close to the Turnbull coefficient for water  $(0.32)^{[37]}$  and in contrast with typical value 0.45 for most metals<sup>[37]</sup>. Therefore, our results not only support Turnbull's conclusion but also indicate that SM model is a reasonable model to describe some common properties of polar fluids such as water.



Solid line represents original data while dash line denotes fitted straight line.

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Interface	Short direction	Interfacial free energy	Interfacial stiffness	
100	001	0.340(5)	0.283(3)	
110	1-10	0.333(5)	0.213(7)	
111	1-10	0.324(5)	0.443(4)	

, where fitting parameters are  $\varepsilon_{\rm 1}=0.0678$  ,  $\varepsilon_{\rm 2}=-0.00825$  and  $\gamma_{\rm 0}=0.333$ 

Interface	Short direction	Interfacial free energy	Interfacial stiffness
100	001	0.385(3)	0.306(2)
110	1-10	0.375(3)	0.243(4)
111	1-10	0.365(3)	0.497(2)
1 0	• •	0.0741 0.0073	4 1 0.075

Table 4-5  $\mu^* = \sqrt{2}$ 

, where fitting parameters are  $\varepsilon_1=0.0741$  ,  $\varepsilon_2=-0.00724$  and  $\gamma_0=0.375$ 

1able 4-6 $\mu = -$	Table	e 4-6	и <sup>®</sup>	=	$\sqrt{3}$
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Interface	Short direction	Interfacial free energy	Interfacial stiffness
100	001	0.461(4)	0.467(1)
110	1-10	0.462(4)	0.326(3)
111	1-10	0.452(4)	0.572(8)
1	<b>C</b>	0.0045 0.00010	1 0.450

, where fitting parameters are  $\varepsilon_1=0.0245$  ,  $\varepsilon_2=-0.00918$  and  $\gamma_0=0.459$ 

## **4.5 Conclusions**

#### 4.5.1 Cleaving wall method

The interfacial free energy of Stockmayer model with  $\mu^* = 1, \sqrt{2}, \sqrt{3}$  for (111), (110) and (100) interface orientations has been calculated by the cleaving wall method with Ewald sum to deal with long range dipole-dipole interactions. In general,  $\gamma_{sl}$  increases with dipolar strength and the anisotropy is also enhanced at higher dipole moment.

#### 4.5.2 Fluctuation method

The interfacial free energy of Stockmayer model with  $\mu^* = 1, \sqrt{2}, \sqrt{3}$  for (111), (110) and (100) interface orientations has been calculated by the fluctuation method with a simple switching function to deal with long range dipole-dipole interactions. In general, results are consistent with those obtained from the cleaving wall method. The major difference is that fluctuation method tends to give a smaller anisotropic effect, which may

be due to indirect measurement of interfacial free energy. Overall, both methods are

effective for determining the anisotropic effect. The trend of anisotropy predicted by the

fluctuation method is similar to that resulting from the cleaving wall method, namely

 $\gamma_{100} > \gamma_{110} > \gamma_{111} \,.$ 

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## Chapter 5 Calculation of liquid-vapor Surface Tension for LJ model and SPC/E water model

## **5.1 Introduction**

In previous two chapters we discussed several methods to calculate liquid-solid interfacial free energy  $\gamma_{st}$ . Actually another important interface, namely liquid-vapor interface, has also been the subject of computer simulation for a long time. A detailed understanding of liquid-vapor interface is crucial to many technological processes, such as adsorption, separation. The liquid-vapor interfacial free energy  $\gamma_{hv}$ , also called surface tension, is one of the most important interfacial properties. In thermodynamics, the surface tension is defined as the work to create a unit surface area. It is the liquid-vapor surface tension that accounts for the spherical shape of a stand-alone liquid drop since the spherical shape has the smallest ratio of surface area to volume. For the same reason the liquid surface in a capillary tube usually exhibits a curved shape to minimize the surface area.

A statistical mechanics definition of the surface tension was introduced by Kirkwood and Buff<sup>[1]</sup> in 1949. This definition states that the surface tension can be determined by the difference between the pressure normal to the interface and that parallel to the interface (KB method). The KB definition laid the foundation for later widely used mechanical approach for computing the surface tension. A year later, Irving and Kirkwood<sup>[2]</sup> proposed another method to compute the surface tension, which is based on the local profile of pressure components that are normal and parallel to the interface

(IK method). A major advantage of the IK method is that only in the interfacial region the difference between pressure component normal and parallel to the interface is non-zero, while the difference is zero in the bulk liquid and vapor region. For the definition involving local pressure, a controversy arose after Hasasima<sup>[3]</sup> introduced a different definition (the H method) in 1958. A major difference between the IK and H definitions is the expression for the pressure component parallel to the interface<sup>[4]</sup>. Nevertheless, both definitions lead to the same expression for the surface tension (KB formula<sup>[1]</sup>) with integration over the direction normal to the interface. However, the so-called surface of tension (the position where the surface tension acts) is still dependent on the definition of local pressure<sup>[4]</sup>. Both IK and H methods have been used to compute the surface tension, for which the IK method has been mostly used for systems described by pairwise-additive potential whereas the H method has been used for systems with non-pairwise additive (e.g. the reciprocal-space part of Ewald sum<sup>[5]</sup>).

Overall, the LJ fluid and water are the two mostly studied systems and are commonly viewed as the benchmark systems for developing and testing new simulation methods.

Thus far, more than 30 papers have been published on computation of liquidvapor interfacial tension of the LJ fluid. In summary, with a special long range correction (LRC) technique<sup>[6-11]</sup> or using a very large cutoff distance<sup>[12]</sup>, similar surface tension results<sup>[6-15]</sup>  $\gamma = 1.1,0.85,0.6,0.45,0.3$  for the approximate non-truncated LJ were obtained at T=0.7,0.8,0.9,1.0,1.1, respectively. In addition, similar surface tension results<sup>[13,16-23]</sup>  $\gamma = 0.58,0.40,0.23,0.08$  for the truncated LJ subjected to a cutoff of 2.5 were also obtained at T=0.7,0.8,0.9,1.0, respectively. In general, an increase of the cutoff distance will cause increased surface tension and decreased vapor density.

Surface tensions of water have also been subjected to intensive studies over the past three decades. Summarizing, previously predicted good match between calculated  $\gamma$  values and experimental values with the SPC/E-FA model, as shown in Ref. [5], may not be sufficiently accurate due to inadequate simulation time<sup>[24]</sup>. Correct  $\gamma$  values with the SPC/E model have been reported as  $\gamma = 61$ , 58, and 53 *m*N/m at 300, 325 and 350 K, respectively<sup>[25-29]</sup>. The best water model to reproduce experimental values appears to be the TIP4P-2005<sup>[25]</sup>. The calculated  $\gamma$  values based on TIP4P-2005 are  $\gamma = 71$ , 67, 52, and 31 *m*N/m at 300, 328, 400 and 500 K, respectively<sup>[25,30,31]</sup>.

In this chapter, we present our results of  $\gamma_{l\nu}$  for LJ fluid and SPC/E water model using both KB and IK methods. Although the two benchmark models have been investigated by many researchers, the obtained  $\gamma_{l\nu}$  values were scattered because many factors can affect calculated  $\gamma_{l\nu}$ . Another main goal of this chapter is to summarize previously reported surface tension values and to examine effects of simulation ensemble, box dimension, particle number, method of pressure calculation (atomic pressure. vs. molecular pressure) on the calculated surface tension.

#### **5.2 Computational Methods**

#### 5.2.1 Kirkwood-Buff (KB) method

In computer simulation of a liquid-vapor interface, typically, a system is set up<sup>[32]</sup> such that a liquid film is sandwiched between two vapor phases in a rectangular box as shown in Fig. 5-1. With the KB method, the surface tension  $\gamma$  can be calculated using the following formula:

$$\gamma = \left\langle \frac{L_z}{2} \left( P_N - P_T \right) \right\rangle \tag{5-1}$$

, where  $L_z$  is the length of simulation box in the direction normal to the interface (z axis).  $P_N = P_{zz}$  is the pressure normal to the interface while  $P_T = \frac{1}{2} (P_{xx} + P_{yy})$  is the pressure parallel to the interface which is also called tangential component or transverse component of pressure.  $P_{xx}$ ,  $P_{yy}$ ,  $P_{zz}$  are instantaneous diagonal elements of the pressure tensor. The bracket  $\langle \rangle$  means an ensemble average. The factor 1/2 in Eqn. (5-1) stems from the presence of two interfaces in our simulation setup. In a constant-volume ensemble (*NVT* or *NVE*) with liquid-vapor coexistence, Eqn. (5-1) can be simplified as:

$$\gamma = \frac{L_z}{2} \left( \left\langle P_{zz} \right\rangle - \frac{1}{2} \left( \left\langle P_{xx} \right\rangle + \left\langle P_{yy} \right\rangle \right) \right)$$
(5-2)



Fig. 5-1 Schematic illustration of the system used to simulate liquid-vapor coexistence<sup>[32]</sup>

For molecular fluids such as water there are two different representations of the pressure tensor, namely atomic pressure tensor and molecular pressure tensor.

In the case of pair-additive potential, the element  $\alpha\beta$  of atomic pressure tensor can be written as:

$$P_{\alpha\beta} = \frac{1}{vol} \left( \sum_{i} \sum_{a} m_{ia} v_{ia,\alpha} v_{ia,\beta} + \sum_{i} \sum_{j>i} \sum_{a} \sum_{b} r_{iajb,\alpha} f_{iajb,\beta} + \sum_{i} \sum_{a} \sum_{b>a} r_{iaib,\alpha} f_{iaib,\beta} \right)$$
(5-3)

, where  $m_{ia}$  and  $v_{ia}$  are mass and velocity of atom *a* in molecule *i*. *vol* is the system volume.  $r_{iajb}$  is the distance between atom *a* in molecule *i* and atom *b* in molecule *j*.  $r_{iaib}$  is the distance between atom *a* in molecule *i* and atom *b* in the same molecule.  $f_{iajb}$  is the intermolecular force due to LJ potential.  $f_{iaib}$  is the intramolecular force due to constraints from intramolecular potentials (bond, angle, dihedral, etc.) or SHAKE algorithm. The first term is the contribution to the pressure tensor from kinetic energy. The second term is from intermolecular interactions while the third term is from intramolecular interactions.

In the case of pair-additive potential, the element  $\alpha\beta$  of molecular pressure tensor can be expressed as:

$$P_{\alpha\beta} = \frac{\sum_{i} m_{i} v_{i,\alpha} v_{i,\beta} + \sum_{i} \sum_{j>i} r_{ij,\alpha} f_{ij,\beta}}{vol} = \frac{\sum_{i} m_{i} v_{i,\alpha} v_{i,\beta} + \sum_{i} \sum_{j>i} \sum_{a} \sum_{b} r_{ij,\alpha} f_{iajb,\beta}}{vol}$$
(5-4)

, where  $m_i$  and  $v_i$  are molecular mass and center-of-mass velocity of molecule  $i \cdot r_{ij}$  is the distance between center-of-mass of molecule i and center-of-mass of molecule j. Eqn. (5-3) and Eqn. (5-4) are completely equivalent due to the equalities

$$\sum_{i}\sum_{a}m_{ia}v_{ia,\alpha}v_{ia,\beta} = \sum_{i}m_{i}v_{i,\alpha}v_{i,\beta}$$
(5-5)

$$\sum_{i} \sum_{j>i} \sum_{a} \sum_{b} r_{ij,\alpha} f_{iajb,\beta} = \sum_{i} \sum_{j>i} \sum_{a} \sum_{b} r_{iajb,\alpha} f_{iajb,\beta} + \sum_{i} \sum_{a} \sum_{b>a} r_{iaib,\alpha} f_{iaib,\beta}$$
(5-6)

However, in the case of non-pair-additive potential such as calculation of reciprocal space contribution to pressure tensor from Coulomb (electrostatic) interactions by Ewald sum, the expression of atomic pressure tensor is slightly different from that of molecular pressure tensor.

The contribution to the pressure tensor from electrostatic interactions calculated by Ewald sum can be written in the same form:

$$P_{\alpha\beta} = P_{\alpha\beta}^{real} + P_{\alpha\beta}^{recip} - P_{\alpha\beta}^{self}$$
(5-7)

In terms of atomic pressure tensor:

$$P_{\alpha\beta}^{real} = \frac{1}{vol} \left( \sum_{i} \sum_{j>i} \sum_{a} \sum_{b} r_{iajb,\alpha} f_{iajb,\beta}^{real} + \sum_{i} \sum_{a} \sum_{b} r_{iaib,\alpha} f_{iaib,\beta} \right)$$
(5-8)

, where the intermolecular Coulomb pair force is  

$$f_{iajb,\beta}^{real} = \frac{q_{ia}q_{jb}}{4\pi\varepsilon_0 r_{iajb}^3} \left( erfc(\kappa r_{iajb}) + \frac{2\kappa r_{iajb}}{\sqrt{\pi}} e^{-\kappa^2 r_{iajb}^2} \right) r_{iajb,\beta}, \kappa \text{ is the convergence parameter in}$$

Ewald sum and erfc(x) is the complementary error function.  $f_{iaib}$  is the intramolecular constraint force from intramolecular potentials or SHAKE algorithm.

$$P_{\alpha\beta}^{recip} = \frac{1}{2vol^2\varepsilon_0} \sum_{\underline{h}\neq 0} Q(h)S(\underline{h})S(-\underline{h}) \left(\delta_{\alpha\beta} - 2\left(\frac{1}{4\kappa^2} + \frac{1}{h^2}\right)\underline{h}_{\alpha}\,\underline{h}_{\beta}\right)$$
(5-9)

, where 
$$Q(h) = \frac{e^{-h^2/4\kappa^2}}{h^2}$$
,  $S(\underline{h}) = \sum_i \sum_a q_{ia} e^{i\underline{h}\cdot\underline{r}_{ia}}$ ,  $S(-\underline{h}) = \sum_i \sum_a q_{ia} e^{-i\underline{h}\cdot\underline{r}_{ia}}$ ,  $\underline{h}$  is the

reciprocal space lattice vector and  $\delta_{\alpha\beta}$  is the Kronecker delta function.

$$P_{\alpha\beta}^{self} = \frac{1}{vol} \sum_{i} \sum_{a} \sum_{b>a} r_{iaib,\alpha} f_{iaib,\beta}^{self}$$
(5-10)

, where the correction force 
$$f_{iaib,\beta}^{self} = \frac{q_{ia}q_{ib}}{4\pi\varepsilon_0 r_{iaib}^3} \left( erf(\kappa r_{iaib}) - \frac{2\kappa r_{iaib}}{\sqrt{\pi}} e^{-\kappa^2 r_{iaib}^2} \right) r_{iaib,\beta}$$
 and  $erf(x)$ 

is the error function.

