Multiscale modeling of clay-water systems

by

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Submitted to the Department of Civil and Environmental Engineering in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the field of Civil and Environmental Engineering

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Abstract

The engineering properties of soils are highly affected by clay content and clay-water interactions. However, existing macro-scale continuum models have no length scale to describe the evolution of the clay microstructure and its role in affecting macroscopic properties. This research proposes a bottom-up multiscale modeling approach to understand the physics underlying macroscopic clay behavior.

Atomistic models are developed to understand clay-water interactions using the ClayFF force field. We simulate water adsorption between clay layers for a reference mineral, Wyoming montmorillonite (Na-smectite) using molecular dynamics simulations. The elastic properties of the system are found to vary with the hydration state (amount of interlayer water) and can be well-approximated using cross-anisotropic symmetries. The simulated adsorption isotherm and stiffness are compared with available experimental measurements.

We develop a perturbation approach to investigate the free energy associated with relative positions of two clay platelets in water. The free energy functions for edge-edge and face-face particle associations are used to calibrate the Gay-Berne (GB) potential that represents each platelet as a single-site ellipsoidal body. A coarse-graining upscaling approach then uses the GB potentials and molecular dynamics to represent the meso-scale aggregation of clay platelets (at submicron length scale). Results from meso-scale simulations obtain the equilibrium/jamming configurations for mono-disperse clay platelets. The results show aggregation for a range of clay platelets dimensions and pressures with mean stack size ranging from 3-8 platelets. The particle assemblies become more ordered and exhibit more pronounced elastic anisotropy at higher confining pressures. The results are in good agreement with previously measured nanoindentation moduli over a wide range of clay packing densities.

The current research represents an important step forward towards multiscale modeling of soils and can be used to study any system composed of platy constituents.

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I wish to thank Professor Andrew Whittle and Professor Roland Pellenq for their valuable advice and insights in supervising this work. Being in Professor Whittle’s lab makes you work harder as he never lets you go out of the group meeting until you understand what you are talking about. I thank him for giving me the room to define my own research problem and for his support and guidance during my stay at MIT. I have learned from the way he shapes the story of the research. Your manuscript becomes fantastic after his review and comments. He is a role model for me to define and tackle new problems. Another aspect that I found amazing to look at and learn from in Professor Whittle’s character is his leadership in both small and large scale as the head of a research group and the head of the department. I hope I have the opportunity to follow his approach.

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It is always good to look out of your home department. You may find wonderful and knowledgeable people like Professor Gregory Rutledge who are willing to help you. I thank him to accept being in my research committee. I am grateful for the comments and suggestions he made during our meetings. The one thing I would like to emphasize about him is his en-
thusiasm for teaching. You can feel eagerness in his eyes whenever he teaches you something and you learn it.

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Chapter 1

Introduction

This thesis follows a multi-scale modeling 'bottom-up' approach to understand and potentially modify or control physical or engineering properties of clays at the macro/continuum-scale. At the finest scale we use atomistic simulations to model the clay-water system and then we present an upscaling approach to investigate the aggregation of clay platelets. The following sections briefly discuss the importance of studying clay in civil engineering, soil science and material modeling and introduce the multi-scale modeling approach used in this research.

1.1 Atomistic structure of clay

Clay minerals have a layered structure. Each layer consists of a combination of two types of mineral sheet referred to as silicon tetrahedra and aluminum octahedra (Figure 1-2). The unit structure of the silicon tetrahedral sheet comprises four $O^{2-}$ around a central $Si^{4+}$, and the sheet is formed by arranging Si tetrahedral units in a hexagonal pattern through sharing three of the four oxygen atoms. The basic unit of the aluminum octahedral sheet is a unit comprising six $O^{2-}$ or $OH^{1-}$ around a central aluminum ion.

The sheet stacking sequence and interlayer bonding define different clay types (see Figure 1-1). In this research, we consider montmorillonite, a member of the smectite clay group. Smectites are 2:1 swelling clay minerals, i.e., two tetrahedral sheets with unshared $O$ atoms come around a central octahedral sheet which has two planes of unshared $O$ atoms and
additional hydroxyl groups (OH) to form a clay layer (TOT) (Figure 1-3). Due to isomorphous substitutions within clay sheets, clay layers have net negative charge which is compensated by exchangeable cations between layers. For example, $\text{Al}^{3+}$ may substitute $\text{Si}^{4+}$ in the tetrahedral sheet and $\text{Mg}^{2+}$ may substitute $\text{Al}^{3+}$ in the octahedral sheet. The amount of isomorphous substitution is characterized by Cation Exchange Capacity (CEC). Typical CEC of clay minerals are summarized in Table 1.1.

This research focuses on Na-Wyoming montmorillonite which has substitutions in all three sheets (CEC = 102 (mequiv/100 g)) and negative charge of clay is balanced by Na$^{1+}$ ions between layers (Figure 1-3). Adsorption of water molecules by this system accompanied by increase in layer spacing or swelling of clay mineral. Swelling of clay significantly impacts structural and mechanical properties of soil.
### Table 1.1: Typical Cation Exchange Capacity (CEC) of clay minerals, according to Mitchell and Soga (1976).

<table>
<thead>
<tr>
<th>Minerals</th>
<th>CEC (meq/100g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaolinite</td>
<td>3-15</td>
</tr>
<tr>
<td>Halloysite</td>
<td>5-40</td>
</tr>
<tr>
<td>Montmorillonite</td>
<td>80-150</td>
</tr>
<tr>
<td>Vermiculite</td>
<td>100-150</td>
</tr>
<tr>
<td>Illite</td>
<td>10-40</td>
</tr>
</tbody>
</table>

**Figure 1-2: Basic units of clay sheets:**

(a) Si Tetrahedral unit  
(b) Al Octahedral unit

### 1.2 Clay usage and properties

The chemical and physical properties of soils are strongly affected by their clay content. In a soil composed of sand or silt particles (round and angular particles dominated by quartz) the contact area is small, the system does not swell or shrink upon wetting or drying, particles are quite inactive (not affected by ionic concentration) since they are neutral and have small surface for interaction, they remain as single grains (don’t aggregate to create secondary structures) by changing concentration or applying confining pressure. All of these properties change with the presence of clay minerals. Clay minerals have large surface area. Table 1.2 summarizes typical Specific Surface Area (SSA) of clay minerals. Montmorillonite platelets can have SSA between 50-120 m²/g.
The smectite clay swells upon water adsorption. They are active and influenced by the ionic concentration in the pore water due to isomorphous substitutions inside their crystal structure. Clays can aggregate by increasing concentration of particles or applying external pressure. Aggregates of montmorillonite can have SSA between 700-840 m²/g (see Table 1.2). All of these properties makes them interesting for different applications in industry or create problems as will be explained:

- The CEC determines the activity of the clay mineral. The substitutions in Wyoming Na-montmorillonite studied in this research corresponds to CEC of 102 mequiv/100 g. According to Mitchell and Soga (1976), CEC of montmorillonite varies between 80-150 mequiv/100 g (see Table 1.1). The layer charge along with very large surface area for interaction are useful properties in some industries including: radioactive
waste disposal to adsorb radioactive cations such as $\text{Cs}^{1+}$ and $\text{Sr}^{2+}$ (Madsen, 1998; Cuadros, 2008), environmental protection to adsorb toxic metals (which cannot be processed by living organisms) such as $\text{Cd}^{2+}$ and $\text{Zn}^{2+}$ from water (Srinivasan, 2011; Bhatnagar, 2013), binding agent (at low water to clay ratio) to bind foundry molding sand and animal feed (Clem and Doehler, 1961), drug carrier to deliver and release the drug (Zheng et al., 2007; Park et al., 2008), carrier for agricultural insecticides and adsorption of animal waste (Murray, 1999).

- Swelling potential of smectite can be problematic for foundations and subgrades where there are seasonal changes in water content (due to rainfall, evaporation, etc.). The potential damage due to swelling requires: (1) the presence of swelling montmorillonite (2) natural water content close to the plastic limit ($W_p$); and a source of water (Holtz and Kovacs, 1981). Swelling potential can be reduced by replacing existing cations with high swelling potential (such as Na$^{1+}$ or Li$^{1+}$) with ones that can stabilize the clay structure (such as K$^{1+}$ or Ca$^{2+}$). Swelling can also block macropore pathways of liquids, fracturing fluids and hydrocarbons resulting in a decrease in the production of hydrocarbons from wells.
Swelling clays (at high water to clay ratio) are often used as drilling fluids in the oil and gas industry or for excavation support in construction of diaphragm walls,

<table>
<thead>
<tr>
<th>Minerals</th>
<th>(SSA) (m$^2$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaolinite</td>
<td>10-20</td>
</tr>
<tr>
<td>Halloysite</td>
<td>35-70</td>
</tr>
<tr>
<td>Montmorillonite</td>
<td>50-120 (primary), 700-840 (secondary)</td>
</tr>
<tr>
<td>Vermiculite</td>
<td>40-80 (primary), up to 870 (secondary)</td>
</tr>
<tr>
<td>Illite</td>
<td>65-100</td>
</tr>
</tbody>
</table>

Table 1.2: Typical Specific Surface Area (SSA) of clay minerals, according to Mitchell and Soga (1976).
drilled shafts, etc. In this application, a thin filter cake forms on the walls of the excavation and prevents ingress ground water or bleed of drilling fluid/slurry (Odom, 1984; Murray, 1999). Swelling clays are also widely used as barriers for the movement of liquids such as in earth dams or landfills (Murray, 1999) or barriers for isolation of radioactive wastes (Gens, 2003).

- The plate-like geometry of the clay at nanoscale and its active properties make it a candidate to design new hybrid materials such as polymer clay nanocomposites (Güven, 2009). The hybrid material shows substantial improvements in mechanical, thermal, barrier and fire retardant properties (Bitinis et al., 2011). Recently, a new class of polymers called biopolymers (which are renewable and biodegradable) are the subject of research for sustainable development applications. For example, the reinforcement of biopolymers with clays makes an alternative material for conventional polymers with wide range of applications in different areas such as food packaging, environmental remediation and fire retardant (Zhu and J Njuguna, 2013).

While results of this research can be applied in some of the areas mentioned above, the main goal is to present a bottom-up multiscale framework for modeling clay materials.

1.3 Multiscale modeling

Any system can be studied at different levels with different resolutions in time and length scales. Figure 1-4 shows five scale modeling of the soil system:

- Quantum scale

This scale deals with chemical reactions (i.e., bond formation or bond breaking like formation of silicon dioxide, dissociation of water molecules or ionic/covalent bonding within tetrahedral or octahedral sheets). This is achieved by modeling electronic configurations and band structures (i.e., ranges of energy levels occupied by electrons). Behavior of the matter at this scale is modeled based on first principles of quantum mechanics. For this reason, the methods are also called ab-initio methods. Electronic motions in atoms and molecules are calculated by approximate solution of the
Figure 1-4: Multiscale modeling.

Schrödinger equation using density functional theory. The results of calculations at this scale are used to parametrize force fields (Section 2.9) that are then used at the atomistic scale.

- **Atomistic scale**

At this scale, interactions between groups of atoms are studied using molecular simulation techniques and empirically calibrated force fields. Two simulation methods can be used in this scale: Molecular Dynamics (MD, Section 2-4) and Monte Carlo (MC, Section 2-7). MD is based on solving classical Newton equations of motion for all the atoms in the system. MC is based on exploring the energy surface by random perturbation of the system. Thermodynamic properties (e.g., pressure, temperature), structural properties (e.g., atomistic structure of clay, water and ions), transport prop-
erties (e.g., diffusion coefficient) and mechanical properties can be calculated at this scale. Coarse Graining (CG) methods are used to transfer information to larger scale. These methods, average out certain degrees of freedoms and replace them with their mean effects. For instance, to study interaction of clay platelets in water, the screening effect of water molecules and ions are averaged out and they are removed from the model at the meso-scale. Moreover, all intramolecular interactions are frozen and each platelet is modeled as a rigid ellipsoidal (oblate) particle to simulate aggregation of clay layers.

- **Meso-scale**

  The Meso (or intermediate) scale refers to length and time intervals that lie between atomistic and micro-scale. Formation of microstructures with mesopores and grain boundaries are studied at this scale. Interaction of clay platelets with the effects captured from atomistic scale forms microstructure within the clay that are used to connect to the Micro-scale. Both simulation methods (MD and MC) can be used at this scale. At this scale particles can have non-spherical rigid bodies with orientational degrees of freedom and trajectories of motion are generated by solving Newton-Euler equations of motion. The mechanical properties of the model are calculated and used as the input parameters for the micro-scale models.

- **Micro-scale**

  This is the last intermediate scale to connect to the macro-scale. What we have calculated in the previous scale doesn’t have the effects of inclusions (solid grains of quartz, black objects in Figure 1-4) and air bubbles (white objects in Figure 1-4). Using micromechanics methods of homogenization, such as Self-Consistent Schemes (Hill, 1965) or Mori-Tanaka Method (Mori and Tanaka, 1973; Benveniste, 1987), we calculate effective medium approximation of the soil properties to be used it in the macro-scale models. For granular materials such as silt or sand, discrete element methods (based on Newtonian mechanics and balance of linear momentum at the
particle level) are used to infer material properties of assemblies of particles from inter-particle interactions (Cundall and Strack, 1979; Andrade and Avila, 2012).

- **Macro-scale**
  Macro-scale is the scale of engineering practice. Finite element and discrete element are methods of formulating and solving engineering problems at this scale. Behavior of the matter is modeled with constitutive relations by using input parameters from the meso-scale modeling. For example, excavation of a tunnel, settlement of the surface and deformation of the lining can be studied at this scale.

There are two main advantages in using the bottom up approach:

- By studying the underlying mechanisms of material behavior, we can address changes in the large scale starting from more fundamental scales. This is the initial step toward designing physically-based models of macroscopic behavior.

- We can manipulate the material at the atomistic scale to design a new material with desired properties at the macro-scale.
  By upscaling, both spatial and temporal resolution of the analysis are decreased. As a result, we can model phenomena at larger scales in time and space (such as the formation of shear band during large deformation of soil masses).

### 1.4 Research objectives

The goal of this research is to study clay-water systems at atomistic-scale in order to understand water adsorption mechanisms during stepwise swelling and their effects on mechanical properties. At the meso-scale we consider aggregation of clay layers, interaction of clay particles and formation of clay microstructure leading to different mechanical properties using molecular simulation techniques. Different aspects of the problem can be summarized as
The existing literature on water adsorption has focused on simulations that assume the clay layers are rigid and reported only on volume changes as a result of increase in basal layer spacing (Boek et al., 1995a; Tambach et al., 2004b). The current research relaxes the rigid layer assumption using the CLAYFF force field (Cygan et al., 2004) which uses partial charges and has been calibrated for clay-water interactions. The CLAYFF potential allows all crystallographic cell parameters which define cell dimensions and all atomic positions to vary during molecular simulations. This sampling leads to comprehensive exploration of the phase space to find the most probable configuration of the system. The CLAYFF force field has been used previously to study interlayer swelling (Kirkpatrick et al., 2005a), structure, dynamics and energetics of mineral-water interface (Kalinichev et al., 2007), x-ray diffraction patterns (Lombardo et al., 2008), elastic constants (Thyveetil et al., 2007), vibrational spectra (Kirkpatrick et al., 2005b), dielectric properties (Wander and Clark, 2008), thermomechanical properties (Mazo et al., 2008) and sorption and diffusion of organic molecules (Zhao and Burns, 2013).