In the expression of molecular pressure tensor:

$$P_{\alpha\beta}^{real} = \frac{1}{vol} \sum_{i} \sum_{j>i} \sum_{a} \sum_{b} r_{ij,\alpha} f_{iajb,\beta}^{real}$$
(5-11)

 $P_{\alpha\beta}^{recip}$  is as same as Eqn. (5-9).

$$P_{\alpha\beta}^{self} = \frac{1}{vol} \sum_{i} \sum_{a} p_{ia,\beta} f_{ia,\alpha}^{recip}$$
(5-12)

, where  $p_{ia} = r_{ia} - r_i$  and  $f_{ia}^{recip} = -\frac{q_{ia}}{vol\varepsilon_0} \sum_{\underline{h}\neq 0} real(i \cdot e^{i\underline{h}\cdot r_{ia}}S(\underline{h}))Q(\underline{h})\underline{h}$  is the total reciprocal

force acting on atom *a* in molecule *i*. The function real(x) returns the real part of a complex number. Alternatively  $f_{ia}^{recip}$  can be written as  $-\frac{q_{ia}}{vol\varepsilon_0}\sum_{\underline{h}\neq 0}img\left(e^{-i\underline{h}\cdot r_{ia}}S(\underline{h})\right)Q(\underline{h})\underline{h}$ ,

where the function img(x) returns the imaginary part of a complex number.

Comparing Eqn. (5-11) with Eqn. (5-8) we can see that the contribution from real space in two representations is actually equivalent due to the equalities shown in Eqn. (5-6). Since  $P_{\alpha\beta}^{recip}$  is same in two different representations, so the major difference between the two representations is the  $P_{\alpha\beta}^{self}$  term. This term is actually inherited from the same intramolecular correction term  $\frac{1}{4\pi\varepsilon_0}\sum_{i}^{N}\sum_{a}\sum_{b>a}\frac{q_{ia}q_{ib}}{r_{iaib}}erf(\kappa_{iaib})$  in the total Coulomb interaction energy expression. However, it leads to two completely different expressions in atomic pressure tensor and molecular pressure tensor, one expressed in real space while the other expressed in the reciprocal space.

#### 5.2.2 Irving-Kirkwood (IK) method

In the case of simulation setup consisting of two interfaces, the surface tension  $\gamma$  can be calculated using the following formula based on the IK method.

$$\gamma = \frac{1}{2} \int_{-\infty}^{\infty} \left[ P_N(z) - P_T(z) \right] dz$$
(5-13)

Since the IK method involves the calculation of local normal pressure  $P_N(z)$  and local
tangential pressure  $P_T(z)$ , we need to divide the rectangular simulation box into many slabs along z axis and calculate the local pressure in each slab. However, there is no unique definition about the way how the contribution to the pressure from the interaction between atom *i* and atom *j* is distributed to each slab, which brings the famous ambiguity between Irving-Kirkwood's definition and Harasima's definition.

In the case of atomic system with pair-wise additive potential, the local normal and tangential pressure based on Irving-Kirkwood's definition can be written as:

$$P_{N}^{IK}(z) = \left\langle \rho(z) \right\rangle k_{B}T + \frac{1}{A\Delta z} \left\langle \sum_{i} \sum_{j>i} z_{ij} f_{ij,z} \frac{1}{N_{s}} \theta\left(\frac{z-z_{i}}{z_{ij}}\right) \theta\left(\frac{z_{j}-z}{z_{ij}}\right) \right\rangle$$
(5-14)

$$P_T^{IK}(z) = \langle \rho(z) \rangle k_B T + \frac{1}{A\Delta z} \left\langle \sum_i \sum_{j>i} \frac{x_{ij} f_{ij,x} + y_{ij} f_{ij,y}}{2} \frac{1}{N_s} \theta\left(\frac{z-z_i}{z_{ij}}\right) \theta\left(\frac{z_j-z}{z_{ij}}\right) \right\rangle \quad (5-15)$$

, where the unit step function  $\theta(x) = \begin{cases} 0, & x < 0 \\ 1, & x \ge 0 \end{cases}$  is introduced to evenly distribute the total contribution to the surface tension from i - j interaction into each slab which contains the line connecting atom *i* and atom *j*. Periodic boundary condition in *z* direction should be considered when choosing  $N_s$  slabs "between" atom *i* and atom *j*.  $\Delta z$  is the width of each slab.

In the case of atomic system with pair-wise additive potential, the local normal and tangential pressure based on Harasima's definition can be written as:

$$P_N^H(z) = P_N^{IK}(z) \tag{5-16}$$

$$P_T^H(z) = \left\langle \rho(z) \right\rangle k_B T + \frac{1}{A\Delta z} \left\langle \sum_i \sum_{j>i} \frac{x_{ij} f_{ij,x} + y_{ij} f_{ij,y}}{2} \delta(z_i - z) \right\rangle$$
(5-17)

, where the Kronecker delta function  $\delta(x)$  is introduced to distribute the total

contribution to the surface tension from i - j interaction into the slab which contains atom i.

In the case of molecular system with pair-wise additive potential, the local normal and tangential pressure based on Irving-Kirkwood's definition can be written as:

$$P_{N}^{IK}(z) = \langle \rho(z) \rangle k_{B}T + \frac{1}{A\Delta z} \left\langle \sum_{i} \sum_{j>i} \sum_{a} \sum_{b>a} z_{ij} f_{iajb,z} \frac{1}{N_{s}} \theta\left(\frac{z-z_{i}}{z_{ij}}\right) \theta\left(\frac{z_{j}-z}{z_{ij}}\right) \right\rangle \quad (5-18)$$

$$P_{T}^{IK}(z) = \langle \rho(z) \rangle k_{B}T + \frac{1}{A\Delta z} \left\langle \sum_{i} \sum_{j>i} \sum_{a} \sum_{b} \frac{x_{ij} f_{iajb,x} + y_{ij} f_{iajb,y}}{2} \frac{1}{N_{s}} \theta\left(\frac{z-z_{i}}{z_{ij}}\right) \theta\left(\frac{z_{j}-z}{z_{ij}}\right) \right\rangle$$
(5-19)

, where  $f_{iajb,x}$ ,  $f_{iajb,y}$ ,  $f_{iajb,z}$  are x, y and z component, respectively, of the pair force between atom *a* in molecule *i* and atom *b* in molecule *j*.

In the case of water with Ewald sum, both the contribution to surface tension from LJ interaction and that from real space Coulomb interaction can be calculated using Eqn. (5-18) and Eqn. (5-19). However, the contribution from the reciprocal space Coulomb interaction is non-pair-wise additive, which can not be handled in a similar way. In 1995 Alejandre et al.<sup>[5]</sup> proposed a method to calculate such contribution based on Harasima's definition of local pressure tensor. As mentioned, the reciprocal space contribution to the pressure tensor in terms of molecular representation includes two terms  $P_{\alpha\beta}^{recip}$  and

$$P_{\alpha\beta}^{self} = \frac{1}{vol} \sum_{i} \sum_{a} p_{ia,\beta} f_{ia,\alpha}^{recip}$$
. Calculation of the contribution from the second term based

on Harasima's idea is relative easy since it is straightforward to decompose it upon each atom. Thus, the contribution to the local normal and tangential pressure from the second reciprocal space term can be written as:

$$P_{N}^{recip2}(z) = \frac{1}{A\Delta z} \left\langle \sum_{i} \sum_{a} p_{ia,z} \left( -f_{ia,z}^{recip} \right) \delta(z_{i} - z) \right\rangle$$
(5-20)

$$P_T^{recip2}(z) = \frac{1}{A\Delta z} \left\langle \sum_i \sum_a \frac{p_{ia,x}(-f_{ia,x}^{recip}) + p_{ia,y}(-f_{ia,y}^{recip})}{2} \delta(z_i - z) \right\rangle$$
(5-21)

However, the calculation of the contribution from the first term is not trivial. Alejandre et al.<sup>[5]</sup> used a simple strategy: To calculate the first term contribution as a function of z, the contribution to the surface tension of each molecule is the same for all molecules and is given by the component divided by the number of molecules. Based on this strategy, the contribution to the local normal and tangential pressure from the first reciprocal space term can be written as:

$$P_{N}^{recipl}(z) = \frac{1}{A\Delta z} \left\langle \sum_{i} \frac{P_{zz}^{recip} vol}{N_{mol}} \delta(z_{i} - z) \right\rangle$$
(5-22)

$$P_T^{recip1}(z) = \frac{1}{A\Delta z} \left\langle \sum_i \frac{P_{xx}^{recip} vol + P_{yy}^{recip} vol}{2N_{mol}} \delta(z_i - z) \right\rangle$$
(5-23)

, where  $\,N_{\rm mol}\,$  is the number of molecules in the system.

However, a serious problem occurs when applying the strategy used in Ref. [5]. Since the contribution to surface tension from each molecule is the same, so the surface tension contribution to each slab only depends on the number of molecules in each slab. Therefore, the generated profile  $P_N(z) - P_T(z)$  must have a similar shape as that of the density profile. In other words, the difference  $P_N(z) - P_T(z)$  does not fluctuate around zero in the bulk liquid region and vapor region, which does not make sense in physical meaning because the source of contribution to surface tension only comes from the interface region.

Recently (2008) Ghoufi *et al.*<sup>[30]</sup> proposed a new method to calculate the contribution to local pressure from the first reciprocal space term, which solved the problem in Ref. [5]. The idea of the new method is similar to that used for calculation of local pressure from the second reciprocal space term. That is to decompose the stress tensor  $\sigma_{\alpha\beta}^{recip} = P_{\alpha\beta}^{recip} vol$  upon each atom in order to use Harasima's definition. The key point is how to decompose it upon each atom. It is difficult to make a good decomposition if we write the stress tensor in the following form:

$$\sigma_{\alpha\beta}^{recip} = \frac{1}{2vol\varepsilon_0} \sum_{\underline{h}\neq 0} Q(h) |S(\underline{h})|^2 \left( \delta_{\alpha\beta} - 2\left(\frac{1}{4\kappa^2} + \frac{1}{h^2}\right) \underline{h}_{\alpha} \underline{h}_{\beta} \right)$$
(5-24)

Eqn. (5-24) is equivalent to Eqn. (5-9) due to the identity  $|S(\underline{h})|^2 = S(\underline{h})S(-\underline{h})$ . Eqn. (5-24) is the usual convenient form for us to calculate the contribution to the total stress tensor.

The only decomposable term in Eqn. (5-29) is  $|S(\underline{h})|^2 = \left|\sum_{i}\sum_{a}q_{ia}e^{i\underline{h}\cdot\underline{r}_{ia}}\right|^2$ . However, we

note that  $\left|\sum_{i}\sum_{a}q_{ia}e^{i\underline{h}\cdot\underline{r}_{ia}}\right|^{2} \neq \sum_{i}\sum_{a}\left|q_{ia}e^{i\underline{h}\cdot\underline{r}_{ia}}\right|^{2}$ . Therefore Eqn. (5-24) is not appropriate for

decomposition upon each atom.

On the contrary the Eqn. (5-9) is suitable for the decomposition because the decomposable term  $S(\underline{h})S(-\underline{h}) = S(\underline{h})\sum_{i}\sum_{a}q_{ia}e^{-i\underline{h}\cdot\underline{r}_{ia}} = \sum_{i}\sum_{a}S(\underline{h})q_{ia}e^{-i\underline{h}\cdot\underline{r}_{ia}}$ . Based on this

strategy the stress tensor for atom a in molecule i can be written as:

$$\sigma_{ia,\alpha\beta}^{recip} = \frac{1}{2vol\varepsilon_0} \sum_{\underline{h}\neq 0} Q(h) \left( \delta_{\alpha\beta} - 2\left(\frac{1}{4\kappa^2} + \frac{1}{h^2}\right) \underline{h}_{\alpha} \underline{h}_{\beta} \right) S(\underline{h}) q_{ia} e^{-i\underline{h}\cdot\underline{r}_{ia}}$$
(5-25)

Then the local stress tensor at z can be written as:

$$\sigma_{\alpha\beta}^{recip}(z) = \frac{\sum_{\underline{h}\neq 0} \mathcal{Q}(h) \left( \delta_{\alpha\beta} - 2 \left( \frac{1}{4\kappa^2} + \frac{1}{h^2} \right) \underline{h}_{\alpha} \underline{h}_{\beta} \right) S(\underline{h}) \sum_{i} \sum_{a} q_{ia} e^{-i\underline{h}\cdot\underline{r}_{ia}} \delta(z_i - z)}{2vol\varepsilon_0}$$
(5-26)

Finally the contribution to the local normal and tangential pressure from the first reciprocal space term can be written as:

$$P_{N}^{recip1}(z) = \frac{1}{A\Delta z} \left\langle \sigma_{zz}^{recip}(z) \right\rangle$$
(5-27)

$$P_T^{recipl}(z) = \frac{1}{A\Delta z} \left\langle \frac{\sigma_{xx}^{recip}(z) + \sigma_{yy}^{recip}(z)}{2} \right\rangle$$
(5-28)

Based on Eqn. (5-27) and Eqn. (5-28), the difference  $P_N^{recip1}(z) - P_T^{recip1}(z)$  will fluctuate around zero in the bulk liquid region and vapor region.

## **5.3 Simulation details**

### 5.3.1 LJ model

Our surface tension calculation source codes were based on the modification of dl\_poly\_2.15 MD simulation package. Since the DL\_POLY\_2.15 does not support LJ reduced units, we select a set of LJ parameters  $\varepsilon$  and  $\sigma$  as the basic energy and length unit for conversion between LJ reduced units and realistic units. Nevertheless, the calculation results are not dependent on the choice of LJ parameters and all final quantities presented are in the reduced units. For convenience, we select the LJ parameters used for describing LJ interactions between oxygen atoms in the SPC/E model water, namely,  $\varepsilon = 0.155406$  kcal/mol and  $\sigma = 3.165555$ Å. We only consider the reduced temperature  $T^* = 0.8$  in our simulation since many published simulation data are available at this temperature. The surface tension calculated in this study is based on a spherical cutoff  $r_c^* = 2.5$  without any special LRC to the inhomogeneous system. The

MD simulation was performed in either NVE or NVT ensemble with a time-step  $\Delta t^* = 0.001$ . The system was first equilibrated for 200000 steps before collecting data of the local stress tensors every 10 steps in another 1000000 steps. Totally 8 systems are examined, each with different particle number, initial lattice structure, or box size. Two different strategies to set up the equilibrium liquid-vapor phases were considered: (1) directly establishing equilibrated liquid-vapor phases from an initial solid lattice by running 200000 steps equilibration simulation, or (2) indirectly establishing the equilibrated liquid-vapor phases from an equilibrated bulk liquid slab (obtained by first melting the solid lattice at a high temperature and then cooled to  $T^* = 0.8$ ) followed by extending the simulation box along the z direction to create two vapor slabs. Verlet neighbor list technique was used to accelerate the force calculation with a neighbor width of 0.2. The surface tension is calculated using both KB and IK methods. Six source subroutine files (dl params.inc, dlpoly.f, forces.f, result.f, srfrce.f, sysinit.f) in the DL POLY 2.15 package are modified with a newly added subroutine file sur ten.f to perform final average of collected local stress tensor, to compute the profile  $P_N(z) - P_T(z)$  and to evaluate the integral  $\int_{-L_z/2}^{L_z/2} (P_N(z) - P_T(z)) dz$ . Major modification is in the subroutine srfrce.f for the short-range force calculation, in which additional lines of FORTRAN codes for calculating the local stress tensor from LJ interaction are added into the loop where the pair forces are calculated.

### 5.3.2 SPC/E water model

We used rigid SPC/E model in this work. Most simulation parameters are similar to that used in Ref. [5]. The equations of motion are solved by Leapfrog Verlet algorithm for systems of 512 molecules. The geometry of water molecule is fixed by two methods. One

is to treat a molecule as a rigid body and solve the rotational equations by Quaternions method with a small time step of 1.25 fs in order to keep the total Hamiltonian well concerved. The other is to use SHAKE algorithm to constrain all bond lengths of water molecule to be desired values with a large time step of 2.5 fs. The initial dimension of the simulation box are (19.7Å×19.7Å×39.4Å) and  $L_z$  was later extended to 100 Å. The initial water molecules are located at  $(4 \times 4 \times 8 \times 4)$  FCC lattice sites with random orientations. PBC is applied in all three directions. The electrostatic interactions are calculated with two methods, the conventional Ewald sum and the SPME Ewald sum. Different Ewald precision levels with different convergence parameter  $\kappa$  and maximum reciprocal lattice vectors  $h_x^{\text{max}}$ ,  $h_y^{\text{max}}$ ,  $h_z^{\text{max}}$  are used. We chose T=328K in order to directly compare results with Ref.[5] and other reported simulation data. Both LJ interactions and real space part of Coulomb interactions were truncated at 9.8 Å without any special LRC for inhomogeneous system. The simulations were tested using both NVE and NVT ensembles. In the case of *NVE* the temperature was kept constant by scaling velocities at every 10 steps during equilibration run. In the case of NVT the temperature was controlled by Nose-Hoover thermostat with a relaxation time of 1 ps. Different lengths of simulation time (0.75ns~2ns) were tested in this work. The surface tension was obtained from both IK method based on molecular pressure tensor and KB method based on atomic pressure tensor. In addition to the seven subroutine files in DL POLY 2.15 package (dl params.inc, dlpoly.f, forces.f, result.f, srfrce.f, sysinit.f, sur ten.f) as in the case of LJ fluid, additional two subroutine files (ewald1.f, ewald2.f) for computing conventional Ewald sum or three subroutine files (ewald2.f, ewald spme.f spme for.f) for computing SPME sum are modified. The calculation of contribution to surface

tension from real space Coulomb interaction is implemented in ewald2.f using Eqn. (5-18) and Eqn. (5-19). The calculations of both the first term based on Ghoufi's strategy<sup>[30]</sup> and the second term, reciprocal-space contribution to the surface tension is implemented in ewald1.f for computing conventional Ewald method. For the SPME method the calculation of the first term reciprocal-space contribution to the surface tension based on Alejandre's strategy<sup>[5]</sup> is implemented in ewald\_spme.f while calculation of the second term reciprocal-space contribution to the surface tension for the second term reciprocal-space contribution to the surface tension for the second term reciprocal-space contribution to the surface tension for the second term reciprocal-space contribution to the surface tension for the second term reciprocal-space contribution to the surface tension for the second term reciprocal-space contribution to the surface tension for the second term reciprocal-space contribution to the surface tension for the second term reciprocal-space contribution to the surface tension for the second term reciprocal-space contribution to the surface tension for the second term reciprocal-space contribution to the surface tension for the second term reciprocal-space contribution to the surface tension for the second term reciprocal-space contribution to the surface tension for the second term reciprocal-space contribution to the surface tension is implemented in spme\_for.f.

## **5.4 Results and Discussion**

### 5.4.1 LJ model

Previously reported liquid-vapor interfacial tensions  $\gamma$  of the LJ fluid at  $T^* = 0.8$ (with cutoff = 2.5) are summarized in Table 5-1. Notable differences in the reported  $\gamma$ values can be seen. Larger system sizes (N > 7000) appear to give converged  $\gamma = 0.39$ . Smaller system sizes (N < 2700) result in  $\gamma > 0.4$  except that reported in Ref. [33]. With the error bar, the  $\gamma$  value ranges from the least 0.37 to the largest 0.426. Many factors can affect the calculated surface tension and associated error bar (see below).

We have studied 8 different cases to examine effects of the chosen ensemble (*NVE/NVT*), initial lattice structure (FCC/SC), box sizes, particle number on the obtained surface tension. The simulation parameters and corresponding results are shown in Table 5-2.

Ref. No	Ν	L <sub>x</sub>	Ly	Lz	ensemble	γ
16	768000	120	120	120	NVT	0.396
23	12432	33.01	33.01	33.01	NVT	0.388±0.004
18	10390	29.1	29.1	29.1	N/A	0.39±0.01
34	7200	12.8	12.8	127	NVT	0.39±0.01
20	7100	N/A	N/A	N/A	NVT	0.391±0.002
22	2700	12.5	12.5	75	NVT	0.403±0.007
13	2048	13.41	13.41	39.81	N/A	0.408±0.018
21	1372	11.896	11.896	35.688	NVT	$0.409 \pm 0.005$
17	1372	11.8959	11.8959	35.6877	N/A	0.404±0.005
33	512	7.0	7.0	28.0	N/A	$0.39\pm0.02$

Table 5-1 Summary of reported  $\gamma$  values for LJ subjected to cutoff=2.5

, where N/A means that the reference did not mention the relevant information. N is the number of particles in the system.

Case	Ν	$L_x = L_y$	$L_z$	ensemble	lattice	equilibrium	$\gamma^{IK}$	$\gamma^{_{KB}}$
1	1372	11.896	35.69	NVT	FCC	indirect	0.403(9)	0.403(9)
2	2048	13.41	39.81	NVT	FCC	indirect	0.406(11)	0.406(12)
3	1000	12	24	NVE	SC	direct	0.393(10)	0.393(12)
4	1000	12	24	NVT	SC	direct	0.404(6)	0.403(6)
5	1000	12	24	NVT	SC	indirect	0.404(7)	0.404(9)
6	512	7	28	NVT	FCC	indirect	0.411(25)	0.411(26)
7	8000	21.54	64.62	NVT	SC	direct	0.398(6)	0.399(8)
8	8788	22.23	66.69	NVT	FCC	direct	0.396(7)	0.397(7)

Table 5-2 Simulation parameters and results for LJ model in this work

, where FCC is Face Centered Cubic lattice while SC means Simple Cubic lattice. Indirect and direct are two different strategies to set up liquid-vapor phases in equilibrium.  $\gamma^{IK}$  is obtained based on Eqns. (5-13), (5-14) and (5-15) while is calculated based on Eqn. (5-2). The error bar is obtained by repeating the same simulation 10 times with the initial configuration of new simulation obtained from the last configuration of previous simulation, which make these 10 simulations independent of each other and give a better estimate of the error bar.

We first tried to reproduce the reported  $\gamma$  values using small system sizes to make sure that our surface tension calculation code is correct. Case 1 and case 2 employed the same simulation box and the same number of particles as that used in Ref. [17] and Ref. [13], respectively. We can see that the calculated results in both case 1 and case 2 are in excellent agreement with those in Ref. [17] and Ref. [13], respectively.

Then we attempted to examine the effect of ensemble by simulating the same small system under *NVE* ensemble (case 3) and *NVT* ensemble (case 4). The *NVE* ensemble gives a slightly lower surface tension and larger error bar. However, the average temperature in *NVE* ensemble (case 3) is 0.812, slightly higher than 0.8. With the *NVE* ensemble, the temperature was controlled by rescaling velocities every 10 steps during equilibration run. However, the temperature cannot be controlled during the production run in the *NVE* ensemble. Indeed, in another independent *NVE* simulation, we obtained an average temperature of 0.795 for which the surface tension is 0.406 (which is slightly greater than the surface tension from the *NVT* ensemble). It is known that  $\gamma$  decreases with the increase of temperature. Hence, the *NVT* ensemble is more convenient to compare  $\gamma$  at a given temperature.

Next we examined the effect of using different strategy to obtain the equilibrated liquid-vapor system. Instead of the simple direct method (the equilibrated liquid-vapor coexisting system is obtained directly by performing the simulation in the final rectangular box  $12 \times 12 \times 24$  at T=0.8 under *NVT*) used in case 4, we performed the simulations in case 5 using the indirect method, where the initial cubic solid box  $12 \times 12 \times 12$  was first melted at T>>0.8 and cooled down to T=0.8 to build a bulk liquid box which was then extended to be a rectangular box for setting up the final equilibrated

liquid-vapor system under *NVT*. Our results show that the difference resulting from two strategies is negligible. The indirect method is a normal way to set up the equilibrated liquid-vapor coexisting system. However, the direct method simplified the process as long as the desired temperature is higher enough than the melting point.

Since the results obtained in Ref. [33] is an exception for small system size (N<2700), we tried to give some explanation by performing the simulation under the same condition in case 6. In contrast with Ref. [33] we obtained a much higher  $\gamma$  value and slightly larger error bar. Actually this is an expected result since Chen<sup>[19]</sup> already showed that the surface tension increases with the decrease of the interface area when  $L_x = L_y < 10$ . Later Orea *et al.*<sup>[35]</sup> further found that  $\gamma$  at T=0.8 only converges when  $L_x = L_y \geq 8$ . Therefore our results supported their conclusions.

Finally we also examined the system size effects by performing simulations in two large systems (case 7 and case 8). Our results confirmed our previous observation based on reported  $\gamma$  values in the literature that large system size tends to give  $\gamma$  values less than 0.4 while small system size will lead to  $\gamma$  values larger than 0.4.

Overall we can see that our calculated  $\gamma$  values all fall within the range (0.37~0.426) reported in the literature. We did not see much difference in  $\gamma$  values obtained from IK method or KB method. This is expected because we calculated the pressure in terms of the same atomic representation for LJ model in both methods. For KB method we calculated the total pressure tensor while the local pressure tensor is calculated in IK method. Integration of local pressure tensor along the z direction will give the same total pressure tensor. Therefore, the simple KB method is reliable to determine  $\gamma$  values. However, the advantage of IK method is to allow us assure that real

liquid-vapor equilibrium is established and the source of surface tension really comes from the interface regions. The typical profile of  $P_N(z) - P_T(z)$  and  $\int_{-L_T/2}^{z} (P_N(z) - P_T(z)) dz$  in case 4 are shown Fig. 5-2.



Fig. 5-2

Due to so many factors affecting the obtained  $\gamma$  values, several rules must be obeyed to obtain consistent, reliable surface tension at a certain temperature. First, *NVT* is the preferred ensemble since it gives the average temperature exactly at the desired temperature. Second, the interface area should be large enough ( $L_x = L_y \ge 10$ ). Third,  $L_z \ge 2L_x$  in order to assure that two interfaces will not affect each other due to PBC. Fourth, the initial density of solid box should be appropriate (a little bit higher than the coexisting liquid density). Too high initial density will lead to abnormal results. Fifth, the center-of-mass (COM) for the whole system should be fixed by removing total momentum every a few steps. Serious drift of COM for the system has been observed in our simulations without any constraints on COM. The drift will not affect  $\gamma$  calculated by KB method. However, it does make  $\gamma$  calculated by IK method difficult to converge and bring a large error bar. Any constraint applied to COM should be checked if the total Hamiltonian is still conserved.

### 5.4.2 SPC/E water model

Since the amazing match between calculated  $\gamma$  values for SPC/E model and experimental values was found in Ref. [5], SPC/E model became the most popular and widely investigated water model for liquid-vapor surface tension calculation of water. However, the obtained results are highly scattered and the real surface tension of SPC/E model is still a controversial issue. The value reported in Ref. [5] was once confirmed by two later studies<sup>[36,37]</sup>, which made many people believe that SPC/E is really the best model to reproduce experimental surface tension of water. However, such belief was completely overthrown in Ref. [24] which stated that the  $\gamma$  values reported in Ref. [5] were highly overestimated due to the short simulation time (~375ps). Nevertheless, the values obtained in Ref. [24] were also much lower than those reported in later references<sup>[25,27,29]</sup>. Summary of reported  $\gamma$  values excluding LRC contribution are shown in Table 5-3.

In this work we would like to investigate the actual surface tension of SPC/E model at T=328K subjected to a cutoff of 9.8Å without applying any special long range correction (LRC) technique. In particular we examined the effects of ensemble, type of Ewald technique, method of keeping molecular shape, method of pressure calculation, the number of maximum reciprocal lattice kmax, strategy of obtaining liquid-vapor coexisting system on the calculated surface tension. The simulation parameters and obtained results are shown in Table 5-4.

Ref. No	T(K)	ensemble	coulomb	constraint	Cutoff (Å)	$\gamma_P$ (mN/m)	LRC
5	328	NVE	Ewald	SHAKE	9.8	60.5±3.0	Blokhuis
38	323	NVT	direct	SHAKE	9.0	58±2	No
36	328	NVT	Ewald	SHAKE	9.8	$60^*$	Blokhuis
37	325	NVT	PPPM	SHAKE	9.8	61.5*	PPPM
24	325	NVT	Ewald	SHAKE	10	$42.9^{*}\pm3.0$	Blokhuis
25	325	NVT	SPME	SHAKE	13	56 <sup>*</sup> ±1.0	Blokhuis
27	325	NVT	PME	SETTLE	9.8	53.6 <sup>*</sup> ±1.5	Blokhuis
29	325	NVT	SPME	SHAKE	9.5	$54.1^* \pm 1.3$	SPME

Table 5-3 Summary of reported  $\gamma_P$  values for SPC/E model

\* The values were obtained from tables, figures in corresponding references or taken from the interpolation between T=300K and T=350K if the value at T=300K is not directly available.  $\gamma_P$  is surface tension value directly obtained from the difference between normal and tangential pressure tensor. The long range correction contribution from LJ part to surface tension is not included in  $\gamma_P$  by assuming  $\gamma_P = \gamma_{total} - 5$ .