Using molecular simulation techniques with the CLAYFF force field, we are able to study the adsorption isotherm and changes in elastic properties of clay at different hydration states, structure of adsorbed water and ion distribution in the system at atomistic scales. These simulations are performed for Wyoming Na-montmorillonite and the force field is validated with available experimental swelling measurements for this type of clay.

To date there have been no meso-scale models of clays derived from atomistic simulations. The current research develops potential of mean force for clay platelets and simulates formation of aggregates through interaction of clay platelets. The proposed potential function is derived from results of atomistic simulations to model interaction between large clay platelets. We have characterized clay particles and reported the
change in the mechanical properties of the system due to changes in the microstructure of clay.

1.5 Structure of presentation

The dissertation is divided into five chapters.

After the introductory chapter, we have a review of the molecular simulation techniques in Chapter 2. The Molecular Dynamics (MD) and Monte Carlo (MC) methods will be presented. Also, some key concepts from the statistical mechanics are described.

In Chapter 3, atomistic simulation of clay-water system is presented. In this chapter interaction of Wyoming Na-montmorillonite with water at different levels of hydration is studied. After simulation of adsorption-isotherm, the swelling mechanism of the clay is explained. Nanoscale elastic properties of the clay-interlayer water system are calculated and the change of the stiffness upon water adsorption is discussed.

Chapter 4, includes the mesoscale simulation of clay-water system. In this chapter, face-to-face and edge-to-edge interactions of Wyoming Na-montmorillonite nanoplatelets were studied and used to build a model system for clay aggregates at the meso-scale. Then we performed simulations at the meso-scale. The microstructure of the stabilized system was characterized and the full elastic properties of the system was reported.

Chapter 5 concludes the dissertation by summarizing the work done in this thesis, presenting the key findings and discussing possible extensions for future research in this area.
Chapter 2

Molecular simulation

2.1 Introduction

This chapter explains the basics of molecular simulation techniques. Classical text books (Allen and Tildesley, 1989; Haile, 1992; Leach and Schomburg, 1996; Frenkel and Smit, 2001; Rapaport, 2004; Hinchliffe, 2005; Tuckerman, 2008) cover the theory and applications of the method in detail.

In molecular simulation we are modeling the interactions in a system of particles. A particle can be an atom when we are in the atomistic scale or some collection of atoms (like one platelet of a clay mineral) when we are modeling at the meso-scale.

There are two types of molecular simulation, Molecular Dynamics (MD) and Monte Carlo (MC) methods. The Molecular Dynamics method shows the time evolution of particles by numerical integration of Newton-Euler equations of motion and are described in section 2.5. At each step, positions (coordinates and orientations) and velocities (linear and angular) of the particles are calculated. The forces are derived from the potentials acting between particles (i.e., force field). Section 2.9 gives an example of a force field used to investigate clay-water interactions. MD can be used to study both equilibrium and time dependent properties of the system.

In the Monte Carlo (MC) simulation method particles are moved randomly, to represent a target probability distribution consistent with the desired state of the system. As a result, MC is not deterministic (i.e., the system does not evolve following a physical path and real
2.2 State variables

The thermodynamic state of a system is defined by a set of parameters called state variables. The internal energy $E$, the volume $V$, the number of particles $N$, the temperature $T$, the pressure $P$ and the chemical potential $\mu$ are the six main state variables. State variables are divided into extensive and intensive variables. Table 2.1 summarizes three pairs of state variables. Extensive variables are size dependent and determine the total amount of material in the system. Their conjugate intensive variables are size independent and each one indicates an average measure of a property for the system. The full thermodynamic state of the system is known by specifying one variable from each pair. There must be at least one extensive variable in the ensemble to set the system size. The combination of three independent specified variables defines the statistical ensemble. There are four commonly used ensembles in statistical mechanics:

- Micro-canonical ensemble, NVE
- Canonical ensemble, NVT
- Isobaric-isothermal ensemble, NPT
• Grand Canonical ensemble, $\mu VT$

When an independent variable is fixed, its associated dependent variable fluctuates. For example in the Canonical ensemble the number of molecules, temperature and volume are fixed and their corresponding dependent variables, the chemical potential, internal energy and pressure fluctuate.

## 2.3 Statistical ensembles

Each macroscopic state of the system is characterized by a collection of microscopic configurations. Distribution of microstates with identical macroscopic or thermodynamic state is called ensemble. Figure 2-1 shows schematic representation of an ensemble of ellipsoidal particles.

Molecular dynamics generates microscopic information of the system: positions and momentums $(q, p)$. Bold-face letters denote vectors, i.e., $(q, p) = (q_i, p_i)$, $i = 1 \cdots N$, where $N$ is the total number of particles. For a spherical particle this set represents six members (three coordinates, three linear momentums) and for a non-spherical particle represents twelve members (three coordinates, three orientations, three linear momentums and three
angular momentums). Therefore each state of the system is characterized by the \((q, p)\) set in a multidimensional imaginary space known as phase space. For a system with \(N\) particles this space has \(6N\) or \(12N\) (spherical or non-spherical) dimensions with positions and momentums of all the \(N\) particles as variables. A single point in the phase space represents state of the system. Molecular dynamics produces a series of such points in the phase space as a function of time.

In order to generate statistical ensemble indicating a specific state of a system, the probability of occurrence of a particular state should follow an appropriate probability distribution. In the following sections some of the most important statistical ensembles will be reviewed.

### 2.3.1 Micro-canonical, NVE

In Micro-canonical ensemble a set of \(N\) particles is enclosed in a thermally isolated box with volume \(V\). This ensemble is characterized by \((NVE)\) symbol representing constant number of particles \(N\), constant volume \(V\) and constant energy \(E\). In this ensemble the conjugate intensive variables, pressure \(P\), and temperature \(T\) of the system fluctuate during the simulation. Figure 2-1 can be a schematic representation of the Micro-canonical ensemble assuming no energy exchange between inside and outside of the box.

We number microstates with the index \(i = 1 \cdots \Omega\) where \(\Omega\) is the number of accessible states with energy \(E\). In a Micro-canonical system, all states have equal probability so the probability of the system to be in a particular state \(i\) will be \(\pi(q_i, p_i) = \frac{1}{\Omega(N, V, E)}\).

\(\Omega(N, V, E)\) is also called the partition function of the Micro-canonical ensemble. The function specifies how particles are partitioned throughout accessible states and is calculated by summation over all possible energy states of the system in phase space.

\[
\Omega(N, V, E) = \frac{1}{N! h^{3N}} \int \delta [H(q, p) - E] \, dq \, dp
\]

(2.1)

Where \(H\) is the Hamiltonian of the system, \(h\) is Planck's constant and prefactor \(h^{3N}\) comes from the consistency between quantum and classical mechanics. \(\delta(\cdot)\) is Dirac delta function. The Hamiltonian is the total energy of the system which is sum of the kinetic \(K(p)\) and
potential energies $U(q)$:

$$H(q, p) = K(p) + U(q)$$

The equilibrium state of this ensemble is characterized by maximum entropy ($S$). The following equation relates the entropy of the Micro-canonical system to its partition function:

$$\text{NVE, Entropy: } S = k_B \ln \Omega(N, V, E)$$

where $k_B$ is the Boltzmann's constant. The constant creates the link between macroscopic and microscopic physics. Macroscopically, the ideal gas law states:

$$PV = nRT$$

the product of pressure ($P$) and volume ($V$) is proportional to the product of amount of substance ($n$, in moles) and temperature ($T$). $R$ is the gas constant ($8.3144621(75)$ JK$^{-1}$mol$^{-1}$).

Introducing the Boltzmann’s constant, the ideal gas law can be written in an alternative form:

$$PV = NK_BT$$

where $N$ is the number of molecules of gas. The left side of the equation is a macroscopic representation of the amount of energy specifying the state of the bulk gas. The right side divides the energy by $N$ units, one for each gas particle, each of them has an average kinetic energy of $K_BT$.

Entropy can be seen as a measure of the system disorder. Larger entropy means there are more possible states for the system.

### 2.3.2 Canonical, NVT

In order to calculate properties of an isothermal system we use Canonical ensemble (NVT). In this ensemble, system is in contact with a heat reservoir at temperature $T$ and the number of particles $N$, the volume $V$ and the temperature $T$ of the system are constant. Figure 2-1 can be a schematic representation of the Canonical ensemble assuming constant temperature
in all of the configurations.

In this ensemble the probability of finding the system in a particular state \(i\) with energy level \(H_i\) is given by:

\[
\pi(H_i) = \frac{\exp(-\beta H_i)}{Q(N,V,T)}
\]  
(2.6)

where \(\beta = (k_B T)^{-1}\) and \(Q(N,V,T)\) is the Canonical partition function:

\[
Q(N,V,T) = \frac{1}{N!h^{3N}} \int \exp (-\beta \mathbf{H} (\mathbf{q}, \mathbf{p})) \, d\mathbf{q} \, d\mathbf{p}
\]  
(2.7)

The equilibrium state of this ensemble is characterized by minimum Helmholtz free energy, \(A\). The following equation relates the Helmholtz free energy to the Canonical partition function:

\[
\text{NVT, Helmholtz free energy: } A = -k_B T \ln Q(N,V,T)
\]  
(2.8)

### 2.3.3 Isobaric-isothermal, NPT

The isobaric-isothermal ensemble represents a system with fixed number of particles \(N\), pressure \(P\) and temperature \(T\). In this ensemble the system is surrounded by flexible walls so the volume can fluctuate. Figure 2-2 shows an example of (NPT) ensemble. In this ensemble

![Figure 2-2: System of particles in isobaric-isothermal ensemble. The number of particles, the pressure and the temperature are constant. The internal configurations, the particle velocities, energy and volume of the system fluctuate.](image)
the probability of finding the system in a particular state \( i \) with the volume \( V_i \) at energy level \( H_i \) is given by:

\[
\pi(H_i, V_i) = \frac{\exp\left(-\beta(H_i + PV_i)\right)}{\Delta(N, P, T)}
\]  

where \( \Delta(N, P, T) \) is the isobaric-isothermal partition function:

\[
\Delta(N, P, T) = \int C Q(N, V, T) \exp\left(-\beta PV\right) dV
\]

where \( C \) is a normalization factor with dimension \([L^{-3}]\). There are several choices for \( C \) to make partition function a dimensionless quantity, e.g., \( C = \frac{N}{V} \), or \( C = \beta P \). The difference vanishes in the limit of infinite number of particles.

The equilibrium state of this ensemble is characterized by minimum Gibbs free energy, \( G \). The following equation relates the Gibbs free energy to the isobaric-isothermal partition function:

\[
\text{NPT, Gibbs free energy: } G(N, P, T) = -k_B T \ln \Delta(N, P, T)
\]

### 2.3.4 Grand Canonical, \( \mu VT \)

First we will define the concept of chemical potential \( \mu \). In statistical mechanics, the chemical potential of a species is defined as the change in the energy of the system when a particle is added while the entropy and volume are kept constant:

\[
\mu = \left(\frac{\partial E}{\partial N}\right)_{S,V}
\]

The relationship between the energy, \( E \) and Helmholtz free energy, \( A \), results the following equivalent definition:

\[
\mu = \left(\frac{\partial A}{\partial N}\right)_{T,V}
\]

So \( \mu \) is the change in the Helmholtz free energy when a particle is added at constant \( T \) and \( V \).

The Grand Canonical ensemble can be viewed as an ensemble of Canonical ensembles for each value of \( N \). It is an ensemble to study vapor liquid equilibrium for the system at constant
volume (V) by maintaining thermodynamic equilibrium (constant chemical potential and temperature) between the system and a reservoir. At constant chemical potential number of particles in the system fluctuates due to exchange of particles with the reservoir. Figure 2-3 shows an example of (μ VT) ensemble. In this ensemble the probability of finding the

![Figure 2-3: System of particles in Grand Canonical ensemble. The chemical potential, the volume and the temperature are constant. The number of particles, the internal configurations, the particle velocities and the energy of the system are changing.](image)

system in a particular state \( i \) with \( N_i \) number of particles at energy level \( H_i \) is given by:

\[
\pi(H_i, N_i) = \frac{\exp\left(-\beta(H_i - \mu N_i)\right)}{\Xi(\mu, V, T)}
\]  
(2.14)

where \( \Xi(\mu, V, T) \) is Grand Canonical partition function:

\[
\Xi(\mu, V, T) = \sum_N Q(N, V, T) \exp(\beta \mu N)
\]  
(2.15)

The equilibrium state of this ensemble is characterized by maximum pressure \( \times \) volume (PV). The following equation relates (PV) to the Grand Canonical partition function:

\[
\mu VT, PV \text{ state: } PV = k_B T \ln \Xi(\mu, V, T)
\]  
(2.16)
2.4 Calculation of properties

The conversion of microscopic variables (points in phase space) to macroscopic observables which can be measured in the lab (e.g. pressure, temperature, energy, moles of substance) requires methods of statistical mechanics. Let $A$ denote average of a macroscopic equilibrium observable and $a(x) = a(q, p)$ denote a microscopic phase space function that is used to calculate $A$. If we have an ensemble of $L$ points in phase space:

$$\langle A \rangle = \frac{1}{L} \sum_{k=1}^{L} a(x_k) \quad (2.17)$$

The brackets denote ensemble average of $A$. Due to ergodic hypothesis, in a long molecular simulation system explores all possible points in the phase space such that the ensemble average of a property is equal to the time average:

$$\langle A \rangle = \lim_{t \to \infty} \langle A \rangle_t \quad (2.18)$$

In other words, in order to calculate equilibrium value of any property like $A$ we can perform molecular simulation and take the time average of that property over a reasonably long time period. In the following the calculation of some of the state variables of the system from the trajectory of the molecular simulation will be explained.

Temperature is one of the state variables of a system that is related to the kinetic energy:

$$T = \frac{2 \langle K \rangle}{k_B N_d} \quad (2.19)$$

where $\langle K \rangle$ is ensemble average of kinetic energy expressed as a function of the masses $m_i$, coordinates $r_i$ and linear and angular velocities of the particles, $v_i$ and $\omega_i$:

$$K = \frac{1}{2} \sum_{i=1}^{N} m_i v_i^2 + \frac{1}{2} \sum_{i=1}^{N} \omega_i \cdot I \cdot \omega_i \quad (2.20)$$
where \( I \) is the inertia tensor, \( v_i \) and \( \omega_i \) are vectors of linear and angular momentums, \( N \) is total number of particles and \( N_d \) is the total number of degrees of freedom:

\[
N_d = 3N - N_c
\]  

(2.21)

where \( N_c \) is the total number of independent constraints such as fixed bond length or bond angle.