Case	kmax	ensemble	equilibrium	coulomb	constraint	$\gamma^{\prime \prime $	$\gamma^{_{KB}}$
1	auto	NVE	direct	SPME	SHAKE	53.7±2.0	53.0±2.1
2	auto	NVT	direct	SPME	SHAKE	52.8±3.2	51.9±3.2
3	auto	NVE	direct	Ewald	SHAKE	52.1±0.9	51.2±1.0
4	auto	NVT	direct	Ewald	SHAKE	52.5±2.8	51.9±3.0
5	auto	NVT	indirect	Ewald	SHAKE	54.1±2.4	53.3±2.6
6	auto	NVT	indirect	SPME	SHAKE	53.3±2.2	52.5±2.4
7	auto	NVT	indirect	Ewald	rigid	53.9±1.7	53.3±1.6
8	auto	NVT	indirect	SPME	rigid	53.4±1.9	52.8±2.0
9	manual	NVE	direct	Ewald	SHAKE	57.2±1.9	52.3±2.0
10	manual	NVE	direct	SPME	SHAKE	57.7±2.4	53.4±2.6

Table 5-4 Simulation parameters and results for SPC/E model in this work

We first examined the effect of ensemble by performing several pair simulations at the same condition except that one is under NVE ensemble (case 1, case 3) and the other is under NVT ensemble (case 2, case 4). The results showed some differences in average  $\gamma$  values. However, these differences are small considering the obtained error bars. Then we tested the effect of equilibration strategy by performing another two simulations (case 5, case 6) using the indirect method to obtain liquid-vapor coexisting system. The results showed that the differences all fall within the obtained error bars. By comparing case 1, case 2, case 6 with case 3, case 4, case 5, we can see that the differences resulting from different Ewald methods are also small. Therefore, the SPME method is the preferred choice since it runs much faster than conventional Ewald method. However, we have to employ Alejandre's simple strategy<sup>[5]</sup> to deal with the first reciprocal space term contribution to the surface tension in case of SPME method, which will lead to an unreasonable profile of  $P_N(z) - P_T(z)$  in the bulk liquid region. On the other hand, the conventional Ewald could allow us to deploy Ghoufi's strategy<sup>[30]</sup> to obtain reasonable profile of  $P_N(z) - P_T(z)$ . Next, we performed another two simulations (case 7, case 8) by treating water molecules as rigid bodies. The results showed that the differences resulting from different molecular shape maintaining methods (SHAKE/rigid body) are small compared to the error bars. So, the SHAKE method is the preferred molecular shape maintaining method since it allows us to use a longer time step in simulations. In the case of rigid body method we have to reduce the time step to 1.25fs in order to maintain a well conserved Hamiltonian. In all these cases, we let the DL POLY2.15 program to automatically select proper Ewald parameters with the precision 1.0E-6. With the conventional Ewald method, the program chooses a convergence parameter  $\kappa = 0.32765$  Å<sup>-1</sup> and the number of maximum reciprocal lattice in three directions  $h_x^{\text{max}} = 7$ ,  $h_y^{\text{max}} = 7$ ,  $h_z^{\text{max}} = 33$ . For the SPME method, the corresponding parameters are  $\kappa = 0.32765$  Å<sup>-1</sup>,  $h_x^{\text{max}} = 8$ ,  $h_y^{\text{max}} = 8$ ,  $h_z^{\text{max}} = 64$ . In the next last two cases, we investigated the effect of reducing these Ewald parameters. In case 9 we manually set these parameters as  $\kappa = 0.284 \text{ Å}^{-1}$ ,  $h_x^{\text{max}} = 5$ ,  $h_y^{\text{max}} = 5$ ,  $h_z^{\text{max}} = 20$ with conventional Ewald method. Actually these parameters are as same as those used in Ref. [5]. In case 10 we manually set these parameters as  $\kappa = 0.284 \text{ Å}^{-1}$ ,  $h_x^{\text{max}} = 8$ ,  $h_y^{\text{max}} = 8$ ,  $h_z^{\text{max}} = 32$  with SPME method. The results showed that the reduced Ewald parameters greatly affect the obtained  $\gamma$  values. Obviously, reduced Ewald parameters lead to overestimated  $\gamma$  values. This may also explain why Ref. [5] obtained an overestimated  $\gamma$ compared to more recent calculations<sup>[27,29]</sup>. We also monitored the movement of COM for the system in all above cases and did not find serious drift of COM. Therefore, we did not apply any COM constraint in our case studies. In addition, we also compared  $\gamma$  values obtained from IK method and KB method. Interestingly systematic small difference between IK and KB method has been observed. It seems that IK method will lead to  $\gamma$ values 0.6~0.9 mN/m larger than those obtained from KB method. This can be explained by the difference of pressure calculation between two methods. With the IK method, we chose the molecular pressure definition, whereas DL POLY2.15 uses the atomic pressure definition with the KB method. This difference disappears in the case of LJ fluids since LJ fluid is an atomic fluid. However, it does exist in the case of molecular fluid like water. The exception appears when we reduced the Ewald parameters (case 9, case 10). In these cases the difference of 7 values between IK and KB methods has increased to 4.3~4.9

mN/m. This exception is unexpected because both IK and KB methods use the same reduced Ewald parameters. The cause of this exception deserves further investigation. Overall, our obtained  $\gamma$  values are 52.1~54.1 mN/m with an error bar of 3.0 mN/m. These results are consistent with more recently reported values<sup>[25,27,29]</sup>. Actually the relative large error bar is the result of difference between two large numbers. In Table 5-5 we showed various components of  $\gamma^{IK}$  due to different interactions. Apparently the contribution from LJ interaction  $\gamma^{LJ}$  is a very negative value while the contribution from the real space Ewald sum  $\gamma^{real}$  is a very positive value. Both  $\gamma^{LJ}$  and  $\gamma^{real}$  have a very large error bar. Although the error bars of contributions from the first reciprocal space term  $\gamma^{recip1}$  and the second reciprocal space term  $\gamma^{recip2}$  are much smaller, the error bar of  $\gamma^{IK}$  is mainly determined by its main contribution  $\gamma^{LJ} + \gamma^{real}$  which still has a relative large error bar. One interesting result is that  $\gamma^{LJ}$  became a very negative value in the case of water while  $\gamma^{LJ}$  is a small positive value in the case of LJ fluid. The reason behind this is the fact that oxygen-oxygen distances between different water molecules are much smaller than those between LJ particles. In other words, the oxygen number density in the case of water is much higher than the number density of LJ particles. The closer oxygenoxygen distance is caused by the strong electrostatic interaction between water molecules.

The typical profiles of various components of  $P_N(z) - P_T(z)$  and  $\int_{-L_z/2}^{z} (P_N(z) - P_T(z)) dz$  in case 5 are shown in Fig. 5-3. In case 5 we used conventional Ewald sum and Eqn. (5-32), Eqn. (5-33) were deployed to calculate the first reciprocal space contribution to surface tension based on Ghoufi's strategy<sup>[30]</sup>. In case 6 we used SPME method and Eqn. (5-27), Eqn. (5-28) were employed to calculate the first reciprocal space contribution to surface tension based on Alejandre's simple strategy<sup>[5]</sup>. In Fig. 5-4 we showed the profile of component  $P_N^{recip1}(z) - P_T^{recip1}(z)$  and  $\int_{-L_Z/2}^{z} (P_N^{recip1}(z) - P_T^{recip1}(z)) dz$  in case 6. Profiles of other components in case 6 are similar to those in case 5. By comparing Fig. 5-3 g, h with Fig. 5-4 a, b we can clearly see that Ghoufi's strategy<sup>[30]</sup> gives a reasonable profile of  $P_N(z) - P_T(z)$  and  $\int_{-L_Z/2}^{z} (P_N(z) - P_T(z)) dz$  which shows that the source of surface tension only comes from interface region. On the other hand, Alejandre's simple strategy<sup>[5]</sup> will lead to a profile of  $P_N(z) - P_T(z)$  similar to the density profile. However, two strategies still give the same average surface tension from the integration of  $P_N(z) - P_T(z)$ .

Case	$\gamma^{LJ}$	$\gamma^{real}$	$\gamma^{LJ} + \gamma^{real}$	$\gamma^{recip1}$	$\gamma^{recip 2}$	$\gamma^{recip1} + \gamma^{recip2}$	$\gamma^{IK}$
1	-280±12	330±13	49.8±2.0	-8.9±0.1	12.9±0.2	3.93±0.23	53.7±2.0
2	274.1±6.6	323.1±6.4	49.0±3.1	8.89±0.08	12.7±0.2	3.79±0.20	52.8±3.2
3	277.9±9.6	326.2±9.7	48.3±1.0	8.87±0.08	12.7±0.4	3.82±0.35	52.1±0.9
4	271.6±8.1	320.2±9.5	48.6±2.8	8.85±0.06	12.7±0.3	3.82±0.33	52.5±2.8
5	-274±11	324±11	50.3±2.5	8.85±0.09	12.6±0.2	3.75±0.18	54.1±2.4
6	277.1±6.3	326.4±7.6	49.4±2.3	8.85±0.04	12.8±0.2	3.9±0.2	53.3±2.2
7	-278±11	329±11	50.2±1.8	8.86±0.10	12.5±0.3	3.69±0.32	53.9±1.7
8	276.9±5.8	326.5±5.4	49.7±1.9	8.90±0.08	12.6±0.2	3.71±0.21	53.4±1.9
9	-280±11	334±11	53.8±2.0	8.05±0.06	11.4±0.2	3.35±0.21	57.2±1.9
10	-283±11	337±11	54.1±2.5	7.89±0.07	11.5±0.2	3.6±0.2	57.7±2.4

Table 5-5 Decomposition of  $\gamma^{IK}$  based on contribution from different interactions









## **5.5 Conclusions**

We have systematically investigated many factors which may affect calculation of crude surface tension subjected to a certain cutoff without any special LRC.

For LJ fluid we found that box size and system size (number of particles) have obvious effects on the obtained surface tension. It seems that small box size tends to give larger  $\gamma$  values while large system size tends to give smaller  $\gamma$  values. We did not observe much difference in  $\gamma$  values obtained from IK method or KB method. Serious drift of COM for the system has been observed in our simulations without any constraints on COM.

For water we found that Ewald parameters may affect the obtained  $\gamma$  values. Too small Ewald parameters will lead to overestimated  $\gamma$  values. Contrary to the LJ case we found a small but consistent difference in  $\gamma$  values obtained from IK method or KB method. It seems that IK method will lead to  $\gamma$  values 0.6~0.9 mN/m larger than those obtained from KB method. This difference may result from different pressure definitions employed in these methods. Atomic pressure is used in KB method while molecular pressure is used in IK method. In contrast with the LJ case, we did not find serious drift of COM for the system. We compared Ghoufi's strategy<sup>[22]</sup> and Alejandre's simple strategy<sup>[5]</sup> in calculating the first reciprocal space contribution to surface tension and clearly showed that Ghoufi's strategy<sup>[30]</sup> gives more reasonable profile of  $P_N(z) - P_T(z)$ although two strategies give the similar average surface tension after the integration of

 $P_N(z) - P_T(z).$ 

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## **Chapter 6 Formation of Ice Nanotubes and Ice helixes**

## **6.1 Introduction**

Bulk ice is known to have 15 crystalline phases<sup>[1]</sup>. In the previous work<sup>[2-5]</sup> of our group we have shown that it is possible to form new ice phases in carbon nanotubes. These new ice phases were named as n-gonal ice nanotubes because they can be viewed as stacked water polygons. Recent XRD<sup>[6]</sup>, NMR<sup>[7]</sup> and neutron scattering<sup>[8]</sup> experiments have proved the existence of these n-gonal ice nanotube inside carbon nanotubes. In addition, more recent MD studies<sup>[9-10]</sup> have shown that odd number n-gonal ice nanotubes such as pentagonal ice nanotube can be used as ferroelectric materials since the direction of its total dipole moment can be reversed with the change of external electric field. Moreover, in 2002 Noon et al.<sup>[11]</sup> showed the possibility of forming single layer ice helixes inside (7,7), (8,8) and (9,9) CNTs at ambient condition. The similar ice helix was also discovered inside (10,10) CNT by Liu et al.<sup>[12]</sup> in 2005. Mashl et al.<sup>[13]</sup> also observed the formation of hexagonal ice nanotube inside (9,9) CNT at ambient condition. Tanaka et  $al^{[14]}$  also showed the formation of a composite ice nanotube with hydrophobic guests inside CNT. Shiomi et al.<sup>[15]</sup> recently obtained the liquid-n-gonal ice nanotube transition temperature and its diameter dependence using MD simulations, which are consistent with their previous XRD results<sup>[6]</sup>. Therefore, the study of ice-like water structures not only enriches our understanding of possible ice phases but also helps the design of new materials based on discovered new structures. In this work, we would like to investigate if we can find more interesting ice-like water structures as we gradually increases the water density inside carbon nanotubes.

## **6.2 Simulation details**

### **6.2.1 Formation of Ice Nanotubes**

All simulations were performed under *NVT* ensemble with a time step of 1 fs. Several water models (TIP4P-Ew, SPC/E, SPC-HW) were tested and all were treated as rigid bodies. The rotational equations were solved by Quaternion algorithm with a precision 1.0E-8<sup>[16]</sup>. Velocities were scaled every 10 steps to maintain the temperature during equilibration stage while the temperature was controlled by Nose-Hoover thermostat with a relation time of 1  $ps^{[16]}$ . The simulation cell is a rectangular box which enclosed a certain carbon nanotube. Carbon atoms were described by uncharged LJ atoms with parameters  $\sigma = 3.4$  Å,  $\varepsilon = 0.086$  kcal/mol<sup>[17]</sup>. PBC were applied in all three directions so that the selected carbon nanotube became infinite long along the tube axis. SPME method was deployed to calculate long range electrostatic interactions with a precision 1.0E-6<sup>[16]</sup>. The short range interaction was cutoff at 9 Å. The Verlet neighbor list was used with a width of 1 Å. All simulations were started with a cylindrical distribution of water molecules inside CNT. Then the system was heated at a high temperature for 1ns to form liquid state inside CNT. After that the system was gradually cooled down until an ice-like structure was formed. The detailed simulation cases under NVT ensemble were shown in Table 6-1.

### 6.2.2 Formation of Ice Helixes

All simulations were performed under  $NP_zT$  ensemble. PBC were applied only in axial direction. Smooth wall CNTs were employed to confine TIP5P water molecules. Both long range charge-charge interaction and the short range LJ interactions were truncated at 8.75 Å by a switching function<sup>[5]</sup>. The simulation cases investigated were shown in Table 6-2.

Case	CNT	Model	$L_x = L_y(\text{\AA})$	$L_z(\text{\AA})$	NW	NC
1	(16,0)	TIP4P-Ew	24	84.9	180	1280
2	(17,0)	TIP4P-Ew	20	50.94	126	816
3	(18,0)	TIP4P-Ew	24	59.43	168	1008
4	(17,0)	TIP4P-Ew	20	38.205	126	612
5	(17,0)	SPC-E	20	38.205	126	612
6	(17,0)	SPC-HW	20	50.94	126	816
7	(17,0)	SPC-HW	20	38.205	126	612
8	(17,0)	SPC-E/SPC-HW	20	38.205	126	612

Table 6-1 Simulation cases under NVT ensemble

Table 6-2 Simulation cases under NP<sub>z</sub>T ensemble

Case	CNT	NW	Pz (MPa)
1	(17,0)	252	1
2	(17,0)	252	1000
3	(17,0)	252	4000
4	(20,0)	300	500
5	(20,0)	300	2000
6	(20,0)	300	3000
7	(22,0)	340	800
8	(24,0)	400	800

# 6.3 Results and Discussion

## 6.3.1 Formation of Ice Nanotubes

Tetragonal, pentagonal, hexagonal and heptagonal ice nanotubes have been observed to form inside CNTs in our group's previous work<sup>[2,5]</sup> using TIP4P water model under  $NP_zT$  ensemble. In this work we would like to examine whether we can observe similar ice nanotubes inside CNT under *NVT* ensemble using different water models.

Since CNTs were usually fixed in simulations of confining water, the usage of *NVT* ensemble could allow us to employ real structured CNTs and avoid the unreasonable change of carbon-carbon bond distances under constant pressure ensemble.

In case 1 we built the initial configuration by placing six water chains (each has 30 molecules) in a hexagonal arrangement as shown in Fig. 6-1 (a). The distance between adjacent water molecules in each chain was set to be 2.83 Å so that all molecules were evenly distributed along the tube axis. The initial orientation of each molecule was randomly chosen from a Gaussian distribution. Then the initial structure was relaxed at 320K for 1ns to form a disordered liquid-like structure. From Fig. 6-1 (b) we can see that water molecules were randomly distributed in a cylindrical water shell except two molecules near the tube axis. Similar structure was observed in our previous work<sup>[18]</sup> investigating a short CNT immersed in a water reservoir. Since then the system was cooled down stepwise from 320K to 300K to 275K. At each temperature 5-to-25ns simulations were carried out, respectively. At the lowest temperature (275K) the confined water was found to spontaneously form a hexagonal ice nanotube after 3ns as shown in Fig. 6-1 (c). Following the similar procedure, a heptagonal ice nanotube was observed to form inside (17,0) CNT at 245K after 6 ns in case 2 as shown in Fig. 6-1 (d) and an octagonal ice nanotube was formed inside (18,0) CNT at 190K after 24.5 ns in case 3 as shown Fig. 6-1 (e). Obviously a general trend can be found that longer simulation time and lower temperature are required to form larger n-gonal ice nanotube.

An interesting phenomenon was observed when we reduced the tube length from 50.94Å in case 2 to 38.205Å in case 4. The change caused the axial pressure increased from -60MPa to 400MPa. In the meantime a new core/sheath ice nanotube instead of a

heptagonal ice nanotube was formed inside (17,0) CNT as shown in Fig. 6-1 (f). The inner core is a single-file water chain while the outer sheath is a regular octagonal ice nanotube. The same core/sheath ice nanotube was also observed by a recent neutron scattering experiment<sup>[8]</sup>.



(e) Snapshot of (18,0) at 190K after 24.5ns



In order to verify that the formation of the core/sheath ice nanotube is not a result of a specific water model, we employed the SPC/E water model in case 5 to investigate the water structure confined in the same short (17,0) CNT under *NVT* ensemble. As shown in Fig. 6-2 a similar core/sheath ice nanotube was also observed at 245K after 6 ns. However, the core/sheath ice nanotube formed by SPC/E water molecules was less perfect than that formed by TIP4P-Ew water molecules.



Fig. 6-2 Snapshot of (17,0) at 245K after 6ns with shorter tube

Next, we deployed a special water model SPC-HW (designed for heavy water) to further verify that the change of tube length really altered the possible water structure formed inside CNT. In case 6 we enclosed 126 SPC-HW  $D_2O$  molecules inside a 5.094 nm long (17,0) CNT while in case 7 we placed the same number of  $D_2O$  molecules within a 3.82 nm long (17,0) CNT. As shown in Fig. 6-3 a heptagonal ice nanotube was formed in the long tube while a core/sheath ice nanotube was formed in the short tube. Compared with results from TIP4P-Ew model, we can see that SPC-HW model results in more perfect ice nanotube structures.



(a) Snapshot of (17,0) at 245K with longer



(b) tube Snapshot of (17,0) at 245K with shorter tube Fig. 6-3

In addition, we also examined the possibility of forming a hybrid ice nanotube consisting of two different water models. In case 8 we enclosed 63 SPC/E H<sub>2</sub>O molecules and 63 SPC-HW D<sub>2</sub>O molecules inside a 3.82 nm long (17,0) CNT. After cooling the system at 245K for 6ns a hybrid core/sheath ice nanotube was formed as shown in Fig. 6-4.



Fig. 6-4 Snapshot of (17,0) at 245K after 6ns with mixed water models

Overall we can see that the tube length under *NVT* ensemble really affects the possible water structure inside CNTs. The actual change resulting from reducing tube length is the increased water density and the increased axial pressure. This further stimulated us to explore the possible high density water structures confined in CNTs resulting from increasing axial pressure under  $NP_zT$  ensemble.

### **6.3.2 Formation of Ice Helixes**

In this part we carried out four series of MD simulations to explore formation of high density ice nanotubes in four smooth wall zigzag CNTs described by (17,0), (20,0), (22,0) and  $(24,0)^{[19]}$ .

In the first series of MD simulations, liquid water was confined in (17,0) CNT. The initial axial pressure was controlled at 1 MPa in case 1. After the system was cooled at 250K for 16 ns the confined water was observed to spontaneously freeze into a

heptagonal ice nanotube. Next, with the temperature controlled at 250K we increased the axial pressure in several steps. As axial pressure increased to 1000 MPa in case 2, we observed that the heptagonal ice nanotube was transformed into a core/sheath ice nanotube with the sheath consisting of an octagonal ice nanotube and a single file water chain forming the core. These observations were consistent with our previous simulations of confined water under *NVT* ensemble. In other words, the low density heptagonal ice nanotube is formed at low axial pressure (long tube length) while the high density core/sheath ice nanotube is formed at high axial pressure (short tube length). An interesting new structure was observed as we increased the axial pressure to 4000 MPa. The core/sheath ice nanotube was transformed into a double-walled ice helix as shown in Fig. 6-5 (a-b). Unlike the regular ice nanotubes whose hydrogen-bond networks can be viewed as an octuple-stranded helix (Fig. 6-5 c), whereas the inner wall is a quadruple-stranded helix (Fig. 6-5 d).



Fig. 6-5 Snapshot of (17,0) at T=250K Pz=4GPa

Like low density n-gonal ice nanotubes, the high density ice helix also satisfies the bulk ice rule with every water molecules hydrogen-bonded to exactly four nearest-neighbor water molecules. Specially, every molecule in the outer wall is hydrogen-bonded to three nearest-neighbors in the octuple helix and to one in the inner wall. Conversely, every molecule of the inner wall is only hydrogen-bonded to two nearest neighbors within the quadruple helix while the other two hydrogen bonds are connected to nearest neighbors in the outer wall<sup>[19]</sup>.



(I) Snapshot of (20,0) at T=250K Pz=500MPa



(II) Snapshot of (20,0) at T=250K Pz=2GPa



(III) Snapshot of (20,0) at T=250K Pz=3GPa Fig. 6-6 Snapshot of (20,0) at T=250K

The second series of MD simulations were performed in a (20,0) CNT with a slightly larger diameter of 1.585 nm. After the confined liquid water reached equilibrium at 250K and 1MPa, the pressure was increased instantly in three steps. As pressure was increased to 500MPa in case 4, we observed that the liquid water froze spontaneously into a new high density double walled ice-like structure (Fig. 6-6 I). The outer wall is a staggered-octagonal ice nanotube, whereas the inner wall is staggered-tetragonal ice nanotube. The double walled structure also contains core water molecules with two molecules per unit cell (Fig. 6-6 I d). Note that a regular octagonal or tetragonal ice nanotube can satisfy the

ice rule by itself. However, because of the existence of the core water molecules, both the outer octagonal and the inner tetragonal ice nanotube adopt the staggered structures to fulfill the ice rule.

A solid-solid transition was observed when the pressure was further increased to 2000 MPa in case 5. Again a double-walled tubular structure was formed, where the outer wall is a hendecagonal ice nanotube and the inner wall is a pentagonal ice nanotube (Fig. 6-6 II e, f). Lastly, at the highest pressure (3000 MPa) simulated in case 6, another solid-solid transition was observed. A new high density double-walled ice nanotube containing a single-file water chain was formed (Fig. 6-6 III g). The outer wall is a weakly helical hendecagonal ice nanotube, whereas the inner wall is a weakly helical hexagonal ice nanotube.



Fig. 6-7 Snapshot of (22,0) at T=250K Pz=800MPa

The third series of MD simulations involved another (22,0) CNT with a diameter of 1.74 nm. After the liquid water was equilibrated at 250K and 1MPa, the pressure was instantly raised to 800MPa. Again, the liquid froze spontaneously into a high-density double-walled tubular structure containing core molecules (Fig. 6-7 a). Here, the outer wall is a decagonal ice nanotube with a structure similar to that of (5,5) armchair CNT (Fig. 6-7 b, c), whereas the inner wall is a staggered pentagonal ice nanotube (Fig. 6-7 d). The core is a single-stranded helix (Fig. 6-7 d). The formation of the armchair tube is particularly noteworthy. It is known that the armchair tube can be viewed as rolling up a graphene-sheet along a carbon-carbon bond direction. Such a graphene-sheet like water structure has been reported previously in the formation of a two-dimensional bilayer ice within a hydrophobic slit pore<sup>[20]</sup>. Therefore, the armchair water tube can be viewed as rolling up one sheet of two dimensional bilayer ice.

Finally the fourth series of MD simulations was performed inside the largest CNT (24,0) investigated in this study. Again the pressure was raised to 800MPa in case 8. In stark contrast with previous cases, the confined liquid froze into a triple-walled helical structure (Fig. 6-8 a, b). Here, the outer wall is an 18-stranded helical nanotube (Fig. 6-8 c), whereas both the middle and inner walls are hextuple-stranded helixes (Fig. 6-8 c, d). Interestingly, the middle wall only serves as a hydrogen-bonding "bridge" to connect the outer wall and the inner wall. Water molecules in the middle wall do not have any hydrogen-bonding neighbors within the middle wall itself<sup>[19]</sup>.


Fig. 6-8 Snapshot of (24,0) at T=250K Pz=800MPa

# **6.4 Conclusions**

### 6.4.1 Formation of Ice Nanotubes

We have performed 8 cases *NVT* simulations to investigate the formation of ice nanotubes inside three CNTs with increasing diameters. Using a special water model (TIP4P-Ew) designed for Ewald sum technique to deal with long range electrostatic interactions, we found that the hexagonal, heptagonal and octagonal ice nanotubes can be spontaneously formed inside (16,0), (17,0) and (18,0) CNTs, respectively. However, it takes longer time and lower temperature to form larger n-gonal ice nanotubes. Interestingly, a new core/sheath ice-like structure was formed inside another (17,0) CNT with reduced tube length. We further confirmed that such core/sheath structure can be

also formed using SPC/E  $H_2O$ , SPC-HW  $D_2O$  or a mixture of and  $H_2O$  and  $D_2O$ . Therefore, the formation of new core/sheath structure is not sensitive to water models.

#### **6.4.2 Formation of Ice Helixes**

In summary, we have demonstrated previously unknown double- and triple-walled ice helixes within CNTs using  $NP_zT$  MD simulations. The water double helix shows structural similarity to the DNA double helix. In the (22,0) CNT, an armchair (5,5) ice nanotube emerges, marking the onset of graphene-like nano-ice in the CNT. The richness of the bulk and nano-ice phases is a testament to the adaptability and versatility of the water hydrogen-bond frame work to a change of external environment, either on the outer planets, or within microscopic nanochannels. We have seen the transitions from the low-density heptagonal ice nanotube, to the medium-density core/sheath ice-like structure, and to the high-density ice helix inside the same (17,0) CNT as we increased the water density.

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# **Chapter 7 Possibilities of Water/Ions Entrance and**

# **Conduction through Carbon Nanotube**

### 7.1 Introduction

Since its discovery in 1991<sup>[1]</sup>, carbon nanotube (CNT) has been a central research topic in nanoscience due to its remarkable structural, mechanical and electronic properties as well as its great potential for applications such as gas storage<sup>[2,3]</sup>. nanoelectronics<sup>[4]</sup>, membrane separation<sup>[5]</sup>, molecular detection<sup>[6]</sup> and AFM probe tip<sup>[7]</sup>. CNT is also an ideal nanoscale tube for conduction of water and ions. Although several molecular dynamics (MD) studies of static<sup>[8,9]</sup> and dynamic<sup>[10,11]</sup> properties of confined water to CNTs were published in the literature long ago, the number of papers on simulation of confined water in CNTs has increased sharply since the discovery of onedimensional (1D) nanoice in CNTs and novel transport behavior of water through CNTs in 2001.<sup>[12]</sup> In the latter work, Hummer *et al.* observed spontaneous entry of water into a narrow (6,6) CNT and pulse-like conduction of single-file water chain through the CNT. They suggested that CNT can be exploited as biological channels for water conduction. Subsequently, the idea of using CNT as prototype systems to study much more complex biological channels such as aquaporin water channel was proposed by many researchers<sup>[13-21]</sup>. In particular, the idea of designing CNT-based artificial ion channel was first proposed by Joseph et al.<sup>[22]</sup>, based on the study of ion transport in modified CNTs under an external electric field along the axial direction. These researchers investigated the possibility of incorporating certain functionality of natural ion channels into CNTs. Their idea was later supported by other researchers<sup>[23-25]</sup>. Especially, Liu *et al.*<sup>[23]</sup> recently

designed a CNT-based artificial water channel, investigated its perturbation to the lipid membrane with the implanted CNT and water conduction through the artificial water channel using MD simulation. They found that a double-walled CNT (DWCNT) shows better biocompatibility with the lipid bilayer than a single-walled CNT (SWCNT). They imposed two positive charges on carbon atoms in the middle of the inner CNT to mimic positively charged residues inside aquaporin-1(AQP-1) water channel, and they found that the imposed charges can affect the single-file water chain to form a bipolar orientation. This could in principle prevent the proton transport across the channel. The computed water permeation rate is also in good agreement with that of AQP-1 water channel.