Internal stress and pressure of a system of interacting particles can be calculated from the virial theorem (Clausius, 1870). The internal stress tensor of the system is given by (Vitek and Egami, 1987):

\[
\sigma_{ij} = \frac{1}{V} \sum_{\alpha} \left( m^\alpha u_i^\alpha u_j^\alpha + \sum_{\beta} f_i^{\alpha \beta} r_j^\alpha \right)
\]  

(2.22)

Where \( V \) is the volume of the system, \( m^\alpha \) and \( u^\alpha \) are mass and velocity of atom \( \alpha \), respectively. \( f_i^{\alpha \beta} \) is the force acting on atom \( \alpha \) by atom \( \beta \) in the \( i \) direction and \( r_j^\alpha \) is the Cartesian component of the vector from atom \( \beta \) to atom \( \alpha \) in the \( j \) direction. Pressure is then evaluated as one third of the trace of stress tensor:

\[
P = \frac{1}{3} tr (\sigma_{ij})
\]  

(2.23)

### 2.5 Molecular Dynamics

The Molecular Dynamics (MD) method is a deterministic technique that describes the time evolution of a system of particles by solving Newton (for spherical particles) or Newton-Euler (for non-spherical particles) equations of motion. The algorithm of the MD simulation is given in Figure 2-4. The first step is to create initial condition that includes coordinates and orientations of particles. Also the force field which is the key driver of the MD simulation is defined. A single particle is affected by the potential energy of the other particles in the system. The force field defines a set of functional forms that are used to calculate the potential energy of the system based on the relative position of particles. More explanations and examples will be provided later. After defining run parameters, the system energy will be minimized. Initial energy minimization finds a configuration corresponding to a local
energy minimum. If in some parts of the model particles are too close to each other, the forces may become very large and the MD simulation may crash. This step eliminates hot spots of the initial configuration.

The next step of the simulation is carried out by solving Newton-Euler equations of motion (described in more detail in Section 2.5.1). All dynamic simulations are performed in two stages: equilibrium and production. In the equilibration stage, the initial random structure is evolved until a steady state is reached. The purpose of this stage is to prepare the system to sample the phase space from the desired probability distribution consistent with the ensemble of the simulation. As the system becomes larger, the amount of time that is needed to equilibrate the system increases since it should explore larger phase space. The state of the system is evaluated by calculating and plotting different thermodynamic variables such as energy, pressure and temperature. When the system reaches the steady state, the state variables will fluctuate around a stable average value. After equilibrating the system at the target ensemble data can be collected for the production stage. The length of the production stage depends on the type of the property being calculated and the size of the model. Plotting running average of the properties is a way to check the convergence of the result.

The methods used for the equilibration and production are the same. Just we need to give the system some time to equilibrate and then we can start sampling and calculating properties. For instance, to keep the temperature at \( T = 300 \) K, we have to modify the Newton-Euler equations of motion (section 2.5.1.2). The physical interpretation is to put the system in contact with a heat reservoir. It takes some time for the system to reach thermal equilibrium with the reservoir. Numerically this is done by the exchange of momentum between particles in the system and the reservoir through solving modified Newton-Euler equations of motion. With the language of statistical mechanics, this means we give some time to the system in order to evolve in the phase space (i.e. to visit different states) until the system starts to sample from a specified probability distribution associated with the ensemble of the simulation (i.e. generate certain states consistent with the ensemble).
1. Create initial condition
   - Initial positions of all atoms
   - Initial velocities of all atoms
   - Force field parameters (interactions, masses of particles)
   - Run parameters: time step, \( n_{\text{steps}} \), ensemble, integrator

2. Find configuration with local minimum energy

3. Calculate forces and torques on each particle

4. Integrate Newton-Euler equations of motion
   - Update positions (coordinates, orientations)
   - Update velocities (linear, angular)

5. Calculate the instantaneous properties

6. Return to step 3 until \( n_{\text{steps}} \)

7. Analyze the trajectory
   - Visualize the results
   - Calculate time average properties

Figure 2-4: The Molecular Dynamics algorithm.

2.5.1 System Dynamics

2.5.1.1 Micro-canonical case, NVE

Figure 2-5 shows a force system acting on a particle. At each time step the total potential, force and torque on a particle are calculated:

\[
U(i) = \sum_{j=1, j \neq i}^{N} U_{ij} \quad (2.24)
\]
Global (fixed) coordinate system

Local (moving) coordinate system

Figure 2-5: The force system acting on a particle.

\[ \mathbf{F}(i) = \sum_{j=1, j \neq i}^{N} -\frac{\partial U_{ij}}{\partial \mathbf{r}_{ij}} \]  \hspace{1cm} (2.25)

\[ \mathbf{T}(i) = \sum_{j=1, j \neq i}^{N} \mathbf{r}_{ij} \times \mathbf{F}_{ij} \]  \hspace{1cm} (2.26)

where \( \mathbf{F}(i) \) and \( \mathbf{T}(i) \) are total force and torque acting on particle \( i \), \( \mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j \) is the distance between particles. \( F_{ij} \) and \( U_{ij} \) are the force and potential between particles \( i \) and \( j \).

The linear and angular velocities are updated by solving Newton-Euler equations of motion:

Micro-canonical system

\[
\begin{align*}
\mathbf{F}(i) &= \frac{d}{dt}(m_i \mathbf{v}_i) = m_i \frac{d}{dt} \mathbf{v}_i \\
\mathbf{T}(i) &= \frac{d}{dt}(\mathbf{I} \omega_i)
\end{align*}
\]  \hspace{1cm} (2.27)

(2.28)

where \( \mathbf{I} \) is the inertia tensor, \( \mathbf{v}_i \) and \( \omega_i \) are vectors of linear and angular velocities. Coordinates and orientations will be updated using linear and angular velocities.

Total potential energy, force and torque are calculated in the global (fixed) coordinate system. Moment of inertia is expressed in the local (moving) coordinate system that is rigidly attached to the particle. For this reason, it is more convenient to write angular equation of motion (Eq.(2.28)) in the local coordinate system (denoted by superscript \( l \)):

\[ \mathbf{T}^l = \mathbf{A} \cdot \mathbf{T}^g \]  \hspace{1cm} (2.29)
\[
\mathbf{T}' = \frac{d}{dt}(\mathbf{I} \omega_i)' + \omega_i' \times (\mathbf{I} \omega_i)'
\]  

(2.30)

where superscript \( g \) denotes global coordinate system and \( \mathbf{A} \) is the rotation matrix. According to Euler theorem, any two independent orthogonal coordinates can be related by a sequence of three rotations about coordinate axes where no two successive rotations should be around the same axis. This limit leads to the following twelve rotation sequences:

\[
\begin{align*}
\text{XYZ} & \quad \text{XZY} & \quad \text{XYX} & \quad \text{XZ}X \\
\text{YXZ} & \quad \text{YZX} & \quad \text{YYX} & \quad \text{YZ}Y \\
\text{ZXY} & \quad \text{ZYG} & \quad \text{ZXZ} & \quad \text{ZZZ}
\end{align*}
\]

(2.31)

In the following we assume ZXZ sequence. The orientation of a particle can be defined by three Euler angles which map the global coordinate to a local one: \( (\phi, \theta, \psi) \). Figure 2-6 shows the sequence of rotations that maps the left coordinate (Figure 2-6(a)) to the right one (Figure 2-6(d)). First of all we rotate by \( \phi \) angle about the Cartesian Z axis. This changes the X and Y axes. Then we rotate by \( \theta \) angle about the new X axis which changes the Y and Z axes. Finally, we rotate by \( \psi \) angle about the new Z axis.

In the following we assume ZXZ sequence. The orientation of a particle can be defined by three Euler angles which map the global coordinate to a local one: \( (\phi, \theta, \psi) \). Figure 2-6 shows the sequence of rotations that maps the left coordinate (Figure 2-6(a)) to the right one (Figure 2-6(d)). First of all we rotate by \( \phi \) angle about the Cartesian Z axis. This changes the X and Y axes. Then we rotate by \( \theta \) angle about the new X axis which changes the Y and Z axes. Finally, we rotate by \( \psi \) angle about the new Z axis.

Angular equations of motion written in terms of Euler angles have singularities at \( \theta = 0 \) or \( \pi \) (Allen and Tildesley, 1989). For this reason, it is common to write these equations in terms of quaternions to eliminate singularities. Quaternions are vectors in four dimensional Euclidean space \( (\mathbb{R}^4) \): \( \mathbf{a} = (a_0, a_1, a_2, a_3) \). The norm of a quaternion is defined as \( |\mathbf{a}| = \sqrt{a_0^2 + a_1^2 + a_2^2 + a_3^2} \).
\[ \sqrt{a_0^2 + a_1^2 + a_2^2 + a_3^2}. \] Unit quaternions \((|a| = 1)\) represent orientations in three dimensional space \((\mathbb{R}^3)\). Any rotation in three dimensional space can be represented as a combination of a unit vector \(\mathbf{u}\) and a scalar angle \(\alpha: a = (\cos \frac{\alpha}{2}, \mathbf{u} \sin \frac{\alpha}{2})\). This quaternion denotes a rotation with an angle \(\alpha\) around the axis defined by the unit vector \(\mathbf{u}\). In other words, for any rotation of the global axis of coordinate to a local axis of coordinate, we can find a unit vector in the space and an angle \(\alpha\) that maps the global coordinate to a local one. The quaternions are defined in terms of Euler angles as:

\[
\begin{align*}
 a_0 &= \cos \frac{\theta}{2} \cos \frac{\phi + \psi}{2} \\
 a_1 &= \sin \frac{\theta}{2} \cos \frac{\phi - \psi}{2} \\
 a_2 &= \sin \frac{\theta}{2} \sin \frac{\phi - \psi}{2} \\
 a_3 &= \cos \frac{\theta}{2} \sin \frac{\phi + \psi}{2}
\end{align*}
\]

(2.32)

The rotation matrix has the following form in terms of quaternions:

\[
A = \begin{pmatrix}
 a_0^2 + a_1^2 - a_2^2 - a_3^2 & 2a_1a_2 - 2a_0a_3 & 2a_1a_3 + 2a_0a_2 \\
 2a_1a_2 + 2a_0a_3 & a_0^2 - a_1^2 + a_2^2 - a_3^2 & 2a_2a_3 + 2a_0a_1 \\
 2a_1a_3 - 2a_0a_2 & 2a_2a_3 - 2a_0a_1 & a_0^2 - a_1^2 - a_2^2 + a_3^2
\end{pmatrix}
\]

(2.33)

In solving standard Newton-Euler equations of motion, the total number of particles \(N\), total volume \(V\) and total energy \(E\) of the system are constant during simulation. In other words, we are sampling from micro-canonical (NVE) ensemble.

2.5.1.2 Canonical case, NVT

There are several ways of performing simulations at constant temperature but only some of them sample from the canonical ensemble like the Nosé–Hoover thermostat (Nosé, 1984; Hoover, 1985). Others satisfy constant kinetic energy constraint like the Andersen (Andersen, 1980) and the Berendsen (Berendsen et al., 1984) thermostats but they don’t sample from a true constant temperature ensemble. In this thesis we will use the extended system method originally formulated by Nosé and Hoover.

In order to keep the temperature at a constant value, the particle velocities should be adjusted in an appropriate way. The Nosé–Hoover thermostat introduces an additional time
dependent frictional parameter, \( \zeta \), to the equations of motion. The value of \( \zeta \) is calculated from the difference between the instantaneous kinetic energy (at temperature \( T(t) \)) and the average target kinetic energy (at temperature \( T_0 \)). As a result, in the Canonical (NVT) ensemble, the Newton-Euler equations (Eqs.(2.27) and (2.28)) are modified to the following:

\[
\begin{align*}
F(i) &= m_i \frac{d}{dt} v_i + \zeta m_i v_i \\
T(i) &= \frac{d}{dt} (I \omega_i) + \zeta I \cdot \omega_i \\
\frac{d}{dt} \zeta &= \frac{g}{Q} (K_B T(t) - K_B T_0)
\end{align*}
\]

where \( g \) is the number of degrees of freedom in the system and \( Q \) is the associated fictitious mass parameter.

There are two criteria (Refson, 2001) to satisfy when choosing the value of \( Q \). The coupling to the heat bath produces a fictitious oscillation to the kinetic energy of the system with the period \( t_0 = \frac{2\pi}{\sqrt{Q/2gK_BT_0}} \). \( Q \) value should be small enough to have lots of oscillations during the production stage. On the other hand, \( Q \) value should be large enough so that the coupling period \( t_0 \) is large compared to the decay time of the dynamical correlation functions. In other words, the fictitious oscillation of the heat bath should be decoupled from the real dynamics of the system. To satisfy both requirements, it might be necessary to increase the total simulation time.

### 2.5.1.3 Isobaric-isothermal case, NPT

There are several methods to control the pressure of the system for NPT simulations. Some definitions of barostats generate the correct average pressure (e.g. Andersen (1980); Berendsen et al. (1984)) but don't sample from the NPT ensemble. The Parrinello-Rahman (Parrinello and Rahman, 1981) barostat can sample from the probability distribution function corresponding to the true NPT ensemble and is the preferred approach used through the thesis.

To keep the pressure at a constant value, the positions of the atoms and the volume of the simulation box should be adjusted in an appropriate way. The matrix of the unit cell vectors \( \mathbf{h} \) is defined as \( \mathbf{h} = [a, b, c] \) where columns represent three vectors of the unit cell, \( \mathbf{a}, \mathbf{b} \) and
c. The Parrinello-Rahman method uses the \( h \) matrix as an extra time dependent parameter to adjust the volume and the shape of the unit cell. The \( h \) matrix is changed in response to the difference between the instantaneous pressures or stresses \((P(t))\) and the target pressures \((P_0)\) through the following equation:

\[
W \frac{d^2 h}{dt^2} = V (h)^{-T} (P(t) - P_0)
\]  

(2.37)

where \( V \) is the volume of the unit cell and \( W \) is a fictitious mass parameter matrix that determines the strength of the coupling. The physical interpretation of the equation is to control the pressure in the system by using a piston that is represented by its weight \( W \). The fluctuations of the volume is affected by the mass of the piston. A large \( W \) represents a heavy piston and slow motion of the unit cell. In the limit of infinite \( W \), cell volume will not change and we get back to constant volume dynamics. On the other hand, small \( W \) results in fast motion of the unit cell. In this case, there may be insufficient time for the equilibration of the system (and the simulation may crash). An appropriate value of \( W \) can be found by trial and error tracking thermodynamic variables to check equilibration of the system.

The matrix form of the equation allows anisotropic coupling between the system and the pressure bath. Also, the linear equation of motion should be modified to generate a constant pressure trajectory. The angular equation of motion will be the same as the canonical ensemble (Eq.(2.35)). As the Parrinello-Rahman barostat is always used in conjunction the Nosé-Hoover thermostat, only the extra modification for pressure coupling need be explained. The matrix of the unit cell vectors, \( h \), is used to define a scaling matrix \( S \) that will be used to modify linear equation of motion:

\[
S = h^{-1} \left[ h \frac{dh^T}{dt} + \frac{dh}{dt} h^T \right] h^{-T}
\]  

(2.38)

\[
F(i) = m_i \frac{d}{dt} v_i + m_i S v_i
\]  

(2.39)
2.6 Monte Carlo

In the previous section we described the generation of statistical ensembles using Molecular Dynamics. In the MD approach statistical ensembles with probability distributions for target ensemble were obtained by solving Newton-Euler equations of motion. Monte Carlo (MC) is an alternative simulation method. In the MD method, the positions and velocities of particles are updated in each time step to generate ensemble of configurations. In contrast, sampling for the MC method depends on positions only (not velocities). In fact, the contribution of kinetic energy to the partition function is integrated analytically as its functional form is known. For instance, the partition function of the canonical ensemble (cf. Eq.(2.7)) can be expressed as:

\[ Q(N, V, T) = \frac{1}{N!h^{3N}} \int \exp(-\beta U(q)) \, dq \int \exp(-\beta K(p)) \, dp \]  

(2.40)

where the integral over the Hamiltonian \((H)\) is divided into two separate integrals over the potential \((U)\) and the kinetic \((K)\) energies since \(U\) depends only on positions and \(K\) depends only on momentums. From statistical mechanics, the integration over particle momentums results in:

\[ Q(N, V, T) = \frac{Z(N, V, T)}{N!A^{3N}} \]  

(2.41)

where \(Z(N, V, T) = \int \exp(-\beta U(q)) \, dq\) is called the conformational integral and \(A\) is the thermal de Broglie wavelength. For a system of spherical particles with mass \(m\):

\[ A = \frac{\hbar}{\sqrt{2\pi m K_B T}} \]  

(2.42)

where \(\hbar\) is Planck's constant. For non-spherical particles the de Broglie wavelength contains contributions from the rotational degrees of freedom. For hetero-atomic systems multiple de Broglie wavelengths representing different atomic masses appear in the partition function. For a separable Hamiltonian, the distribution of positions (configurations) and momentums are separable and the probability of finding a configuration with positions \(q_i\) and momentums \(p_i\) can be written as:

\[ \pi(q_i, p_i) = \pi(q_i)\pi(p_i) \]  

(2.43)
where

\[
\pi(p_i) = \frac{\exp(-\beta K(p_i))}{\hbar^{3N} \Lambda^{-3N}} \tag{2.44}
\]

and

\[
\pi(q_i) = \frac{\exp(-\beta U(q_i))}{Z(N,V,T)} \tag{2.45}
\]

Eq.(2.45) defines probability of finding a configuration with positions \(q_i\) in the configuration space (space of positions with dimension \(3N\) for spherical particles and \(6N\) for non-spherical particles). It should be noted that the probability density of the canonical ensemble in the phase space (Eq.(2.6)) is different from the one in the configuration space (Eq.(2.45)). Consequently, statistical ensemble with canonical probability distribution can be generated by changing configurations in configuration space (with changing positions of particles) rather than phase space (with changing positions and momentums).

In molecular simulations, we can use the Monte Carlo method for random sampling of a target probability distribution corresponding to a statistical ensemble. While Molecular Dynamics is a method for deterministic sampling of the phase space, the Monte Carlo method performs stochastic sampling of the configuration space. The MC method is a Markov Chain process in which the current configuration (old state) is randomly perturbed to find the next configuration (new state). The perturbation can be a random movement (like translation or rotation) or insertion/removal of a particle. The accessibility of the new state is checked using an acceptance criterion. We construct a chain of states started from an arbitrary configuration and iterate the Markov Chain many times. The system will equilibrate in the initial sampling process after a finite number of iterations. Then, the production stage of the simulation can be carried out in which we are sampling from the target probability associated with the statistical ensemble of the Monte Carlo method. We measure the equilibrium properties of the system by taking ensemble averages at the production stage. The system has reached to the stationary state of sampling the target ensemble if the following equation known as detailed balance (or microscopic reversibility) is satisfied:

\[
P(i) \pi(i \rightarrow j) = P(j) \pi(j \rightarrow i) \tag{2.46}
\]

49
where $P(i)$ is the probability of state $i$ and $\pi(i \rightarrow j)$ is the transition probability of reaching state $j$ from state $i$. The Markov Chain transition probability ($\pi(i \rightarrow j)$) is defined in such a way to satisfy the above condition. There are different methods to construct a Markov Chain (e.g. Gibbs sampler (Gelfand and Smith, 1990; Casella and George, 1992), Metropolis-Hastings algorithm (Metropolis et al., 1953; Hastings, 1970)). In the following the Metropolis-Hastings algorithm will be explained.

### 2.6.1 The Metropolis-Hastings algorithm

The Metropolis-Hastings (MH) algorithm (Metropolis et al., 1953; Hastings, 1970) is a technique that generates a Markov Chain process with a specified target probability distribution $\pi(q)$ in configuration space. The limiting distribution of the MH algorithm is the $\pi(q)$ probability distribution. The algorithm of the Metropolis-Hastings Monte Carlo simulation is given in Figure 2-7. The first step is to create an arbitrary initial configuration, to define force field parameters (that determine interactions between particles) and to specify run parameters. After minimizing energy in this configuration (to remove hot spots from the model), the system is ready to begin Markov-Chain Monte Carlo (MCMC). The main part of the algorithm has two steps. In the first step, the configuration is randomly perturbed (for instance by random movement of a particle) to create a new configuration. In the second step, the new configuration is tested and accepted or rejected with a defined acceptance probability. There is no force calculation in the MC. Similar to the MD method, the system will equilibrate after performing this algorithm for a finite number of steps. In the production stage, the algorithm performs stochastic sampling of the target $\pi(q)$ distribution in the configuration space corresponding to the probability distribution of the desired statistical ensemble. Both of the MD and MC methods create same ensemble averages at the production stage due to ergodic hypothesis ($\langle A \rangle = \langle A \rangle_{MD} = \langle A \rangle_{MC}$).

It is not easy to simulate open systems (e.g. systems that exchange particles with an external reservoir such as the Grand Canonical ensemble) using the MD method since the insertion or omission of particles introduces discontinuities in the integration of Newton-Euler equations of motion (Ungerer et al., 2005). The MC is the preferred method for such ensembles. The next section describes the Grand Canonical Monte Carlo technique (GCMC-$\muVT$).
1. Create initial condition
   - Initial positions of all atoms
   - Force field parameters (interactions)
   - Run parameters: \( n_{\text{steps}} \), ensemble

2. Find configuration with local minimum energy

3. From configuration \( i (q_i) \) create
   new configuration \( j (q_j) \) by random perturbation

4. Accept the new configuration with the
   acceptance probability of
   \[ P_{\text{acc}} = \min \left\{ 1, \frac{\pi(q_j)}{\pi(q_i)} \right\} \]
   This step can be performed as follows:
   a. Compute the probability ratio \( X = \frac{\pi(q_j)}{\pi(q_i)} \)
   b. Pick a random number \( Y \) between 0 and 1
   c. If \( Y \leq X \), make \( q_n = q_j \)
      otherwise, make \( q_n = q_i \)

5. Calculate the instantaneous properties

6. Replace \( q_i \) by \( q_n \) and return to step 3 until \( n_{\text{steps}} \)

7. Analyze the configurations
   - Visualize the results
   - Calculate ensemble average properties

Figure 2-7: The Metropolis-Hastings Monte Carlo algorithm.
2.6.2 Grand Canonical Monte Carlo (GCMC-$\mu$ V T)

In the Grand Canonical Monte Carlo (GCMC-$\mu$V$T$) simulation particles are inserted or removed in a Markov Chain process with a probability distribution that depends on the chemical potential $\mu$ of the reservoir. In the $\mu$ V T ensemble, the chemical potential $\mu$, volume V and temperature T of the system are constant, while the total number of particles N is allowed to fluctuate. In the algorithm of the (GCMC) method, step 3 of the Metropolis-Hastings Monte Carlo (Figure 2-7) consists of three types of random perturbation of the configuration: particle movement (translation or rotation) , particle insertion and particle removal. Also, step 4 of the MHMC algorithm (Figure 2-7) is divided into three acceptance criteria corresponding to the three types of changing the system configuration. After the random perturbation, the change in the potential energy from the previous to the new configuration ($\Delta U = U_{\text{new}} - U_{\text{old}}$) is calculated and used to accept or reject the new configuration based on the following acceptance criteria:

1. **Particle movement:** A particle is selected at random and given a new position. The move is accepted with the probability:

   $$P_{\text{acc}} = \min \{1, \exp [-\beta \Delta U]\}$$  \hspace{1cm} (2.47)

   If a particle moves to a favorable position, the energy change would be negative and the new configuration is likely to be accepted.

2. **Particle insertion:** A particle is inserted at a random position so the number of particles is changed from $N$ to $N + 1$. The probability of accepting an insertion is:

   $$P_{\text{acc}} = \min \left\{1, \frac{V}{\Lambda^3(N + 1)} e^{\beta (\mu - \Delta U)} \right\}$$  \hspace{1cm} (2.48)

   If the insertion creates favorable interactions with the rest of the particles, the energy change would be negative and the new configuration is likely to be accepted.

3. **Particle removal:** A randomly selected particle is removed so the number of particles
is changed from $N$ to $N - 1$. The particle removal is accepted with the probability:

$$P_{\text{acc}} = \min \left\{ 1, \frac{A^3N}{V} \exp \left[ -\beta (\mu + \Delta U) \right] \right\}$$  \hspace{1cm} (2.49)

If the particle selected for removal has a favorable interaction with the rest of the particles, the energy change would be positive and the new configuration is unlikely to be accepted. The perturbation to the configuration is tuned by changing perturbation size so that approximately half of the trials are accepted. For a very large perturbation (like large movement of a particle) the change in the potential energy is likely to be a large positive value (due to the large probability of particles overlapping on each other). As a result the new configuration will be rejected. On the other hand, for a very small perturbation (like small movement of a particle), the step size will limit the sampling of the configuration space. As a result, the number of steps required for the equilibration of the system increases. There are methods to increase efficiency of sampling the configuration space known as biased sampling or important sampling methods. For instance, to increase efficiency of inserting particles (Mezei, 1987) proposed a biased sampling algorithm. In the Mezei method, attempts for particle insertion favor empty spots and discount areas filled with particles. To maintain detailed balance in the Mezei algorithm, the inverse of the bias is applied to the acceptance criteria.

### 2.7 Periodic boundary condition and minimum image convention

The molecular simulations are performed within a unit cell containing small number of particles. The size of the system is constrained by computation time which scales with the square of the number of particles ($N^2$). On the other hand, we are interested to calculate bulk properties of the material. Results of a simulation in a small unit cell are affected by the boundaries due to high percentage of the surface atoms. Hence, periodic boundary conditions are used to simulate bulk properties with relatively small number of particles. Figure 2-8 shows periodic boundary conditions which are developed by replicating the central unit cell (calculation cell) in all directions. Particles leaving the calculation cell enter into the
Figure 2-8: Periodic boundary conditions in 2D. The central box (solid lines) is the calculation cell. The rest (dashed lines) are image cells. If a particle leaves the calculation cell, its image enters to one of the image cells on the opposite side. Each atom interacts with the particles and their nearest images within a cut off sphere.

image cells in the opposite direction. For short range potentials such as Lennard-Jones the interaction of each particle with all atoms and their images within a cut off radius, \( r_c \), is calculated. In order to prevent double summation of a particle contribution (i.e., considering both particle and its image interacting with another particle) the cut off radius should be smaller than the half length of the shortest vector for the unit cell:

\[
  r_c < \frac{1}{2} \min \{ a, b, c \} \quad (2.50)
\]
The above relation is called minimum image convention.

2.8 Ewald summation

Long range interactions such as Coulombic potentials decay slowly with distance ($\sim \frac{1}{r}$). As a result, truncation of the interactions at a certain cut-off can introduce large errors (Lau et al., 1994; Patra et al., 2003). The Ewald summation (Ewald, 1921) is one of the methods to calculate the total electrostatic interactions in a periodic system. Figure 2-9 shows schematic representation of the Ewald summation for a 1D system. In this method the original problem

\[ \sum q_x V_x = \sum q_x + \sum q_x' \]

is written as summation of two parts: the direct part (to be calculated in the real space) and the reciprocal part (to be calculated in the fourier space). The direct part contains the original point charges plus Gaussian charge distributions with the opposite charge. The direct part can be calculated in the real space similar to the short range interactions within a specified cut off. The reciprocal part contains collection of canceling Gaussian charge distributions. The electrostatic interactions of this infinite periodic part is calculated in the fourier space. Then the result is converted back to the real space and added to the direct part. The method is accurate but computationally expensive. For large systems, more efficient methods like the Particle Mesh Ewald summation (Darden et al., 1993; Essmann et al., 1995) can be used. Also, the Wolf method (Wolf et al., 1999) is an alternative non-Ewald method.
of calculating electrostatic energy of a periodic system. Although, there are arguments that the Wolf method converges to the result of the Ewald summation (Angoshtari and Yavari, 2011) but there are reports that this method performs poorly for zeolites (Vlugt et al., 2008).

2.9 Energy landscape and CLAYFF force field

The energy landscape defines the way the energy of a system changes as a function of its configuration and is described by force field functional forms (which are mathematical description for the chemical bonds and angles in the system). Force field describes potential energy of the system of atoms (i.e., the internal energy that keeps atoms in their equilibrium positions) as a function of their relative positions. In classical molecular dynamics each atom is considered as a single point which is defined by its position and velocity. Force field parameters are calculated by fitting experimental data to the functional forms for small set of molecules (i.e., combinations of atoms). In order to choose a force field we look to see if the system has been already studied with MD or MC and which force field has been used. The force field should have interactions between components of the system to be able to define the problem. The success of a force field is assessed by comparing its results with experiment.

There are two main force fields in the literature which have been used to simulate clay minerals: Skipper and Smith force field, SSFF (Skipper et al., 1995; Smith, 1998), and CLAYFF (Cygan et al., 2004). CLAYFF (Cygan et al., 2004) shows better agreement with experimental results compared to SSFF which was developed by Skipper et al. (1995) and modified by Smith (1998). For instance, Marry et al. (2011) showed that SSFF overestimated the diffusion coefficient of water in montmorillonite compared with CLAYFF which shows better agreement with experiment. There are many more successful examples of using CLAYFF for instance Greathouse and Cygan (2005); Liu et al. (2007); Suter et al. (2007) to name a few. Although CLAYFF is the most successful force field in simulating clay minerals, Ferrage et al. (2011) recently proposed some corrections to the force field to have better agreement with diffraction patterns of X-ray and neutron diffraction experiments. There are other choices as well, for instance, Heinz et al. (2005) proposed a force field which has been
used mostly to simulate clay minerals in contact with (bio)organic molecules and polymers. In this work, we will use CLAYFF (Cygan et al., 2004) force field which was parametrized using structural and spectroscopic data fitted to some simple hydrated compounds. CLAYFF is a flexible force field within the clay lattice that was developed for simulating aluminum hydroxide minerals and clays. In this force field, total potential energy of the system has contributions from bonded and nonbonded interactions. Bonded interactions include bond stretching and angle bending. Nonbonded interactions include long range electrostatic (Coulombic) interactions and short range (van der Waals) interactions.

\[ U_{\text{total}} = U_{\text{bond stretch}} + U_{\text{angle bend}} + U_{\text{Coulomb}} + U_{\text{vdW}} \]  

(2.51)

The only three body term in CLAYFF is angle bending in water and the rest of the energies are pairwise interactions. Bond stretching is only used to define O-H bond in hydroxyl and water. Bonded interactions are described by simple harmonic forms:

\[ U_{ij}^{\text{bond stretch}} = k_r (r_{ij} - r_0)^2 \]  

(2.52)

\[ U_{ijk}^{\text{angle bend}} = k_\theta (\theta_{ijk} - \theta_0)^2 \]  

(2.53)

where \( k_r \) and \( k_\theta \) are force constants and \( r_0 \) and \( \theta_0 \) are equilibrium bond length and equilibrium bond angle. For water molecules, CLAYFF uses a flexible version of the simple point charge (SPC) water model (Teleman et al., 1987; Berendsen et al., 1987). The parameter values of the bonded interactions of the CLAYFF force field are listed in Table 2.2.

<table>
<thead>
<tr>
<th>bond</th>
<th>( k_r ) (eV/Å²)</th>
<th>( r_0 ) (Å)</th>
<th>( k_\theta ) (eV/rad²)</th>
<th>( \theta_0 ) (deg)</th>
</tr>
</thead>
</table>

Table 2.2: Bonded interactions, bond stretching and angle bending parameters of the CLAYFF force field

The long range coulombic interaction of two atoms \( i \) and \( j \) with charges \( q_i \) and \( q_j \) at a
separation of $r_{ij}$ is calculated using Coulomb's law:

$$U_{ij}^{\text{Coulomb}} = \frac{e^2 q_i q_j}{4\pi\varepsilon_0 r_{ij}}$$  \hfill (2.54)

where $e$ is the charge of the electron, and $\varepsilon_0$ is the dielectric permittivity of vacuum.