In 2003 Kalra *et al.*<sup>[26]</sup> investigated the flow of water through aligned (6,6) CNT membranes under osmotic pressure. They showed that water molecules flow spontaneously from the pure-solvent compartment to the concentrated solution compartment through CNT-based membranes at a fast rate, while the (6,6) CNT-based membranes completely blocked the passage of both Na<sup>+</sup> and Cl<sup>-</sup> ions. If a hydrostatic pressure, strong enough to overcome the osmotic pressure, is applied to the solution compartment, water molecules are expected to flow from solution compartment into pure-solvent compartment as a result of reverse osmosis. This led to the idea of using CNT-based semi-permeable membranes for desalination of CNT-based membranes for efficient sea water desalination <sup>[27]</sup>. He investigated conduction of water and NaCl through (5,5), (6,6), (7,7) and (8,8) CNT-based membranes driven by a hydrostatic pressure. The results show that water can easily pass through all considered CNTs and the

conduction rate increases with the tube diameter, while ions can only pass through two wider tubes (7,7) and (8,8) among the four. The length of CNTs does not affect rate of water conduction too much as shown in the case of doubling the length of (6,6) CNT. More specifically, no Cl<sup>-</sup> is observed to pass though (7,7), while five Cl<sup>-</sup> can pass through (8,8) in 25 ns, compared to 23 Na<sup>+</sup>. The salt rejection rate can still be as high as 95% in (7,7) while it drops to 58% in (8,8). Therefore, (7,7) CNT appears to be an ideal tube for efficient sea water desalination since the water conduction rate can be four times of that of (5,5) while the salt rejection rate is only changed from 100% to 95%. In reality, the packing density of CNT in membranes should be as high as possible to achieve the highest conduction rate of water.

Despite of these previous studies illustrated above, systematic studies of possibilities for water/ions to enter into and to pass through various CNTs are still lacking. In this work, we investigate effects of uniform external electric field and charged walls of CNTs on the entry and conduction behavior of water and ions in CNTs. More specifically, we have examined: (1) The possibility of unidirectional single-file water flow through a narrow (9,0) CNT; (2) the narrowest CNT that allows water to enter under an uniform electric field; (3) the narrowest CNT that allows ions (Na<sup>+</sup> and Cl<sup>-</sup>) to enter without any external driving force; (4) the narrowest CNT that allows ions (Na<sup>+</sup> and Cl<sup>-</sup>) to enter under a uniform electric field; (5) the possible selectivity between Na<sup>+</sup> and K<sup>+</sup> to enter CNTs, with and without the external field.

## 7.2 Simulation details

MD simulations were carried out in a constant-temperature and constant-volume (*NVT*) ensemble using DLPOLY programs of version  $2.17^{[28]}$ . The long-range

electrostatic interactions among charged species (including oxygen and hydrogen of water, and ions) were treated using a smooth-particle-mesh Ewald (SPME) technique with a convergence precision of  $1.0 \times 10^{-6}$ , and the short-range van der Waals (vdW) interactions were spherically cut off at 9 Å. A Verlet neighbor-list width of 1 Å was adopted. The Newton's equations of motion were solved using the leap-frog Verlet algorithm with a time step of 2.5 fs. The carbon atoms were fixed during the simulations as uncharged Lennard-Jones (LJ) particles whose parameters were taken from the AMBER96 force field<sup>[29]</sup> unless specified in some cases. The cross interaction parameters between carbon and oxygen were derived based on the Lorentz-Berthlot combining rule. The constant temperature (298.15 K) was controlled by a Nose-Hoover thermostat with a relaxation time of 1ps. In most cases, water molecules were described by the TIP3P model and the geometry of water molecules was constrained using the SHAKE technique with a tolerance of  $1.0 \times 10^{-8}$ . Ions (Na<sup>+</sup>, K<sup>+</sup>, Cl<sup>-</sup>) were treated as charged LJ particles with parameters taken from Spohr's work<sup>[47]</sup>. We followed a widely used method to simulate CNT-based membrane systems where the CNT, as a channel, bridges two parallel graphene sheets (as the membranes) on which some atoms are removed at desired sites to accommodate the CNT tube as shown in Fig. 7-1. To be compatible with the rhombic shape of the graphene sheets with a side length of 24.7 Å, a monoclinic simulation cell with a length of 40 Å along the CNT axial direction was constructed with the parallelepiped periodic boundary condition.



Fig. 7-1 (9,0) CNT-membrane system

## 7.2.1 Possibility of unidirectional single-file water passing through (9,0) CNT

A 15.8 Å long (9,0) CNT with a (carbon-to-carbon) diameter of 7.02 Å was imposed between two parallel graphene sheets and fixed at the center of the monoclinic supercell as shown in Fig. 7-1. Initially, no water molecules were inside the CNT although the entire CNT-membrane system was immersed in a water reservoir consisting of 352 TIP3P water molecules (per supercell) on both entrances of the CNT. A uniform electric field with varying strength was applied along the tube axis, pointing from the left to right (defined as the positive *z*-axis). The system was equilibrated for  $1 \times 10^5$  steps, followed by  $4 \times 10^6$  steps (10 ns) of production run during which coordinates of all particles were recorded every 1000 steps. Each 10 ns simulation was resumed at least 5 times so that the total simulation time exceeded 50 ns for a given field strength.

### 7.2.2 The narrowest CNT allowing water entry under uniform electric field

Three different CNTs, (7,0), (8,0) and (5,5) with diameters of 5.46 Å, 6.24 Å and 6.76 Å, respectively, were tested with varying the strength of electric field from 0 to 2.778 V/Å and the length of CNT from 13.5 Å to 50.2 Å. The water reservoir includes 453 water molecules per supercell. Initially, no water molecules were inside CNT. Again, the system was equilibrated for  $1 \times 10^5$  steps, followed by  $5 \times 10^5$  steps of production run. In

addition, the same simulations were repeated using the SPC/E water model and carbon parameters based on the OPLS-AA force field<sup>[30]</sup>.

# 7.2.3 The narrowest CNT allowing ions (Na<sup>+</sup> and Cl<sup>-</sup>) entry with no assist of external driving force

Three different ionic concentrations (0.12 M, 0.6 M, 1.2 M) were considered to examine dependence of the minimum diameter of the CNT on the ion concentration for allowing ion (Na<sup>+</sup> and Cl<sup>-</sup>) entry. Three ways of restricting movement of ions were undertaken, namely, mobile cations/fixed anions, mobile anions/fixed cations and mobile cations/mobile anions. In addition, effects of charged walls on the entry of water into CNT were also investigated. In each CNT case, the system was equilibrated for  $1 \times 10^5$  steps followed by  $4 \times 10^6$  steps of production run. Whenever a negative result (i.e., ions cannot enter CNT) was seen, the simulation was resumed two more times to ensure validity of obtained results.

# 7.2.4 The narrowest CNT allowing ions (Na<sup>+</sup> and Cl<sup>-</sup>) passing through in uniform electric field

Most simulation details are the same as those discussed in subsection 2.3 except different strengths of the electric field were applied along the tube-axis direction.

# 7.2.5 Possible selectivity between $Na^+$ and $K^+$ to enter CNT with and without external electric field

Four different CNTs (7,7), (8,8), (9,9) and (10,10) with the same length of 25.7 Å were used in the simulations. In the first series of simulations, a cation was initially imposed in the middle region of CNT while the counter ion Cl<sup>-</sup> was randomly placed in the outer water reservoir so that we can test how long the cation is able to stay inside the

tube. In the second series of simulations, both  $Na^+$  and  $K^+$  were initially set in the middle region of CNT, while two Cl<sup>-</sup> were put into water reservoir to balance the positive charge. This allows us to directly compare relative stability of  $Na^+$  and  $K^+$  inside different CNTs. Lastly, a gravitational field or a uniform electric field was applied along the tube axis to calculate the conduction rate of ions through different CNTs that is immersed in a water reservoir containing  $Na^+$ ,  $K^+$  and Cl<sup>-</sup>. The conduction rates can be used to assess relative selectivity of  $Na^+$  and  $K^+$  by different CNTs.

## 7.3 Overview of Previous Work, Results and Discussion

#### 7.3.1 Possibility of unidirectional single-file water passing through (9,0) CNT

In 2007 Gong *et al.*<sup>[16]</sup> observed a unidirectional flow of water through a (6,6) CNT, by asymmetrically imposing three positive charges 0.5 Å away from the wall of CNT, implying a possibility of designing water transport devices that could function without a hydrostatic pressure gradient. Later, however, Zhuo *et al.*<sup>[17]</sup> observed an apparent bidirectional flow of water through the (6,6) CNT based on the same charge distribution, even though the accumulated net flux is still along one direction. Meanwhile, Wan *et al.*<sup>[31]</sup> discovered an orientation induced unidirectional water transport through the (6,6) CNT using MD simulation. They found that the single-file water chain inside CNT with concerted dipole orientations can collectively flip between the left state (all dipoles of single-file water molecules pointing to the left entrance of CNT) and the right state (all dipoles of single-file water molecules pointing to the right entrance of CNT) in the simulations. Interestingly, the net water flux is along the left direction when single-file water chain is in the left state even though the flow of water is still bidirectional. Likewise, the net water flux is along the right direction when the single-file water chain is

in the right state. This finding suggests a new way to achieve high flux water conduction as long as the orientation of single-file water chain can be maintained at either the left or the right state.

One simple way to control the orientation of the single-file water chain is to apply an external electric field along the tube axis. Here, we applied a varying uniform electric field with different strengths along the tube axis of (9,0) CNT to investigate the possibility of implementing unidirectional water flow in CNT. We also performed a simulation without the external field as a reference case.

From the trajectory movies we observed that the initially empty CNT was quickly filled with a single-file water chain and the filling speed increases under the electric field, consistent with previous studies<sup>[15,32]</sup>. The average number of water molecules inside CNT also increases with the strength of electric field as shown in Table 1a, indicating that the electric field can drive more water molecules into the CNT and promote water occupying the hydrophobic channel much more quickly.

The results of water flow from the left to right entrance of CNTs (Flow+), water flow from right to left entrance (Flow-), net water flux (Flux), total conduction events (Flow) and the average number of water molecules inside the CNT (<N>) are listed in Table 7-1a. In Table 7-1b the duration time in which the single-file water chain is in the left dipole state or the right dipole state is shown. In addition, we counted how many water molecules passed through the CNTs along the right direction and in the left dipole state (Left Dipole+), or along the left direction in the left dipole state (Left Dipole-), along the right direction in the right dipole state (Right Dipole+), and along the left direction in the right dipole state (Right Dipole-). The results in the reference case (E = 0) are consistent with those reported by Wan *et al.*<sup>[31]</sup>. With no external driving force, the probability of water conduction along the direction to the right entrance should be the same as that to the left entrance. Therefore, the net flux during the 50 ns simulation is only -1, very close to zero. The duration time of the left dipole state (26.13 ns) is also close to that of the right dipole state (23.87 ns). Most importantly, 155 molecules were conducted from the left to right entrance, compared to 284 molecules conducted from the right to left entrance when the single-file chain is in its left dipole state, which resulted in a net flux of 129 water molecules along the direction to the left entrance and in the left dipole state. Similarly, a net flux of 128 water molecules along the direction to the right entrance was observed in the right dipole state. Hence, a clear unidirectional net flux was seen in either the left or the right dipole state.

When a uniform electric field was applied along the tube axis direction, some new phenomena emerged. Expectedly, the right dipole state became dominant. In fact, the left dipole state completely disappeared when  $E \ge 0.02 \text{ V/Å}$ . Unexpectedly, however, the net water flux in a weaker electric field (E < 0.04 V/Å) is along the direction to the left entrance, contrast to the result in the zero field. The trend is reversed when  $E \ge 0.04 \text{ V/Å}$ , even though the net water flux decreases dramatically due to the reduction of the total conduction flow. The reduction of total flow suggests that mobility (diffusion) of water in (9,0) CNT is reduced under an external electric field, consistent with the observation by Garate *et al.*<sup>[25]</sup> in their study of CNT-assisted water self-diffusion across a lipid membrane in the absence/presence of the electric field.

Overall, our results indicate that it is possible to achieve unidirectional water flow

inside narrow CNTs (in which a single-file water chain can be formed) in the presence of an external electric field. The direction and magnitude of the net water flux can be altered by the electric field strength. These findings can be useful for future design of energy efficient CNT-based sea water desalination devices.

E(V/Å)	Flow	Flow+	Flow-	Flux	<n></n>
0.0	829	414	415	-1	6.51(2)
0.004	819	354	465	-111	6.54(1)
0.02	805	382	423	-41	6.62(1)
0.04	779	434	345	89	6.76(1)
0.2	414	222	192	30	8.25(1)
0.4	265	139	126	13	9.45(1)

Table 7-1a Conduction of water through (9,0) CNT under electric field in 50 ns

Table 7-1b Conduction of water during different dipole states in 50 ns

$E(V/\lambda)$	Left	Right	Left	Left	Right	Right
E(V/A)	Dipole(ns)	Dipole(ns)	Dipole+	Dipole-	Dipole+	Dipole-
0.0	26.13	23.87	155	284	259	131
0.004	7.42	42.58	48	87	306	378
0.02	0	50	0	0	382	423
0.04	0	50	0	0	434	345
0.2	0	50	0	0	222	192
0.4	0	50	0	0	139	126

#### 7.3.2 The narrowest CNT allowing water entry under a uniform electric field

As shown by several previous studies<sup>[15,32-33]</sup> including ours, an external electric field can drive more water molecules into CNTs and allow water occupying the hydrophobic channel more easily. In particular, Dzubiella *et al.*<sup>[33]</sup> showed that an electric field is capable of reducing the minimum diameter of hydrophobic nanochannel required for water passage. However, to what extent the minimum diameter of CNTs for water entry can be reduced has not yet been studied systematically. Here, we search for the narrowest CNT that allows water entry under a uniform electric field.