The van der Waals interaction between a pair of atoms is represented by the (12-6) Lennard Jones potential (Figure 2-10):

$$U_{ij}^{\text{VWD}} = \epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - 2 \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right]$$ \hfill (2.55)

where $\epsilon$ is the depth of the potential well and $\sigma$ is the distance at which the potential reaches its minimum. The interaction parameters $\epsilon$ and $\sigma$ between unlike atoms are calculated using the geometric mean for the interaction energy and arithmetic mean for the equilibrium interatomic distance:

$$\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j}$$ \hfill (2.56)

$$\sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j)$$ \hfill (2.57)
<table>
<thead>
<tr>
<th>atom type</th>
<th>q (e)</th>
<th>$\epsilon$ (eV)</th>
<th>$\sigma$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al, octahedral</td>
<td>1.5750</td>
<td>$5.76 \times 10^{-8}$</td>
<td>4.7943</td>
</tr>
<tr>
<td>Al, tetrahedral</td>
<td>1.5750</td>
<td>$7.98 \times 10^{-8}$</td>
<td>3.7064</td>
</tr>
<tr>
<td>H, water</td>
<td>0.4100</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>O, water</td>
<td>-0.8200</td>
<td>0.0067387</td>
<td>3.5532</td>
</tr>
<tr>
<td>O, clay</td>
<td>-1.0500/-1.1808/1.1688/1.2996</td>
<td>0.0067387</td>
<td>3.5532</td>
</tr>
<tr>
<td>O, hydroxyl</td>
<td>-0.9500/-1.0808</td>
<td>0.0067387</td>
<td>3.5532</td>
</tr>
<tr>
<td>H, hydroxyl</td>
<td>0.4250</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Si, tetrahedral</td>
<td>2.1000</td>
<td>$7.91 \times 10^{-8}$</td>
<td>3.7064</td>
</tr>
<tr>
<td>Mg, octahedral</td>
<td>1.3600</td>
<td>$3.91 \times 10^{-8}$</td>
<td>5.9090</td>
</tr>
<tr>
<td>Na</td>
<td>1.0000</td>
<td>0.0056416</td>
<td>2.6378</td>
</tr>
</tbody>
</table>

* when connected to octahedral substitution
* when connected to tetrahedral substitution
* when connected to double substitution.

Table 2.3: Nonbonded interactions, charges $q$ and Lennard-Jones parameters $\epsilon$ and $\sigma$ of the CLAYFF force field (Cygan et al., 2004)

The parameter values of the nonbonded interactions of the CLAYFF force field are listed in Table 2.3.

Intramolecular nonbonded interactions between oxygen and hydrogen in hydroxyl groups and water molecules are excluded since they are covered by bonded terms.
Chapter 3

Atomistic simulation of clay-water system

3.1 Introduction

The engineering properties of soils are highly affected by their clay content (Murray, 1999; Boivin et al., 2004). Similarly, the hydration state of the clay mineral plays an important role in physical properties such as the mechanics and transport of ionic substances. This work is motivated by the lack of a universal constitutive model to explain the effect of water adsorption on clay behavior (i.e., from partially saturated clay to fully saturated states). The fundamental understanding of the clay hydration process impacts several application fields from engineering estimates of ground movements caused by seasonal changes in moisture content (Jones and Jefferson, 2012) to swelling pressures exerted by compacted bentonite on nuclear waste canisters (Gens, 2003). Knowledge of elastic properties is critical in back-analyzing geophysical seismic exploration data and interpreting acoustic scattering measurements (Wang, 2001). Fundamental mechanical properties of clays are also required to model hydraulic fracturing of oil and gas shale source rocks (Waters et al., 2011). Clays are being used to improve mechanical and thermal properties of polymers, via polymer clay nanocomposites (PCNs) (SinhaRay and Biswas, 1999). These applications also require knowledge of fundamental properties of clay to design properties of the PCN composite materials.
Clay minerals have a layered structure at the nano-scale. Each layer consists of some combinations of two sheet types with silicon tetrahedra and aluminum octahedra as basic units. This work considers montmorillonite, a member of the smectite group that comprises two tetrahedral silicate sheets each with unshared oxygen, O, atoms around a central octahedral hydroxide sheet which has two planes of unshared O atoms and additional hydroxyl groups, OH, to form the base lamellae. Due to isomorphous substitutions of metal ions within the clay sheets, each lamellae has a net negative charge which is compensated by positive exchangeable interlayer cations. Adsorption of water molecules by this system is accompanied by a large increase in the basal layer spacing. This swelling process significantly impacts the structural and mechanical properties of the clay.

It is very challenging to measure the fundamental mechanical properties of clay due to their high affinity for water and their platy geometry (Vanorio et al., 2003). Plan dimensions of each lamellae are typically one hundred times larger than the 2:1 layer thickness. All of the reported direct measurements are for clay minerals that are dry or have a very small amount of water (often ill-defined). Most of the available experimental results report only isotropic elastic moduli of clay minerals (Faust and Knittle, 1994; Pavese et al., 1999; Smyth et al., 2000; Pawley et al., 2002; Kopycinska-Müller et al., 2007). However, clay minerals have inherent anisotropy due to their layered structure as shown experimentally in the case of muscovite mica, phlogopite and biotite (Vaughan and Guggenheim, 1986; McNeil and Grimsditch, 1993; Alexandrov and Ryzhova, 1961). For example, Vanorio et al. (2003) reported isotropic elastic moduli of montmorillonite samples from extrapolation of acoustic measurements on cold-pressed samples at different porosities but with no control of water content. Similarly, Wang et al. (2001) presented a method to calculate elastic properties of clay from elastic wave velocity measurements on composite samples prepared by mixing the clay with an epoxy resin of known elastic properties. Chen and Evans (2006) argued that this method does not necessarily measure the moduli of individual clay platelets.

To the best of our knowledge, successful direct anisotropic experimental measurements on montmorillonite mineral are currently not available in the literature, so theoretical and computational methods can provide useful estimates of these properties.
Molecular simulation is a computational technique that is used to model behavior of the matter at atomic scale. The existing literature on molecular simulation of clay water systems has focused on crystalline swelling behavior of the clay and on the interlayer distribution of water and ion molecules (Skipper et al., 1991; Delville, 1992; Delville and Sokolowski, 1993; Skipper et al., 1995; Chang et al., 1995; Delville, 1995; Boek et al., 1995b; Teppen et al., 1997; Chang et al., 1998; Smith, 1998; Greathouse and Sposito, 1998; Shroll and Smith, 1999; Young and Smith, 2000; Chávez-Páez et al., 2001b,a; Sutton and Sposito, 2001; Hensen et al., 2001; Marry et al., 2002; Hensen and Smit, 2002; Marry and Turq, 2003; Arab et al., 2003; Zaidan et al., 2003; Odriozola and Guevara-Rodríguez, 2004; de Lourdes Chávez et al., 2004; Whitley and Smith, 2004; Tambach et al., 2004b,a; Heinz et al., 2005; Smith et al., 2006; Tambach et al., 2006; Marry et al., 2008; Liu et al., 2008; Suter et al., 2008; Cygan et al., 2009; Anderson et al., 2010; Liu et al., 2011). There are very few reported elastic properties for clay minerals from numerical simulations. Most of the reported elastic moduli from computer simulations are for non-expanding minerals with small interlayer spacing. For example, Sato et al. (2005) reported the first principle calculation of the full elastic stiffness matrix of kaolinite, a non-expanding clay with small adsorption of water. Recently, Militzer et al. (2011) reported the first principle ab initio calculations of full elastic stiffness constants for dry silicate minerals including muscovite, kaolinite, dickite, nacrite as well as a dry illite-smectite mineral. Suter et al. (2007) and Mazo et al. (2008) calculated in-plane elastic moduli of hydrated Wyoming Na-montmorillonite clay.

In this research we will derive the full elastic tensor calculations for Wyoming Na-montmorillonite over a range of hydration conditions using Molecular Dynamics (MD) simulations.

3.2 Methodology

3.2.1 Simulation Detail

The crystallography for 2:1 clay mineral has been taken from Refson et al. (2003). The specific structure of natural Wyoming Na-montmorillonite includes isomorphous
substitutions in both tetrahedral and octahedral sheets with the following experimental formula (Newman, 1987): \( \text{Na}_{0.75} \text{nH}_2\text{O[Si}_{7.75}\text{Al}_{0.25}][\text{Al}_{3.5}\text{Mg}_{0.5}]\text{O}_{20}(\text{OH})_4 \). The isomorphous substitutions in Wyoming Na-montmorillonite corresponds to cation exchange capacity of \(102 \, \text{meq/100g} \). The simulation cell consists of sixteen unit cell (4x2x2 array of clay unit cell) with initial plan dimensions \((X - Y)\) of \(\sim 20.87 \, \text{Å} \times \sim 18.15 \, \text{Å}\). Sodium ions, Na, were randomly distributed in the interlayer space. Each simulation contains between 0 to 258 water molecules that corresponds to water contents in the range \(M_{\text{H}_2\text{O}}/M_{\text{clay}} = 0\) to 0.4 g/g.

The analyses are based on the CLAYFF (Cygan et al., 2004) force field that has been developed successfully for structural simulation of clay minerals (Liu et al., 2007; Suter et al., 2007). CLAYFF is a versatile force field built around the flexible version of the simple point charge (SPC) water model (Teleman et al., 1987). All parameters and equations were given in the previous chapter.

Two simulation packages were used in this work: GROMACS (Van Der Spoel et al., 2005) and GULP (Gale, 1997). GROMACS was used for molecular dynamics simulations while GULP was used to create the initial structure of the adsorbed water, to perform static energy minimization and to calculate the elastic stiffness matrix. The visualization of the molecular configurations was carried out using the molecular graphic software VMD (Humphrey et al., 1996). For each hydration state we displaced clay layers to have basal layer spacing of a little (\(\approx 1\, \text{Å}\)) more than the anticipated equilibrium from experiment (Fu et al., 1990). Using GULP program, the initial state of the adsorbed water in each simulation was generated through conventional Grand Canonical Monte Carlo (GCMC - \(\mu\)-V-T) simulations at 300K until we have number of water molecules that corresponds to that state of hydration. This step provides the starting configuration at defined hydration states related to the experiment. Three-dimensional, periodic boundary conditions were applied along with the minimum image convention (a cutoff radius of 8.5Å was used for short range interactions). The long range electrostatic coulombic interactions were calculated using Particle Mesh Ewald summation (Darden et al., 1993; Essmann et al., 1995).
Isomorphous substitution was carried out randomly by replacing one Si$^{4+}$ with Al$^{3+}$ in each tetrahedral sheet, and four Al$^{3+}$ with Mg$^{2+}$ in each octahedral sheet. We obeyed Lowenstein's rule for distribution of defects as observed by Si-NMR experiments (Lipsicas et al., 1984; Sanz and Serratosa, 1984; Herrero and Sanz, 1991). The resulting negative charge was compensated with sodium ions between the clay layers. This type of substitution strategy was also used by Abdolhosseini Qomi et al. (2012) to study the effect of elemental substitution on elastic properties of calcium-silicate-hydrate (CSH)-another mineral with layered structure. We carried out two different random isomorphous substitutions in the octahedral layer and created two distinct atomic structures for the computer simulations. Figure 3-1 shows the radial distribution functions of Mg-Mg defects of the two structures. In simulation (1), the two defects have a separation greater than 7.9Å, while in simulation (2) they are separated by more than 5.2Å. Figure 3-2 shows the typical structure of the simulated clay-water system. Clay swelling was simulated at an isothermal temperature, $T=300$ K, and isobaric pressure, $P=0$ GPa, using $NPT$ ensemble over a time period, $\Delta t=900$ ps (pico second). The Nosé-Hoover thermostat (Nosé, 1984; Hoover, 1985) is used to control temperature together with the Parrinello-Rahman (Parrinello and Rahman, 1981) barostat to control pressure in the system. All properties are calculated from the last 500 ps of the simulations when the system has reached its equilibrium state. An integration time step of 1 fs (femto second) was used in all simulations.

### 3.2.2 Calculation of Elastic Properties

The single crystalline elastic stiffness properties were calculated using energy minimization of the structure obtained from MD simulation in GULP program. We use the Voigt notation in representing components of the fourth order elasticity tensor $C_{ijkl}$ that changes the indices in the following way: $11 \rightarrow 1, 22 \rightarrow 2, 33 \rightarrow 3, 23 \rightarrow 4, 13 \rightarrow 5$ and $12 \rightarrow 6$. In this notation, fourth order elasticity tensor can be represented by a symmetrical matrix with components $C_{ij}$. We will use cartesian coordinate system with direction 3 as the one normal to the clay layers (Z) and directions 1 and 2 in the plane of the clay layer (XY)(see Figure 3-2). The generalized
The expression for calculating elastic constants is (Theodorou and Suter, 1986):

$$C_{ij} = \frac{1}{\Omega} \frac{\partial^2 A}{\partial \epsilon_i \partial \epsilon_j} \quad i, j = 1, 2, \ldots, 6$$

(3.1)

where $\Omega$ is the volume of the unit cell, $A$ is the Helmholtz free energy, $\epsilon_1, \epsilon_2$ and $\epsilon_3$ are the longitudinal strains in the $X$, $Y$ and $Z$ directions and $\epsilon_4, \epsilon_5$ and $\epsilon_6$ are the shear strains in the $YZ$, $XZ$ and $XY$ planes, respectively.

We have reported elastic stiffness constants based on the second derivative of potential energy density with respect to strain:

$$C_{ij} = \frac{1}{\Omega} \frac{\partial^2 U}{\partial \epsilon_i \partial \epsilon_j} \quad i, j = 1, 2, \ldots, 6$$

(3.2)
Figure 3-2: Typical unit cell in periodic crystal of the simulated clay mineral at d=12Å.

The effects of temperature are handled by equilibrating the clay-water system at 300K such that the interatomic distances are modified to represent the behavior of system at this temperature. The same interatomic distances are then used to calculate elastic properties which leads to a proper approximation of the elastic tensor at finite temperature.

There are two alternative methods for computing the system stiffness that are illustrated here for the $C_{33}$ stiffness component using a reference system with water content, $\frac{M_{\text{water}}}{M_{\text{clay}}} = 0.0367$ and basal layer spacing, $d=12.1Å$. Within the framework of MD, there are two alternative approaches to compute elastic properties at finite temperature using, quasi-static or rate dependent approaches:

In the quasi-static approach, the Z-dimension of the box model is extended by applying different strains perpendicular to the clay layers. Each case is equilibrated in an NVT ensemble ($T=300K$, $dt=1$ fs). Each point in the strain-stress curve is the mean value of the pressure component in the vertical direction. Figure 3-3 shows the results of applying a total strain $\epsilon_{33} = 0.7\%$ in 0.1% increments. Each stress point is averaged over a simulation period of 1ns. The results show apparent linear stress strain response with an initial linear
stiffness of $C_{33} = 33$ GPa. The initial part of the curve does not go back to zero stress at zero strain since the configuration is taken at the end of the NPT ($P=0$ GPa and $T=300$K) with pressure oscillating around zero (and not being exactly zero). Convergence can be considered by using smaller strain steps (0.01%). Figure 3-4 shows the computed strain-stress behavior up to $\epsilon_{33} = 0.05\%$. In this case the stress level at each strain state is averaged over the last 10ns of a 60ns simulation in the NVT ensemble ($T=300$K, $dt=1$ fs). It can be seen that the stresses oscillate around $\sigma_{33} = 0$ for $\epsilon_{33} < 0.03\%$. This result occurs as there is a large fluctuation of instantaneous stress compared to the mean shown in Figure 3-5 over 60ns of NVT simulation (for strain $\epsilon_{33} \leq 0.05\%$). As the strain level increases the mean stress value increases. However, the system is far from its initial configuration. Therefore, it is practically impossible to define the elastic response from equivalent strain-stress properties computed at small strains using a quasi-static method.