Our previous study<sup>[20]</sup> predicted that (5,5) CNT is the narrowest tube, when immersed in water, that can be filled by single-file water chain. Thus far, few studies have been reported on filling water into a CNT narrower than (6,6). Noon et al.<sup>[34]</sup> predicted that (5,5) CNT is too small to accommodate any water molecules. They used the TIP3P water model and carbon parameters taken from CHARMM force field. Similarly, Won et al.<sup>[35]</sup> reported that (5,5) CNT can be barely filled by water. Their LJ energy parameter is  $\varepsilon_{C-O} = 0.4340$  kJ/mol, which is slightly less than our value  $\varepsilon_{C-O} = 0.4784$  kJ/mol. Corry<sup>[27]</sup>, showed that (5,5) CNT can be either fully filled by water or completely empty in his MD simulation for which the carbon parameters were taken from CHARMM27 force field. However, Garate et al. <sup>[25]</sup> showed that (5,5) CNT with a length of 36.9 Å can be quickly filled with the TIP3P water using the same carbon parameters taken from CHARMM27 force field. Also, Mashl et al.<sup>[36]</sup> found that (5,5) CNT can be filled with the SPC/E water. They used a relatively large parameter  $\varepsilon_{C-O} = 0.5146 \text{ kJ/mol}$  than ours. To verify that our finding of water filling in (5,5) CNT is not too sensitive to selected water model and carbon parameters, we repeated our previous simulations<sup>[20]</sup> using TIP3P and SPC/E water models, respectively, as well as carbon parameters taken from both AMBER96 and OPLS-AA force fields. The new results still show that (5,5) CNT can be filled with water based on any combination of one of two water models with a carbon force field. In addition, we examined if the water filling of (5,5) CNT depends on the length of CNTs, when the tube length is elongated from 13.5 Å to 50.2 Å. Still, we found that the water can fill the (5,5) CNT regardless of the CNT's length.

Next, we examined the possibility of water filling in a (8,0) CNT which is slightly narrower than (5,5). As expected, water cannot fill the (8,0) CNT, consistent with our previous study<sup>[20]</sup>. Even under a 0.0434 V/Å electric field, water still cannot fill the (8,0) CNT [see Fig. 7-2(a)]. When the strength of electric field is increased to 0.0868 V/Å,

however, the 13.5 Å long (8,0) CNT can be quickly filled with a single-file water chain in a 1.25 ns simulation [see Fig. 7-2(b)]. From the trajectory movie, we can see that dipoles of all water molecules inside CNT always point to the right entrance of CNT since the applied electric field points to the left entrance. We conclude that there exists a critical strength of electric field beyond which water can fill the (8,0) CNT. In some sense, this phenomenon is similar to the voltage-induced gating mechanism of biological ion channels. The trans-membrane voltage difference between the intracellular domain and extracellular domain keeps varying in certain range. When the voltage difference is less than a critical value, the membrane-spanning ion channel is in the closed state whereas it is in the open state once the voltage difference exceeds the critical value<sup>[37]</sup>.







(b) E=0.0868 V/Å

Fig. 7-2 Water filling of a short 13.5Å (8,0) CNT under electric field

Furthermore, we investigated dependence of the critical strength of electric field on the tube length. As shown in Fig. 7-3 (a), water can no longer enter (8,0) CNT if the tube length exceeds 26.2 Å even under the 0.0868 V/Å electric field. However, water can fill the longer (8,0) CNT if the strength of electric field is also doubled (0.1736 V/Å) as shown in Fig. 7-3(b). If the tube length increases to 51.6 Å, the strength of electric field has to be doubled again (0.3472 V/Å) to allow water to enter the CNT. It seems that the critical strength of electric field required for forcing water into the (8,0) CNT is proportional to the tube length. Previously, Crozier *et al.*<sup>[38]</sup> showed that the electrostatic potential drop due to an external electric field occurs mainly at the channel membrane region while the water reservoir region remains neutral due to rearrangement of water molecules to resist the external electric field. Thus, the electric static potential drop, 3.472 V (0.0868 V/Å×40Å), across the simulation cell with a length of 40 Å mainly occurs within the 13.5 Å tube length region. As the tube length is increased to 26.2 Å while maintaining the same field strength 0.0868 V/Å, the actual electrostatic potential drop over the 26.2 Å tube length is 4.577 V (0.0868 V/Å×52.735 Å, for the cell length being 52.735 Å). However, this increased electric potential drop is still not large enough to allow water to fill the tube. As we doubled the electric field strength to 0.1736 V/Å, the resulting electrostatic potential drop across the tube-length region is up to 9.154 V (0.1736 V/Å×52.735 Å), strong enough to force water into the tube. Therefore, the actual electrostatic potential drop has to be at least doubled (9.154 V  $\geq 2\times3.472$  V) to allow water to fill the tube length is doubled.



<sup>(</sup>a) E=0.0868 V/Å

(b) E=1.736 V/Å

Fig. 7-3 Water filling of a long 26.2Å (8,0) CNT under electric field
Motivated by above findings, we further examined the possibility of water filling a
(7,0) CNT which is slightly narrower than (8,0). The results show that no water can enter
the 13.5 Å long (7,0) CNT with a diameter of 5.46 Å, even a very strong electric field

(0.868V/Å) was applied. From MD snapshots, we can see the formation of ice-like layered structure in the water reservoir region under such a strong electric field. Actually, this result can be understood because the effective internal diameter of (7,0), taken out vdW radius of 1.7Å of a carbon atom, is 5.46-1.7×2=2.06Å which is already smaller than the vdW diameter of an oxygen atom 3.15 Å. Note, however, that, a recent Raman experiment<sup>[46]</sup> has demonstrated that a single-file water chain can fill in chiral (5,3) CNT with the same diameter as (7,0) CNT. We therefore re-examined such a possibility, using both TIP3P and SPC/HW<sup>[48]</sup> models. The results show that no single-file water chain can be formed inside (5,3) tube even with an extremely strong electric field (0.868V/Å). Further, we performed the same simulations using SPC/E model and carbon parameters from OPLS-AA force fields. No qualitative differences were found. So the difference between the simulation and experiment for the narrowest CNT is likely due to the inaccuracy of water model and oxygen-carbon interaction parameter.

# 7.3.3 The narrowest CNT allowing ion (Na<sup>+</sup> and Cl<sup>-</sup>) entry with no assist of external driving force

Both Kalra *et al.*<sup>[26]</sup> and Peter *et al.*<sup>[39]</sup> showed that (6,6) CNT is impermeable for ion passage under a concentration gradient. Peter *et al.*<sup>[39]</sup> found that Na<sup>+</sup> can pass through (10,10) CNT while Cl<sup>-</sup> cannot. For a dilution solution (containing only one Na<sup>+</sup> in the supercell), they only observed entry of Na<sup>+</sup> into (10,10) CNT once during 10 ns simulation. At a higher concentration (0.2 M, five NaCl pairs), Na<sup>+</sup> can pass through (10,10) CNT. Later Liu *et al.*<sup>[40]</sup> showed that both Na<sup>+</sup> and Cl<sup>-</sup> can be driven into (15,0) and (16,0) CNTs at a high concentration of 2.26 M. More recently, Corry<sup>[27]</sup> showed, based on his MD simulation, that ions cannot pass through narrow CNTs like (5,5) and (6,6) but can pass through wider CNTs like (7,7) and (8,8) under a hydrostatic pressure difference. In particular, he found that no Cl<sup>-</sup> can pass through (7,7) CNT, but he did observe 5 Cl<sup>-</sup> passing through (8,8) CNT during 25 ns simulation, compared to 23 Na<sup>+</sup>. Hence, study of the possibility of ion passage through various CNTs is relevant to the design of CNT-based membranes for sea water desalination. In this subsection, we examined possibilities for ion passage through CNTs without applying any external driving forces such as hydrostatic pressure or electric field.

First, we consider a system which includes a single Na<sup>+</sup> (0.12 M) and a CNT with varying diameter. To keep the entire system neutral, we fixed a counter ion (Cl<sup>-</sup>) in vacuum at the boundary of the simulation cell outside the CNT. Following the same simulation condition as used by Peter *et al.*<sup>[39]</sup>, we chose (10,10) and (17,0) CNTs as two test cases. Our simulation shows that Na<sup>+</sup> cannot enter into (17,0) but can enter into (10,10) CNT. However, the Na<sup>+</sup> inside the (10,10) CNT never passed through the 13.5 Å-long tube during 30 ns simulation. These results are consistent with those of Peter *et al.*<sup>[39]</sup>. Cl<sup>-</sup> was also found to be able to enter into (10,10) in a separate test.

Next, we increased the ion concentration to 0.6 M by placing 5 Na<sup>+</sup> or 5 Cl<sup>-</sup> in the water reservoir while immobilizing five counter ions in the middle region of empty space outside CNT. Through a series of trial simulations, we found that the narrowest CNT that allows entry of Na<sup>+</sup> and Cl<sup>-</sup> is (11,0) and (7,7), respectively. We then further increased the ion concentration to 1.2 M by placing 10 Na<sup>+</sup> or 10 Cl<sup>-</sup> in the water reservoir while fixing 10 counter ions around the cell edge to keep the system neutral. Again after a series of trial simulations, we found that the narrowest CNT that allows entry of Na<sup>+</sup> and Cl<sup>-</sup> is (6,6) and (10,0), respectively.

Third, instead of immobilizing counter ions in the simulation cell, we tested another model system such that all counter charges are uniformly distributed on each atom of CNT to neutralize the entire system. This charged-wall setup was inspired by a recent simulation<sup>[41]</sup> of ion partitioning from water reservoir into charged CNT. Our simulation results show that at a low concentration (0.12 M) the narrowest CNT allowing entry of Na<sup>+</sup> and Cl<sup>-</sup> is (8,8) and (15,0), respectively. Simulation trajectories show that neither Na<sup>+</sup> nor Cl<sup>-</sup> is trapped in the CNT with a weakly charged wall. When the concentration is increased to 0.6 M, both Na<sup>+</sup> and Cl<sup>-</sup> are weakly trapped in the narrowest (12,0) CNT with a moderately charged wall. In particular we found that 3 out of 5 Na<sup>+</sup> are trapped inside the (12,0) CNT while 1 out of 5 Cl- is trapped inside the (12,0) CNT. At the highest concentration considered (1.2 M), six Na<sup>+</sup> and one Cl<sup>-</sup> are strongly trapped inside the narrowest (6,6) and (10,0) CNTs, respectively. It is interesting to see the partitioning of Cl<sup>-</sup> into a narrower (10,0), in contrast to the partitioning of Na<sup>+</sup> into the wider (6,6).

Fourth, we randomly distributed ion pairs in the water reservoir so that neither fixed counter ions nor charged walls are needed to neutralize the entire system. This is the most realistic system setup. Again, by varying the concentration from low to high, we found that the narrowest CNT that allows entry of Na<sup>+</sup> or Cl<sup>-</sup> (in most cases Na<sup>+</sup>) is (10,10) for 0.12 M solution, (13,0) for 0.6 M and (8,8) for 1.2 M, respectively. Unexpectedly, the predicted narrowest CNT (8,8) for 1.2 M solution is even wider than that (13,0) for 0.6 M solution. This can be understood as the chance of forming ion pairs is dramatically increased at the higher concentration. All the simulation results discussed above are summarized in Table 7-2, and the diameters of various CNTs considered in this

work are given in Table 7-3 as a reference.

	O $T$ $(1 + 1)$		Charged	Charged	Neutral
Concentration(M)	CNI(Na)	CNI(CI)	$CNT(Na^+)$	CNT(Cl <sup>-</sup> )	CNT(NaCl)
0.12	(10, 10)	(10, 10)	(0,0)	(15.0)	(10,10)
0.12	(10, 10)	(10,10)	(8,8)	(15,0)	(10, 10)
0.6	(11,0)	(7,7)	(12,0)	(12,0)	(13,0)
1.2	(6,6)	(10,0)	(6,6)	(10,0)	(8,8)

Table 7-2 Narrowest CNT which allows Na<sup>+</sup> or Cl<sup>-</sup> to enter

Table 7-3 Diameters of various CNTs investigated in this work

(n,m)	D(Å)	(n,m)	D(Å)	(n,m)	D(Å)
(6,0)	4.681	(6,6)	8.107	(15,0)	11.702
(4,4)	5.405	(11,0)	8.581	(9,9)	12.161
(7,0)	5.461	(12,0)	9.362	(16,0)	12.482
(8,0)	6.241	(7,7)	9.459	(17,0)	13.262
(5,5)	6.756	(13,0)	10.142	(10,10)	13.512
(9,0)	7.021	(8,8)	10.810	(18,0)	14.042
(10,0)	7.801	(14,0)	10.922		

7.3.4 The narrowest CNT allowing ion (Na<sup>+</sup> and Cl<sup>-</sup>) entry under uniform electric field

Many reverse osmosis devices are often operated under an external electric field besides a hydrostatic pressure because the applied electric field can be useful to reduce the requirement for a large hydrostatic pressure. This combination renders the whole desalination process more energy efficient. Conventionally, the permeation of water driven by the ion movement under an external electric field is called electro-osmosis. Computer simulations of osmosis, reverse osmosis and electro-osmosis can be traced back to a series of work done by Murad *et al.*<sup>[42,43]</sup> They used two semi-permeable membranes consisting of uncharged LJ particles to separate the solvent compartment and the solution compartment. The LJ length parameter for membrane particles is adjusted so that only solvent can pass through the membranes. The permeation rate of osmosis or reverse osmosis increases with both temperature and the electric field strength due to the reduced stability of ion and solvent clusters. At extremely high temperature, and/or under extremely strong electric field, the ions do permeate the membranes. Therefore, investigation of the narrowest CNT that allows entry of ions into the CNT under a uniform electric field is also very useful for designing energy efficient sea water desalination membranes with high salt rejection rate.

Similar to several simulation conditions discussed in subsection 3.3, first, we examined the possibility of a single Na<sup>+</sup> (0.12 M) entry into various CNTs under E = 0.2 V/Å, while fixing a counter ion (CI<sup>-</sup>) on the edge of the simulation cell. After a series of trial simulations, we found (6,6) is the narrowest CNT to allow Na<sup>+</sup> entry. In contrast to zero electric field, Na<sup>+</sup> not only can enter the CNT but can also pass through it from the left to right entrance, when the applied electric field points to the left entrance. When the electric field strength is increased to a higher value of 0.4 V/Å, Na<sup>+</sup> is able to conduct through the very narrow (8,0) CNT, recalling that (8,0) is the narrowest CNT that allows water molecules to fill under an electric field. When the concentration of Na<sup>+</sup> is increased to 0.6 M, the narrowest CNT that allows Na<sup>+</sup> to pass through is again (8,0) under both E = 0.2 V/Å and 0.4 V/Å. The same result is obtained for E = 0.2 V/Å and 0.4 V/Å at the highest concentration considered (1.2 M) as shown in Table 7-4.