In the rate-dependent approach, we apply a constant strain rate in the vertical direction in an NVT ensemble ($T=300$ K, $dt=1$fs) and report the average of the corresponding pressure component. Figure 3-6 (a) shows the resulting stress-strain response over 10% strain (applied for a simulation of $10^5$ fs) corresponding to strain rate of $10^{-6}$ fs$^{-1}$. Fitting a straight line to the initial part of the strain-stress curve (Figure 3-6 (b)) results in $C_{33} = 86$ GPa. In Figure 3-7 (a), 1% strain is applied over $10^5$ fs of simulation corresponding to strain rate of $10^{-7}$ fs$^{-1}$. Fitting a line to the initial part of the curve (Figure 3-7 (b)) results in $C_{33} = 624$ GPa. Again, it is practically impossible to define an elastic regime from strain-stress plots using a constant strain rate loading method. This approach generates stiffness values that are highly sensitive to the strain rate.

Given the illustrations described above, we believe that the proposed approach based on the curvature of the energy landscape is the best appropriate way to interpret elastic properties for the clay water system. The derived elastic constants of the clay mineral are generally in good agreement with available results from acoustic and nanoindentation measurements. Provided that the potential between atoms are known, one can calculate analytical derivatives of the energy with respect to the strain tensor to find second order elastic properties of
Figure 3-3: Strain-stress curve for $C_{33}$ with strain steps of 0.1%

Figure 3-4: Strain-stress curve for $C_{33}$ with strain steps of 0.01%

the crystal. Following the derivation of Catlow and Mackrodt (1982), to obtain energy change due to deformation, the strain energy density can be written as a power series expansion
Figure 3-5: Instantaneous values of \( \sigma_{33} \) for \( \varepsilon_{33} = 0.05\% \)

Figure 3-6: Strain-stress curve for strain rate of \( 10^{-6} \text{ fs}^{-1} \) (a) 0 - 10\% (b) 0 - 1\%

about its equilibrium configuration at zero strain as:

\[
u(R) = u(R_0) + \frac{1}{2}\delta^T \cdot W \cdot \delta
\]  

(3.3)

In which \( R_0 \) denotes equilibrium configuration and \( \delta \) is generalized vector consisting of 3N
Figure 3-7: Strain-stress curve for strain rate of $10^{-7}$ fs$^{-1}$ (a) 0 - 1% (b) 0 - 0.2%

(N being number of atoms in the unit cell) internal deformation and 6 external strain acting on the unit cell. Homogeneous strain on the unit cell can result in inhomogeneous internal deformation to maintain internal equilibrium of each atom in the crystal.

$$\delta = [\delta_T, \delta \varepsilon]$$

and $\overline{W}$ is the matrix of second derivatives of the energy:

$$\overline{W} = \begin{bmatrix} u_{rr} & u_{r \varepsilon} \\ u_{r \varepsilon} & u_{\varepsilon \varepsilon} \end{bmatrix}$$

in which "\(^2\)" stands for derivative i.e. $u_{rr} = \partial^2 u / \partial r \partial r$, etc. New configuration, $R = \{ r \}$, is related to the old one, $R_0$, by the following transformation:

$$r = \Delta \varepsilon \cdot (r_0 + \delta r)$$
in which $\Delta \varepsilon$ is a matrix formed from components of $\delta \varepsilon$:

$$\Delta \varepsilon = \begin{bmatrix} \delta \varepsilon_1 & \frac{1}{2} \delta \varepsilon_6 & \frac{1}{2} \delta \varepsilon_5 \\ \frac{1}{2} \delta \varepsilon_6 & \delta \varepsilon_2 & \frac{1}{2} \delta \varepsilon_4 \\ \frac{1}{2} \delta \varepsilon_5 & \frac{1}{2} \delta \varepsilon_4 & \delta \varepsilon_3 \end{bmatrix}$$  \hspace{1cm} (3.7)

expanding Eq.(3.3) we get:

$$u(R) = u(R_0) + \frac{1}{2} \delta r^T \cdot u_{rr} \cdot \delta r + \delta r^T \cdot u_{\varepsilon \varepsilon} \cdot \delta \varepsilon + \frac{1}{2} \delta \varepsilon^T \cdot u_{\varepsilon \varepsilon} \cdot \delta \varepsilon$$  \hspace{1cm} (3.8)

equilibrium condition requires:

$$u_{\varepsilon} = 0$$  \hspace{1cm} (3.9)

which results in:

$$\delta r_i = \left[ u_{rr}^{-1} \cdot u_{\varepsilon \varepsilon} \cdot \delta \varepsilon \right]_i$$  \hspace{1cm} (3.10)

substituting Eq.(3.10) in Eq.(3.8) gives

$$u(R) = u(R_0) + \frac{1}{2} \delta \varepsilon^T \cdot \left[ u_{\varepsilon \varepsilon} - u_{\varepsilon \varepsilon} \cdot u_{rr}^{-1} \cdot u_{rr} \right] \cdot \delta \varepsilon$$  \hspace{1cm} (3.11)

from which the elastic constant tensor with voigt notation can be identified:

$$C = u_{\varepsilon \varepsilon} - u_{\varepsilon \varepsilon} \cdot u_{rr}^{-1} \cdot u_{rr}$$  \hspace{1cm} (3.12)

Formulae and expressions of the second derivatives can be found in Catlow and Mackrodt (1982). Energy minimization was accomplished using the BFGS steepest descent algorithm (Press et al., 1992). It should be noted that the minimizer switched to a Rational Function Optimization (RFO) algorithm (Banerjee et al., 1985) when the gradient norm fell below $5 \times 10^{-3} \frac{eV}{A}$. The RFO approach guarantees to find configurations with positive definite stiffness matrix which corresponds to a stable minimum. A similar procedure has been used to find equilibrium structure at the extrema of the energy surface with positive curvature for other layered minerals (Auzende et al., 2006; Pellenq et al., 2009; Manzano et al., 2011; Abdolhosseini Qomi et al., 2012).
3.3 Force field validation

Figure 3-8 displays swelling curve of Na-Wyoming montmorillonite as the results of series of MD simulations at different levels of hydration defined in the form of the mass ratio of water to clay. The experimental curve obtained from Fu et al. (1990). Results of the simulations are in very good agreement with the experiment. Same results were obtained to examine performance of CLAYFF (Cygan et al., 2004) in predicting swelling behavior of clay.
3.4 Results and discussion

3.4.1 Swelling Mechanism

In this section we will discuss mechanism of swelling by extracting structural results from the second simulation as an example. The first simulation produces similar results. The mechanism of swelling can be explained by considering the average number of hydrogen bonds per water molecule and the density of the interlayer water as a function of the basal layer spacing, d, as shown in Figure 3-9. We have used the common geometric definition of hydrogen bond (Luzar and Chandler, 1996) in calculating the number of hydrogen bonds that each water molecule creates with surrounding water molecules. A hydrogen bond is assigned when the O-O distance is less than 3.5Å and simultaneously the H-O-O angle is less than 30°. The average number of hydrogen bonds per water molecule at 300K in bulk water is 3.6 which corresponds to the density of 1.0 g/cm³. Three regions are identified in Figure 3-9: in region A, the density of the interlayer water ($\rho_w$) and number of hydrogen bonds ($N_{HB}$) increase rapidly to a threshold condition at $d \approx 12.8$ Å corresponding to the formation

![Figure 3-9: Change in average number of hydrogen bonds per water molecule and density of interlayer water during swelling of Wyoming Na-montmorillonite.](image-url)
Figure 3-10: Change in derivative of the density with respect to basal layer spacing during swelling of Wyoming Na-montmorillonite.

of mono-layer water-clay system. In transition from region A to B, the density of water and number of hydrogen bonds remains constant which indicates that the rate of water adsorption and increase in basal layer spacing are (almost) the same until the system reaches region B. Region B, d\(\approx\)14.3-15.6 Å, corresponds to the formation of the second water layer. The transition from B to C is identified by the change in slope of both \(\rho_w\) and \(N_{HB}\). Figure 3-10 shows the derivative of water density with respect to the basal layer spacing with maxima at d\(\approx\) 12Å and 15Å. We will show that these also correspond to maxima in some of the elastic stiffness constants. The formation of the third water layer (region C) is less visible. Figure 3-11 shows the density profile for interlayer species in the direction normal to the clay layers for three different basal layer spacings (d\(\approx\)12, 15 and 17.8 Å). These results show clearly the formation of the first, second and third layer of water molecules between clay sheets from the number of peaks in the water oxygen, Ow, distribution. Density profiles of water and ions between clay layers are in good agreement with previous simulations (Smith, 1998; Chávez-Páez et al., 2001b; Marry and Turq, 2003; Tambach et al., 2004b; Whitley and
Figure 3-11: Density profile of water oxygen (Ow) and water hydrogen (Hw) and sodium (Na) in the direction normal to the clay layers.

Smith, 2004; Mazo et al., 2008). For the two layer system (d≈15Å), the water molecules are distributed evenly between layers while for the three layer system there are more water molecules close to the clay surfaces than in the middle layer. Following Sposito et al. (1999) the adsorption of interlayer cations in smectite can be classified as 'inner-sphere' or 'outer-sphere' complexes. Inner-sphere surface adsorption describes the condition where there is no water molecule between the cation and the clay surface, while an outer-sphere surface adsorption has at least one water molecule between the cation and the clay sheet. Formation of these surface complexes depends on both the charge and size of the cations and the location of the charged sites due to substitutions in clay layers (Skipper et al., 1995; Greathouse and Sposito, 1998). For Wyoming Na-montmorillonite which has isomorphous substitutions in both tetrahedral and octahedral layers and (Na) cations as charge compensating ions, we expect to find formation of both inner and outer sphere complexes (Sposito et al., 1999). Our
simulation results show that upon increasing water content, Na ions become more hydrated and detached from the clay surface (Boek et al., 1995b). Figure 3-11, confirms the formation of inner-sphere complexes by having peaks in (Na) cation distributions closer than peaks in (Ow) for all basal layer spacings. For d=15Å through 17.8Å, there is a high concentration of Na ions in the middle water layer. This shows an increase in outer-sphere complexes in agreement with Chávez-Páez et al. (2001c). It should be noted that in our simulations, tetrahedral charge sites represent only 33 percent of the total clay layer charge. This explains the decrease of the number of inner-sphere complexes, as hydration proceeds. One can expect a different situation with a larger number of inner-complexes for a pure tetrahedrally substituted clay (the layer charge being then localized very close to the clay layer surface). The type of substitution (tetrahedral/octahedral layer) and the amount of substitutions define the resulting ion distribution that in turn affects the mechanical properties of the material in terms of the layer-to-layer cohesive pressure as shown with primitive model simulations (Pellenq et al., 1997).

3.4.2 Elasticity

For each hydration state, the full elastic stiffness tensor ([C_{ij}] i, j = 1, 2, . . . , 6) has been calculated. It is usually desirable to approximate the full tensor (with 21 independent parameters) using assumptions of material symmetry. For a stack of clay lamellae, we expect good approximations with an equivalent transversely isotropic tensor composed of five independent engineering elastic constants: E_p, E_z, G_{pz}, \nu_p and \nu_{zp}. E_p and E_z are the Young’s moduli in the plane of the basal layer and in the direction normal to it; G_{pz} is the shear modulus in planes normal to the isotropic plane; \nu_p and \nu_{zp} are the Poisson’s ratios characterizing the lateral strain response in the plane of transverse isotropy to a stress acting parallel and normal to the isotropic plane. Values of the elastic constants of the transversely isotropic plane are calculated by averaging over x and y directions and over the two sets of simulations (denoted as \overline{[C_{ij}]}).

In the following discussion, we will show the variation of elastic stiffness constants \( C_{11} \) (and \( C_{22} \)), \( C_{33} \), \( C_{44} \) (and \( C_{55} \)), \( C_{12} \), \( C_{13} \) (and \( C_{23} \)) as a function of the degree of hydration for two structures with different locations of isomorphous substitutions. These constants can
be directly related to the above listed set of engineering elastic constants. The mean and standard deviation between two simulation results will be reported.

Figure 3-12: The $C_{33}$ elastic constant as a function of basal layer spacing. Filled symbols represent data points from simulation (1) and hollow symbols represent data points from simulation (2). Triangular symbols represent equivalent transversely isotropic stiffness constants.

Figure 3-12 shows the variations of $C_{33}$ upon hydration. There is a sudden decrease in the mean value from $\overline{C}_{33} = 48.5\pm3.8$ GPa to $16.8\pm1.2$ GPa from the dry state to the mono layer hydration. The modulus increases upon further water adsorption to a local maximum, $\overline{C}_{33} = 30.0\pm0.5$ GPa at $d\approx12\text{Å}$ (middle of region A). As the basal layer expands to accommodate more water molecules, there is a decrease in $\overline{C}_{33}$ (to $20.7\pm2.3$ GPa at $d\approx14\text{Å}$), until region B. Formation of the second layer of water is associated with another local maximum, $\overline{C}_{33} = 26.2\pm3.0$ GPa at $d\approx15\text{Å}$ (middle of region B). Further increase in basal layer spacing has only a small impact on the modulus with $\overline{C}_{33} = 21.6\pm1.08$ GPa for $d \geq 15.6\text{Å}$.

Ortega et al. (2007) reported values of the elastic stiffness constants of the clay phase of
deviates from the dry state. During formation of the first layer of water in region A, there is a slight increase in shear stiffness with maximum $\overline{C}_{44}=5.4\pm0.1$ GPa. In this region, the clay surface creates strong Coulombic bonding with the adsorbed water, confirming Sayers (2005) argument that water bounded to the clay surface may create an ordered structure with non-zero shear modulus. Between region A and region B, the shear stiffness remains approximately constant. During the formation of the second layer of water shear stiffness decreases slightly and reduces to a constant value $\overline{C}_{44}=4.1\pm0.3$ GPa for $d\geq15.6$ Å. Ortega et al. (2007) reported UPV (level II) measurements for clay shales of $C_{44}=2.9-8.9$ GPa and interpreted the stiffness for the clay lamellae (level 0), $C_{44}^*=3.7$ GPa. These values are generally in good agreement with the current numerical calculations for Wyoming Na-montmorillonite.

Figure 3-14: The $C_{13}$ and $C_{23}$ elastic constants as a function of basal layer spacing. Legend as in Figure 3-12.