Table 7-4 Narrowest CNT which allows Na<sup>+</sup> or Cl<sup>-</sup> to enter

under electric field with fixed counter ions

Concentration(M)	CNT(Na <sup>+</sup> ) E=0.2V/Å	CNT(Cl <sup>-</sup> ) E=0.2V/Å	CNT(Na <sup>+</sup> ) E=0.4V/Å	CNT(Cl <sup>-</sup> ) E=0.4V/Å
0.12	(6,6)	(8,8)	(8,0)	(13,0)
0.6	(8,0)	(7,7)	(8,0)	(12,0)
1.2	(8,0)	(10,0)	(8,0)	(12,0)

Next, we examined the possibility of  $Na^+$  or  $Cl^-$  entry into various CNTs in a more realistic case that ion pairs (NaCl) are placed in water reservoir with different concentrations. The simulation results are shown in Table 7-5. Again, entry of ions into narrower CNTs becomes more easily with increasing electric field strength, consistent with the conclusion by Murad *et al.*<sup>[43]</sup> Stability of hydrated ion is gradually reduced with increasing electric field strength. As a consequence, ions are partially dehydrated and can enter into the CNT more easily under stronger electric field. Moreover, ions can enter narrow CNTs more easily at higher ion concentration due to the increased probability for ions to be close to both entrances of the CNT. Note, however, that this increased probability does not always lead to more entry of ions into narrower CNTs with increasing the concentration, especially under stronger electric fields. One possible reason is that the probability of forming ion pairs is also increased at higher concentration, which may prevent ions from entering CNTs. Such a case seems more evident under stronger electric fields.

Table 7-5 Narrowest CNT which allows Na<sup>+</sup> or Cl<sup>-</sup> to enter under electric field

Concentration(M)	CNT(NaCl)	CNT(NaCl)	CNT(NaCl)	CNT(NaCl)
	E=0.02V/A	E=0.04V/A	E=0.1V/A	E=0.2V/A
0.12	(9,9)	(15,0)	(12,0)	(10,0)
0.6	(8,8)	(12,0)	(11,0)	(10,0)
1.2	(13,0)	(7,7)	(11,0)	(6,6)

7.3.5 Possible selectivity between  $Na^+$  and  $K^+$  to enter CNT with and without external electric field

One fundament question regarding potassium ion channel is why the narrow hydrophilic filter (length of 12 Å, diameter of 4 Å) prefers to select the larger-size  $K^+$  rather than the smaller-size Na<sup>+</sup>. A widely accepted explanation by biologists is that the narrow selectivity filter requires cations to dehydrate (i.e., to lose part of its hydration shell) before entering into the channel. The energy cost for dehydration must be compensated by the binding energy of cations with negative residues. The weaker binding of smaller Na<sup>+</sup> ions is not enough to compensate the energy cost for

dehydration<sup>[44]</sup>.

Recently Shao et al.<sup>[45]</sup> offered another explanation of K<sup>+</sup> preference over Na<sup>+</sup> inside narrow CNTs such as (7,7) and (8,8), based on MD simulations of hydration shells of these ions inside CNTs. They found that more water molecules prefer an ideal orientation, compared to their hydration in the bulk, such that their dipoles tend to point away from the cations as much as possible in their first hydration shell when cations are solvated inside (7,7) and (8,8) CNTs. More importantly, the increased number of water molecules in the ideal orientation is more evident for K<sup>+</sup> than for Na<sup>+</sup>. In addition, they found that the percentage of water molecules in the ideal orientation in the first hydration is directly related to the ion-water interaction energy in the first hydration shell. Hence, a higher percentage of ideal orientation is a manifestation of stronger ion-water interaction energy. Therefore, inside narrow (7,7) or (8,8) CNT, it is more favorable to stabilize  $K^+$  than  $Na^+$ because the increased percentage of ideal orientation or the increased ion-water interaction energy, compared to the bulk, is more substantial for  $K^+$ . On the contrary, it is more favorable to confine  $Na^+$  than  $K^+$  inside a wider (9,9) or (10,10) CNT because the decreased percentage of ideal orientation or the decreased ion-water interaction energy, compared to the bulk, is more substantial for  $Na^+$ .

One possible reason for  $K^+$  preference over  $Na^+$  for entry into CNT is due to the higher energy cost for  $Na^+$ 's dehydration outside the channel than for  $K^+$ 's, rather than due to the weaker binding of smaller  $Na^+$  ions inside the channel. Although dehydration of  $Na^+$  and  $K^+$  outside the channel can be compensated by the hydrations of  $Na^+$  and  $K^+$  inside the channel, the dehydration cost can be better compensated by the hydration gain for  $K^+$ . Even though the hydration energy of  $Na^+$  is greater than that of  $K^+$  inside the

channel,  $Na^+$  has to overcome a much higher dehydration cost than  $K^+$  in the bulk before entering the channel. In any case, the CNT-based explanation may shed some light on the selectivity mechanism of biological potassium channel.

Nevertheless, several technique issues are still not fully resolved regarding previous explanation of K<sup>+</sup> selectivity inside potassium channel based either interaction energy criterion<sup>[44]</sup> or the first-hydration model by Shao *et al.*<sup>[45]</sup> First, calculation of the radial distribution function (RDF) inside nanotubes can be problematic. The standard method to calculate RDF is to count the number of particles inside a spherical shell, which is then divided by the ideal number of particles within the same shell. This method works well for homogeneous system like bulk water. However, for inhomogeneous systems such as confined water in nanotubes, calculation of the ideal number of particles within a spherical shell can be troublesome because some part of the spherical shell will be beyond the nanotube region if the radius of a spherical shell is larger than that of nanotube. In principle, one could exclude the volume of partial spherical shell outside the nanotube while calculating the ideal number of particles. However, it is challenging to calculate such a volume. Shao et al.<sup>[45]</sup> chose not to consider the exclusion of such a volume, which will render their calculated RDF to approach zero instead of one near the potential cutoff distance. Second, the Gibbs free energy should be considered as the criterion to determine whether Na<sup>+</sup> or K<sup>+</sup> is preferentially solvated inside a channel because the entropy contribution can be important as well besides the ion-water interaction energy. For example, Shao et al.<sup>[45]</sup> showed that the ion-water interaction energies of both  $Na^+$  and  $K^+$  inside (7,7) and (8,8) are stronger than the corresponding values in the bulk. In other words, ions seem like to stay inside CNTs rather than in the

bulk because this would lead to the system with a lower total energy. However, this is not the case based on our test simulations of ion's stability inside various CNTs. Third, Shao et al.<sup>[45]</sup> only calculated the interaction energy between ion and its first hydration shell (reported in their Table 3). In principle, one should use the interaction energy between a cation and all water molecules in the system to examine relative stability of K<sup>+</sup> vs. Na<sup>+</sup> since the second hydration shell and the rest water molecules can contribute to the interaction as well, especially for the long-range electrostatic interaction between the ion and partial charges of water molecules. Fourth, it may not be sufficient to examine the selectivity between Na<sup>+</sup> and K<sup>+</sup> only based on thermodynamic perspective because the conduction of ions through CNT is a dynamic process. For example, it may be more energetically favorable to confine  $K^+$  rather than  $Na^+$  inside a narrow (7.7) CNT from thermodynamic viewpoint, but the confined  $K^+$  may be trapped in a deeper local minimum, which could also block its conduction, whereas the confined Na<sup>+</sup> may move more easily in the channel. MD simulations appears to be effective to assess relative selectivity of ion conduction through nanochannel as  $Na^+$  and  $K^+$  can be placed in the water reservoir region. To this end, we systematically examined relative selectivity between Na<sup>+</sup> and K<sup>+</sup> passing through (7,7), (8,8), (9,9) and (10,10) CNTs located between two parallel graphene membranes.

First, we examined the residence time of Na<sup>+</sup> and K<sup>+</sup> inside each of four CNTs by initially placing either one Na<sup>+</sup> or one K<sup>+</sup> in the center of the CNT that is already filled by water, with one Cl<sup>-</sup> randomly placed in the water reservoir region. The tube length of all CNTs is the same (25.7Å). Two sets of potential parameters were used: The first set is the SPC/E water model together with carbon LJ parameters taken from OPLS-AA force field, which was also used by Shao *et al.*<sup>[45]</sup>. The second set is the TIP3P water model together with carbon LJ parameters taken from AMBER96 force field, which has been used in our study. The residence time is recorded by monitoring when the cation leaves the CNT and enters the water reservoir region. The obtained residence times for Na<sup>+</sup> and K<sup>+</sup> in four CNTs with two different parameter sets are listed in Table 7-6. Our results support the conclusion by Shao *et al.*<sup>[45]</sup> in that K<sup>+</sup> appears more stable inside (7,7) and (8,8) but less stable inside (9,9) and (10,10) compared to Na<sup>+</sup>, because K<sup>+</sup> stays much longer than Na<sup>+</sup> inside narrower CNTs and much shorter inside wider CNTs. However, we found that this behavior may depend on the potential parameters used as illustrated based on TIP3P-AMBER96 parameter set. Eventually, both K<sup>+</sup> and Na<sup>+</sup> leave the narrow CNTs and enter into the water reservoir region, even though the ion-water binding is stronger inside (7,7) and (8,8) than that in the bulk.

Table 7-6 Residence times of Na<sup>+</sup> and K<sup>+</sup> with one cation inside CNT initially

SPC/E-OPLS-AA	Na <sup>+</sup> (ps)	$K^{+}(ps)$	TIP3P-AMBER96	Na <sup>+</sup> (ps)	K <sup>+</sup> (ps)
(7,7)	225	263	(7,7)	210	165
(8,8)	308	369	(8,8)	1250	258
(9,9)	1250	728	(9,9)	453	258
(10,10)	1250	358	(10,10)	768	195

Second, we applied an external electric filed along the tube axis direction to examine conduction capabilities of Na<sup>+</sup> and K<sup>+</sup> through the CNTs. The obtained results are listed in Table 7-7. As expected, the minimum electric field required to allow entry of ions through CNTs also increases with the decrease of tube diameter. For SPC/E-OPLS-AA parameter set, the results are mostly consistent with those of Shao *et al.*<sup>[45]</sup> except in the case of (7,7). Again, it appears that the narrower CNTs prefer K<sup>+</sup> while wider CNTs prefer Na<sup>+</sup>, but this conclusion apparently depend on the chosen parameter set as shown by results based on theTIP3P-AMBER96 parameter set.

SPC/E-OPLS-AA	$Na^+$	$K^+$	TIP3P-AMBER96	$Na^+$	$K^+$
(7,7) E=0.2V/Å	5	5	(7,7) E=0.1V/Å	6	4
(8,8) E=0.2V/Å	8	12	(8,8) E=0.1V/Å	7	9
(9,9) E=0.08V/Å	8	5	(9,9) E=0.04V/Å	9	10
(10,10) E=0.04V/Å	16	9	(10,10) E=0.02V/Å	18	24
~					

Table 7-7 Conduction of Ions through CNTs in 40 ns under an electric field

#### 7.4 Conclusions

We have performed five series of MD simulations to examine trend and possibility of water/ions entry into various CNTs. We confirm that in the absence of an external electric field, unidirectional and short-time water flow through narrow CNTs in the form of single-file water chain can be observed. We also find the long-time unidirectional water flow through narrow CNTs under an electric field. The direction and magnitude of the net water flux through the CNTs can be controlled by the strength of the electric field. We predict the narrowest CNT that allows entry of water under a strong electric field, is (8,0). The critical field strength for forcing water into the CNTs is proportional to the tube length. In addition, we have studied the narrowest CNTs that allow ions (Na<sup>+</sup> and Cl<sup>-</sup>) to enter into, with and without electric field, as well as the effects of ion concentration and field strength on the obtained results. Finally, we confirm the prediction by Shao *et al.*<sup>[45]</sup> that narrow CNTs such as (7,7) and (8,8) prefer  $K^+$  while wider CNTs (9,9) and (10,10) prefer Na<sup>+</sup>. However, we also find that this conclusion can be sensitive to the chosen model parameter set. Our study may shed some light on the transportation of water/ions through biological ion channels and may be helpful for future design of highly efficient CNT-based membranes for sea water desalination.

## 7.5 References

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## **Concluding Remarks**

In retrospective of the entire dissertation, my Ph.D research basically covers two directions. The first one is to study thermodynamic properties of simple model fluids such as Lennard-Jones and Stockmayer models. The specific thermodynamic properties investigated include the melting temperature and surface tension involving both liquidvapor and liquid-solid interfaces. Although the results obtained from the simple models cannot be directly compared with experimental data, simple models are particularly useful as benchmark to test the validity of the calculation methods for various properties such as Irving-Kirkwood method for liquid-vapor surface tension, Superheatingundercooling, cleaving wall and fluctuation methods for liquid-solid surface tension. In the case of melting temperature calculations for four water models we found large difference of the calculated melting temperature among different water models. Although TIP5P model gives a melting temperature closest to the experimental value, it does not mean it is the best model to represent water because every model has its pros and cons to describe different properties. Therefore, model dependence is the major limitation of classical mechanics simulations. One promising solution is the usage of modelindependent quantum mechanics calculations. However, a recent *ab inito* MD simulation based on DFT theory also gave a melting temperature of water much higher than the experimental value. In other words, simplified quantum mechanics method such as DFT may not precisely reflect the interactions between the actual molecules. In principle, quantum mechanics methods based on directly solving Schrodinger equation are supposed to give correct description of various interactions between real molecules. However, they may be limited by the small system size affordable to current computational facilities.

The second direction of my Ph.D research is to investigate water and ions confined in carbon nanotube. In particular, I found the transition from low density heptagonal ice nanotube to medium density core/sheath composite ice tube, and to the high density double-walled ice helix in the same (17,0) carbon nanotube as we increased the water density. Such findings are not sensitive to the selected models based on our tests using different models and help us understand why water is the most complicated substance in the world though the form of a single water molecule is quite simple. In addition, I also examined the possibilities of water and ions to enter and pass various carbon nanotubes. Some of our findings are not model dependent such as the controllable water filling inside a narrow (8,0) tube by adjusting strength of an external electric field. However, some results are definitely dependent on the chosen models such as the relative selectivity between Na<sup>+</sup> and K<sup>+</sup> inside four different carbon nanotubes. So, the understanding of the selectivity K<sup>+</sup> and Na<sup>+</sup> at molecular level is still not clear. In the future, we would like to use *ab inito* MD simulation program such as CP2K to further examine such selectivity issue.