Figure 3-14 shows change in the $C_{13}$ and $C_{23}$ elastic components during hydration. The trend of the $\overline{C}_{13}$ is similar to $\overline{C}_{44}$, decreases from a dry state maximum, $\overline{C}_{13}=18.0\pm1.6$ GPa to $4.9\pm0.6$ GPa, at region A, rising to a local maximum $9.7\pm0.01$ GPa with a constant value $7.7\pm0.6$ GPa for $d>14.3$ Å. Ortega et al. (2007) reported a wide range of $C_{13}$ (6.1-24.3 GPa) from UPV tests and interpreted $C_{13}^*=18.1$ GPa for the clay lamellae. The $C_{13}$ and $C_{23}$
are related to the lateral Poisson's ratio connecting deformation between the vertical and horizontal axes. Although the fundamental stiffness component for the solid clay lamellae is consistent with the numerical simulations at small basal layer spacing, the UPV data are generally higher than the computed range for $C_{13}$. This discrepancy may relate to effects of the finite aggregate size on UPV measurements, while the results of the molecular dynamics simulation corresponds to lamellae of infinite length.

The stiffness components $C_{11}$, $C_{22}$ and $C_{12}$ are mainly affected by the strong iono-covalent bonding inside the clay layers. Figures 3-15 and 3-16 show the variations in $C_{11}$, $C_{22}$ and $C_{12}$ elastic constants during hydration. The $C_{11}$ and $C_{22}$ elastic constants represent Young's moduli in the plane of transverse isotropy. Both $C_{11}$ and $C_{12}$ continuously decrease by increasing basal layer spacing from $290.5 \pm 3.7$ GPa at $d=9.3$ Å to $154.5 \pm 1.6$ GPa at $d=19.5$ Å. These values are 5 to 8 times larger than corresponding values in the direction normal to the clay layers. The large difference between $C_{11}$ or $C_{22}$ and $C_{33}$ values comes from the difference between iono-covalent bonding inside the clay crystal layer and screened
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electrostatic bondings between layers. The average values of Young’s moduli at \( d \approx 12\AA \) are \( E_x = 180\text{GPa} \) and \( E_y = 172\text{GPa} \) that are in very good agreement with values from MD simulations by Suter et al. (2007) \( (E_x = 185\text{GPa} \) and \( E_y = 175\text{GPa} \)). The calculated engineering elastic moduli and the results obtained by Mazo et al. (2008) (at \( T = 300 \text{K} \)) are presented in Table 3.1. We can see good agreement between values of Poisson’s ratios for both monolayer and bilayer systems. The in-plane Poisson’s ratios \( (\nu_{xy} \text{ and } \nu_{yx}) \) close to 0.5 indicate rigidity of the clay-water system in the bedding direction. Also, in-plane elastic moduli \( (E_x, E_y \text{ and } G_{xy}) \) of monolayer system from both analyses are in good agreement. As explained earlier, the planar stiffness are mainly affected by the strong iono-covalent bonding inside the clay layers while the stiffness perpendicular to the layers are mainly due to the screened electrostatic bondings between layers. As the amount of water increases, the contribution of the long range Coulombic interaction in the planar direction also increases. We believe the difference between stiffness values perpendicular to the layers from our calculations \( (E_z = 28.83 \pm 4.21 \text{ for monolayer and } 27.82 \pm 0.12 \text{ for bilayer}) \) and Mazo et al. (2008) \( (E_z = 78.1 \pm 0.1 \text{ for monolayer and } 61.7 \pm 0.1 \text{ for bilayer}) \) are due to the following factors:

- Mazo et al. (2008) used cut-off for long-range Coulombic interactions. Long range interactions such as Coulombic potentials decay slowly with distance \( (\sim \frac{1}{r^2}) \). As a result, truncation of the interactions at a certain cut-off can introduce large errors (Lau et al., 1994; Patra et al., 2003). We have used Particle Mesh Ewald summation (Darden et al., 1993; Essmann et al., 1995) to calculate the total electrostatic interactions in a periodic system. As explained the effect is more pronounced in the direction perpendicular to the layers.

- Mazo et al. (2008) used rate-dependent approach to construct stress-strain curve. As we showed in section 3.2.2 the result of this approach is highly sensitive to the applied strain rate. The effect is less pronounced in the planar direction due to rigidity of the clay crystal and more pronounced perpendicular to the layers.

- Mazo et al. (2008) used the CLAYFF (Cygan et al., 2004) force field but they chose
Table 3.1: Engineering elastic moduli (in GPa) calculated for hydrated montmorillonite

<table>
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<th>our calculations</th>
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<td>bilayer</td>
<td>monolayer</td>
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<tr>
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</tbody>
</table>

TIP3P potential for water molecules (Jorgensen et al., 1983) which is inconsistent with the force field. CLAYFF is built around the flexible version of the simple point charge (SPC) water model (Teleman et al., 1987).

- Mazo et al. (2008) used cut-off radius equal to 10.5 Å for short range van der Waals interactions while CLAYFF has been calibrated for cut-off radius of 8.5 Å.

The computed results are much higher than the UPV data ($C_{11}=13.8-46.1$ GPa) and the calculated value for the clay lamellae ($C'_{11}=44.9$ GPa). This discrepancy is almost certainly related to finite length of the clay aggregates affecting experimental measurements at the UPV scale (sliding between layers etc.)

Figure 3-16 shows the variation of stiffness component $\overline{C}_{12}$ upon hydration. The elastic constant $\overline{C}_{12}$ continuously decreases by increasing basal layer spacing from $140.8\pm3$ GPa at $d\approx9.3$ Å to $77.6\pm1.5$ GPa at $d\approx19.5$ Å. Ortega et al. (2007) reported UPV measurement of $C_{12}=6.9-17.8$ GPa and calculated the stiffness for the clay lamellae $C'_{12}=21.7$ GPa which is less than the values from MD simulation and can also be attributed to finite length effect in the clay aggregation.

Nano-indentation is one of the sub-micron experiments used to measure material stiffness.
parameters. To the best of our knowledge, there are no nanoindentation measurements on Wyoming Na-montmorillonite. However, Bobko and Ulm (2008) performed a series of nanoindentation tests on the same shale samples analyzed by Ortega et al. (2007). By doing statistical analysis of the results, they extracted nanoindentation moduli for the clay phase. They carried out indentation measurements normal and parallel to the bedding plane defining $M_z$ for indentation modulus normal to the bedding plane and $M_p$ for the one parallel to the bedding plane. They reported solid phase nanoindentation moduli extrapolated to zero meso-scale porosity, $M_z^e = 16$GPa and $M_p^e = 25$GPa. Zhang et al. (2009) have also reported a series of nanoindentation results on muscovite and rectorite. The atomic structure of rectorite consists of alternating sequence of fixed and expandable clay layers. They reported a range for the nanoindentation modulus of rectorite $M_z = 19.5 \pm 4.9$GPa. It should be noted that relative humidity is not controlled or measured during these tests. Indentation moduli can be computed from transversely isotropic stiffness components using the derivation by Delafargue and Ulm (2004):
\[ M_z = 2 \sqrt{\frac{C_{11}C_{33} - C_{13}^2}{C_{11}}} \left( \frac{1}{C_{44}} + \frac{2}{\sqrt{C_{11}C_{33} + C_{13}}} \right)^{-1} \]  

(3.13)

\[ M_p \approx \sqrt{\frac{C_{11}C_{33}^2 - C_{12}^2}{C_{33}}} M_z \]  

(3.14)

Figure 3-17: Indentation modulus in z direction as a function of basal layer spacing. Legend as in Figure 3-12.

Figures 3-17 and 3-18 show the computed nanoindentation moduli of Wyoming Na-montmorillonite from molecular dynamics simulations using an equivalent transversely isotropic elastic stiffness matrix as functions of the basal layer spacing. Figure 3-17 shows that the variation of \( M_z \) is similar to change in \( C_{33} \) stiffness component (Figure 3-12). After a sudden decrease from \( 31.2 \pm 7.0 \text{GPa} \) to \( 13.3 \pm 0.1 \text{GPa} \) for \( d \approx 9 \text{Å} \), there are local maxima \( 22.8 \pm 1.1 \text{GPa} \) at \( d \approx 12 \text{Å} \) and \( 20.8 \pm 1.6 \text{GPa} \), at \( d \approx 15 \text{Å} \). For \( d \geq 15.6 \text{Å} \) the \( M_z \) value is approximately constant \((17 \pm 0.3 \text{GPa})\). Results of the simulations are in very good agreement with the nanoindentation experiments (Bobko and Ulm, 2008; Zhang et al., 2009) from region B onward to larger basal layer spacing.

Figure 3-18 shows the modulus parallel to the basal planes \( M_p \) decreases from \( 133.5 \pm 6.2 \text{GPa} \)
(d\approx9.3\text{Å}) to 96.5 \pm 3.4\text{GPa} (d\approx11.5\text{Å}). There is a small increase to 106.0 \pm 0.2\text{GPa} at region A which corresponds to the building up of the first water layer which has strong interaction with the clay surface. After region A, \(M_p\) continuously decreases to 72.8 \pm 0.03\text{GPa} at d\approx19.5\text{Å}. The experimental estimates for clay plates, \(M_p^e\) (Bobko and Ulm, 2008) is much smaller than our simulated values. This difference can be explained by the fact that nanoindentation parallel to the clay layers measures elastic stiffness due to sliding of finite clay layers against each other (similar to \(C_{11}, C_{22}\) and \(C_{12}\)) and not the stiffness of infinitely long clay layers as modeled in MD simulation.

Following the methodology of Shahsavari et al. (2010), the Euclidean and Riemannian distance metrics are used to evaluate the accuracy of the equivalent transversely isotropic parameters (\(\overline{C}_{ij}\)) in representing the full elastic stiffness matrix (\(C_{ij}\)) of the clay-water system. The Euclidean distance metric is one of the most commonly used distance metrics (Alexander et al., 1999) that relates two square matrices, \(A_1\) and \(A_2\), as follows:

\[
d_E(A_1, A_2) = \|A_1 - A_2\|_E
\]  

(3.15)
and the associated norm is defined by:

\[ ||A||_E = \sqrt{\text{tr}((A^T A)} \]  

(3.16)

where \( \text{tr}(\cdot) \) stands for the trace and the superscript \( T \) denotes the transpose. The classical Euclidean distance metric is fast and easy to compute but lacks certain physically meaningful properties (Arsigny et al., 2005) and can generate symmetric matrices with null or negative eigenvalues. These problems are avoided using the Riemannian metric. The Riemannian metric is independent of the coordinate system, preserves material symmetries and is invariant under inversion (Moakher, 2006). Having two positive definite matrices, \( P_1 \) and \( P_2 \), the Riemannian metric is defined as follows:

\[ d_R(P_1, P_2) = \left\| \ln \left( P_2^{1/2} P_1^{-1} P_2^{1/2} \right) \right\|_R = \left[ \sum_{i=1}^{n} \ln^2 \lambda_i \right]^{1/2} \]  

(3.17)

where \( \lambda_i \) are the eigenvalues of \( P_1^{-1} P_2 \).

These metrics are means of measuring similarity between two matrices. For both metrics the smaller value means better approximation in representing full matrix with its equivalent transverse isotropic one.

Figures 3-19(a) and 3-19(b), show relative Euclidean and Riemannian distance metrics of full and transversely isotropic elastic stiffness matrices as a function of the basal layer spacing. The results shows that the transversely isotropic approximation is a good representation of elastic stiffness parameters for \( d \geq 12\AA \), but becomes less reliable for conditions approaching the dry state.

### 3.5 Conclusion

This paper has presented a complete set of elastic stiffness constants for Wyoming Namontmorillonite based on computational molecular dynamics simulations. The results show the variation in elastic constants as a function of the hydration state and basal layer spacing. Key findings for the individual stiffness components can be summarized as follows:
Figure 3-19: (a) Relative Euclidean Metric as a function of basal layer spacing. (b) Riemannian Metric as a function of basal layer spacing. Legend as in Figure 3-12.
(1) The normal stiffness $\bar{C}_{33}$ oscillates with hydration level linked to the formation of mono and double layer of inter-lamellae water.

(2) The $\bar{C}_{33}$, $\bar{C}_{44}$ (and $\bar{C}_{55}$) and $M_s$ values are in good agreement with acoustic and nano-indentation experiments for basal layer spacing $d \geq 15.6 \text{Å}$ corresponding to a system with two layers of water.

(3) The computed in-plane stiffness parameters $\bar{C}_{11}$ (and $\bar{C}_{22}$), $\bar{C}_{12}$ and $M_p$ (and to a less degree $\bar{C}_{13}$ (and $\bar{C}_{23}$)) differ from the experimental measurements. However the latter are illustrated by the finite length of clay particles while the current simulations represent conditions for infinitely long plates.

(4) Transverse isotropic assumption of mechanical properties for the clay mineral is a good approximation after the formation of the first layer of water but is less reliable for representing the dry state of the clay lamellae.
Chapter 4

Mesoscale simulation of clay-water system

4.1 Introduction

Clay is the most abundant mineral on the earth (Meunier, 2006) and one of the most important industrial materials with a wide range of applications in construction, environmental, pharmaceutical and process industries (Murray, 2000). Aggregation of clay mineral plays an important role in calculating the physical properties of soils such as elastic stiffness properties that control elastic wave propagation and the transport of ionic substances required for applications in waste management and environmental protection. Aggregation or dispersion of clay particles also affects the viscosity of drilling fluids. For these reasons, the coagulation of clay particles has received prominent attention in the literature (Goldberg and Glaubig, 1987; Tombácz et al., 2001; Lagaly and Ziesmer, 2003; Tombácz et al., 2004; Michot et al., 2004, 2006; Garcia-Garcia et al., 2007; Michot et al., 2008; Zhou et al., 2012; Michot et al., 2013; Carrier et al., 2013).

Clay minerals have a layered structure at the nanoscale. Each layer consists of some combinations of two sheet types with silicon tetrahedra and aluminum octahedra as basic units. For instance, the structure of natural Wyoming Na-montmorillonite has the following experimental formula (Newman, 1987): $\text{Na}_{0.75} \text{nH}_2\text{O}\text{Si}_{7.75}\text{Al}_{0.25}[\text{Al}_{3.5}\text{Mg}_{0.5}]\text{O}_{20}(\text{OH})_4$. This structure comprises two tetrahedral sheets sandwiching an octahedral sheet. Due to iso-
morphous substitutions of metal ions, the clay has a net negative surface charge. For the Wyoming Na-montmorillonite, 3.125% of the silicon ions, Si$^{4+}$, in the tetrahedral sheet are substituted by aluminum, Al$^{3+}$, while 12.5% of the aluminum ions, Al$^{3+}$, in the octahedral sheet are substituted by magnesium, Mg$^{2+}$. In the current research the negative charge is balanced by sodium ions, Na$^{1+}$ between the clay layers. In a recent study (Ebrahimi et al., 2012), we characterized structural and mechanical properties of montmorillonite at the atomic scale. This chapter presents a methodology to describe clay aggregates at the meso-scale from a simulation point of view.

The fundamental multi-scale approach toward the understanding clay behavior at the macroscopic scale (to address practical applications in geotechnical and petroleum engineering) aims at modeling the material at scales ranging from the atomistic level to the macroscopic system. Molecular dynamics simulation (MD) is a versatile technique to study interaction between colloidal nanoplatelets at the atomistic scale. In order to represent clay aggregates with mesopores and grain boundaries, the model must be scaled up from the atomistic level to the submicron length scale. This exceeds the computational possibilities of full atomistic models and motivates a multiscale and consistent approach. Previous attempts to study clay aggregates were based on using quadrupoles (Dijkstra et al., 1995, 1997) or pseudo charge sites to represent clay platelets (Mourchid et al., 1995; Kutter et al., 2000; Meyer et al., 2001; Odriozola et al., 2004; Mossa et al., 2007; Jönsson et al., 2008; Jardat et al., 2009; Thuresson et al., 2013). The multipole representation of platelets might not be effective because of difficulties in modeling the charge distributions and existence of local defects associated with isomorphous substitutions. To overcome these limitations, we have used an upscaling strategy to run MD at meso-scale through calculation of free energy for face-to-face and edge-to-edge configurations of clay nanoplatelets using full atomistic representation of platelets, water molecules and ions. We then use the thermodynamic perturbation method to calculate the potential of mean force (PMF) (e.g. free energy) as a function of the distance between the centers of two platelets, an approach previously used for interaction between two graphene sheets (Choudhury and Pettitt, 2005). The free energy is then used to calibrate the Gay-Berne (GB) potential (Gay and Berne, 1981) for different platelet sizes to study meso-scale interactions of multiple platelets with different orientations. The resulting
arrangements of particles determine the microstructure of clay aggregates that control mechanical properties such as elastic stiffness. We characterize microstructure of the stabilized systems and report their full elastic properties.

4.2 Nano-scale PMF calculation

The proposed methodology begins with the calculation of the free energy along a reaction coordinate which corresponds to the separation distance (Figure 4-1) for face-to-face and edge-to-edge interactions of two Wyoming Na-montmorillonite platelets in liquid water. In order to calculate the change in free energy of the system from state A, when clay platelets are far from each other, to state B, when they are in close proximity, we define several intermediate states covering the change from state A to state B in small increments to enhance sampling of the phase space. Using stratification strategy, successive states are separated by low energy barriers such that the phase space is fully explored enabling statistical averaging of the states (Chipot and Pohorille, 2007). We construct series of MD trajectories, each one representing one value of center to center distance. The trajectory of the MD simulation at one state is perturbed along the reaction coordinate to the target state while all other degrees of freedom are frozen. Free energy differences between two successive reference and target thermodynamic states will be calculated and added along the transformation path from state A to state B.

The analyses are carried out using the CLAYFF (Cygank et al., 2004) force field that has been used successfully for simulation of clay minerals (Liu et al., 2007; Suter et al., 2007). CLAYFF is a versatile force field built around the flexible version of the Simple Point Charge (SPC) water model (Berendsen et al., 1987).

Full atomistic MD simulations were carried out by using the GROMACS (Van Der Spoel et al., 2005) simulation package. The atomic structures were visualized using VMD (Humphrey et al., 1996) molecular graphic software.

The crystallography for 2:1 clay mineral was taken from Refson et al. (2003). Isomorphous substitution was carried out randomly. We obeyed Lowenstein’s rule for distribution of defects. Depending on the statistical ensemble, the Nosé-Hoover thermostat (Nosé, 1984;
Hoover, 1985) is used to control temperature and the Parrinello–Rahman barostat (Parrinello and Rahman, 1981) to control pressure in the system. An integration time step of 1 fs (femto second) was used in all full atomistic simulations. Three-dimensional, periodic boundary conditions were applied along with the minimum image convention (a cutoff radius of 8.5 Å was used for short range interactions). The long range electrostatic coulombic interactions were calculated using Particle Mesh Ewald summation (Darden et al., 1993; Essmann et al., 1995). Bond lengths and angles of the water molecules were constrained using the SHAKE algorithm (Ryckaert et al., 1977) and clay platelets were kept frozen and rigid at each specific separation distance. The following sections summarizes the simulation details for edge-to-edge and face-to-face interactions.

### 4.2.1 Edge to edge

Two identical clay platelets were placed at center-to-center separations ranging from $r_i = 39.75\text{-}61.25$ Å with an increment of 0.25 Å. Figure 4-1(a) shows the typical structure of the simulated system at one of the separation distances. From now on, each separation distance is called one state, unless otherwise stated. We performed 87 separate simulations at 300 K in the canonical (NVT) ensemble. Each platelet consists of 4 x 4 unit cells with the longest dimension along $y$ axis. Four edge sites on each side (along $y$) corresponding to $[0 1 0]$ edges obtained by cutting the unit cell. Broken bonds were saturated with H or OH groups. Figure 4-1(b) shows the geometry of the edge sites taken from ab initio simulations of Churakov (2006, 2007). Edge corrections introduce $H_{32}O_{16}$ extra atoms on each platelet. The average length of the platelet in the $y$ direction is ~40 Å. We assigned a partial charge equal to 0.45e for a hydrogen atom on the edge (H) to keep the system neutral. Platelets are continuous in the $x$ direction. The two platelets were solvated in the center of a rectangular box. The solvation process was performed by stacking equilibrated boxes of SPC water molecules (Berendsen et al., 1987) to form a rectangular box of $20.87$ Å($x$) x $140$ Å($y$) x $46.56$ Å($z$) containing 3882 water molecules which is constant for all states. Water molecules have been removed from the box if the distance between an atom in the water molecule and an atom in the clay structure is less than sum of their van der Waals radii. It has been shown that structure and dynamics of water molecules on the clay
surface are only affected over two to three molecular layers from the surface (Marry et al., 2008). In our simulations, the thickness of water phase on each side of the clay platelet or on each edge at the largest separation distance is about 20 Å corresponding to more than six molecular water layers (diameter of a water molecule ~ 3 Å). As a result, the interaction of two clay platelets (edge-to-edge or face-to-face) separated by water layers with 40 Å thickness is efficiently shielded to have no interaction between a platelet and its image. Moreover, the simulation box is large enough so that properties of water molecules near to the boundaries of the box approximate closely to those of bulk water. After solvation, each system was equilibrated for 0.5 ns (nano second). Free energy differences between successive states are calculated over a 2.5 ns production period. Each state, $r_i$, was perturbed in two directions: forward and reverse, $r_i ± 1 = r_i ± d r_i$, where $d r_i = 0.25$ Å (except for the end states which perturbed in one direction only). Following Zwanzig (1954), the free energy difference between the reference state, $r_i$, and target state, $r_i ± 1$, can be calculated using free energy perturbation theory:

$$\Delta G (r_i \rightarrow r_i±1) = G(r_i±1) - G(r_i) = -\frac{1}{\beta} \ln \langle \exp (-\beta \Delta U) \rangle_i$$

(4.1)

$$\Delta U = U(r_i±1) - U(r_i)$$ and $\beta = (k_B T)^{-1}$ where $T$ is the temperature, $k_B$ is Boltzmann’s constant and $U$ denotes the potential energy of the system. The brackets denote canonical ensemble average over the trajectory and subscript $i$ indicates that the average is taken in the reference state. We calculated 172 free energy differences between successive states. In order to eliminate systematic sampling bias due to exponential averaging we used simple overlap sampling (SOS) of the forward and reverse perturbation as an estimate of $\Delta G$ (Lee and Scott, 1980; Chipot and Pohorille, 2007):

$$\Delta G (r_i \rightarrow r_i±1) = -\frac{1}{\beta} \ln \left[ \frac{\langle \exp (-\beta \Delta U / 2) \rangle_i}{\langle \exp (\beta \Delta U / 2) \rangle_i±1} \right]$$

(4.2)

The total potential of mean force at each separation distance ($r=r_i$) was calculated by sequentially summing up all the free energy changes from the largest separation ($r=61.25$ Å) to that state ($r=r_i$) assuming zero value for the free energy of the system at the largest separation ($r=61.25$ Å). Figure 4-2(a) shows the potential of the mean force for edge-to-edge
interactions calculated over the range of states for selected analysis production periods. The results converge after averaging over 2.5 ns (i.e., 3 ns simulation and perturbation for each MD state). The PMF shows an oscillatory behavior with distance between energy minimums (or plateau) reflecting size of a water molecule (~3 Å). In other words, rearrangement of the water molecules determines favorable positions of the clay platelets. As platelets come closer to each other, system crosses energy barriers to reach to the lowest free energy at $r=45.5$ Å. For $r<45.5$ Å, repulsion dominates the interaction of platelets indicating work needed to remove water molecules and bring platelets close together. Figure 4-2(b) shows PMF per unit length of the platelet which will subsequently be scaled for different platelet sizes (assuming 'D' as diameter of the platelet, values of the 'x' axis are modified to 'new $r_i = old r_i - 40$ Å + D' and values of the 'y' axis are multiplied by the diameter of the platelet).
Figure 4-2: Potential of mean force for edge-to-edge interaction of clay platelets. (a) total PMF, \(a,b = 3.25, 3 \, \text{Å}\), respectively. (b) PMF per length.
4.2.2 Face to face

Two identical clay platelets were placed at center to center separations of $r_i = 9.23-18.47$ Å with an increment of 0.25 Å. Figure 4-1(c) shows the typical structure of the simulated system in one of the separation distances. Platelets are continuous in x and y directions. We performed 38 separate simulations at $T = 300$ K in the canonical (NVT) ensemble. Table 4.1 summarizes the distribution of water molecules between the platelets (I) and outside (O). In order to create structures with different amount of water between clay platelets, we displaced them to put different number of water molecules in between and the rest outside. Then for each state, we ran a 2 ns (NPT) simulation. Initial states of each (NVT) simulation was taken from trajectories of (NPT) simulations. Each platelet consists of $4 \times 4$ unit cells with the longest dimension along y axis. In order to be consistent with edge-to-edge simulations, we put $3882+2 \times 16$ (taking into account extra H and OH due to edge corrections) = 3914 water molecules in each system. The initial dimension of the rectangular box in each (NPT) simulation was $20.87$ Å(x) $\times 36.31$ Å(y) $\times 179.62$ Å(z). The average final dimensions of the system were $20.72$ Å(x) $\times 36.05$ Å(y) $\times 179.07$ Å(z). From this point, each (NVT) simulation was equilibrated for 0.5 ns. Free energy difference between successive states was calculated from a 3 ns production period. Each state was perturbed in two directions to create 74 perturbed states. The energy differences between successive states are then reported using the SOS method (Equation(4.2)). Total potential of mean force at each separation distance ($r = r_i$) was calculated by sequentially summing up all the free energy changes from the largest separation ($r = 18.47$ Å) to the state of interest ($r = r_i$) assuming zero value for the free energy of the system at largest separation ($r = 18.47$ Å).

Free energy for face-to-face interaction of clay platelets for different lengths of MD trajectory are shown in Figure 4-3(a). The calculated free energy converges after averaging over 3 ns (3.5 ns MD simulation). Similar to edge-to-edge interaction, local minima of the free energy curve are separated by distances comparable to the diameter of a water molecule. This is in agreement with previous studies reporting oscillatory changes in the interaction between two surfaces with periodicity corresponding to the diameter of a water molecule (Israelachvili and Pashley, 1983; Pashley and Israelachvili, 1984; Antognozzi et al., 2001). To have par-
Table 4.1: Center to center distances (r$_i$) and number of water molecules (N$_w$) inbetween (I) and outside (O) of the clay platelets for each state.

<table>
<thead>
<tr>
<th>state</th>
<th>r$_i$ [Å]</th>
<th>N$_w$</th>
<th>state</th>
<th>r$_i$ [Å]</th>
<th>N$_w$</th>
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Particles approach each other and reach the minimum free energy around 11 Å, they should overcome energy barriers at larger distances. Due to large repulsive interactions at smaller distances (r<11 Å), removing more water molecules is not favorable for the system. This is an indication of the existence of some bonded water molecules which cannot be removed easily. This is consistent with the experimental measurements using infrared spectroscopy (Fripiat et al., 1960; Russell and Farmer, 1964; Malhotra and Ogloza, 1989; Johnston et al., 1992; Xu et al., 2000). Figure 4-3(b) shows PMF for face-to-face interactions per surface area which will be scaled for different platelet sizes (values of the 'y' axis are multiplied by the surface area of the platelet).

Our simulations are performed in NVT ensemble to calculate the potential of mean force corresponding to relative Helmholtz free energy. It is well established that the cohesion between charged lamellae (with counter ions and solvent molecules) arises from so-called ionic correlation forces that relate to the thermal fluctuation, here associated with the distribution of Na$^+$ ions in the inter-lamellar void. These can be obtained by taking the z-derivative of the PMF presented in Figure 4-3.
Figure 4-3: Potential of mean force for face-to-face interaction of clay platelets. (a) total PMF, $a,b = 3, 3.22$ Å, respectively. (b) PMF per surface area. Width of the second energy well is wider than the first one (i.e., $d>c$).
The so-called primitive model was first used to establish the existence of the ionic correlations forces between structure-less charged plane objects immersed in a bath of counter-ions (considered as charged hard spheres with an effective diameter taken to be that of their hydration shell) in a dielectric continuum that mimics the screening effects of ion-ion, ion-lamella and lamella-lamella Coulombic interactions (Jonsson et al., 1984; Valleau et al., 1991; Pellenq et al., 1997; Delville et al., 1997). By definition, the primitive model is therefore a meso-scale approach as it ignores any explicit atomistic texture of both the substrate and solvent molecules.

The limitation of the primitive model lies mainly in the fact that the solvent dielectric constant is considered to be that of the bulk as it ignores solvent structure close to the surface (adsorption) and in the neighborhood of ions (hydration shell). The landmark of the primitive model was that one could predict that same-charged colloidal objects such as clay layers can be attracted through the ionic correlation forces akin to the dynamic distribution of ions in the inter-lamellar void, hence predicting phenomenon such as the flocculation of Ca-rich clays. The primitive model when implemented in a Monte-Carlo simulation numerical approach, allows in a very straight fashion to describe ion density thermal fluctuations that are by construction completely ignored in the well-known DLVO theory that is only a mean-field approach (i.e. the ion density distribution being the straight solution of the static Poisson-Boltzmann equation, we do not discuss here the fact that the only way the DLVO theory can predict cohesion is though van der Waals interactions, its coulombic part being only able to predict repulsion between same charged objects immersed in an electrolyte). Hence the electrostatic Poisson-Boltzmann part of the DLVO theory is an exact solution of the primitive model in the limit of weak electrostatic coupling (low substrate charge, low ionic charge, high temperature, high dielectric solvent constant).

Very recently Carrier (2013) reconciled the molecular scale and the meso-scale of the primitive model using Molecular dynamics by solving first long standing statistical physics ergodic problems for coulombic systems. From full atomistic simulation, Carrier showed that the ionic correlation forces are indeed the origin of the cohesion between clay layers. He also showed that the solvent dielectric constant is strongly decreased in the nanometric width on the interlayer void. He then introduced an explicit solvent primitive model that fully
mimics the computationally heavy results of the full atomistic approach as presented in the current thesis. Carrier showed that the ionic correlation forces can be quantified from the magnitude of system’s instantaneous effective ionic dipole moment obtained by dividing the interlayer void in two equivalent volume separated by a fictitious mid plane and counting the number of ions in each two sub-systems over time and calculating the effective system’s dipole moment with respect to the mid-plane. This can be done at various pressures in NPT simulations at constant water content.

We chose one of the systems (state 12) in Table 4.1 to study the effect of pressure. The dipole moment of the sodium ions is calculated using \[ \mu = \sum_{i=1}^{\text{last ion}} (z_i - z_0)q_i \] where \( q_i = 1e \), \( z_0 \) is the \( z \) position of the plane in the middle of two platelets and \( z_i \) is the \( z \) coordinate of the ion \( i \).

Figure 4-4 shows fluctuation of the calculated dipole moment for two different pressures on the system. The average values over the last 3 ns of trajectory (from 0.5 ns to 3.5 ns) are 1.02 and 0.92 e.nm for \( P = 1 \) atm and 800 atm respectively. Clearly the magnitude of the interaction between these effective dipole moment values does not change significantly when considering a pressurized system (compared to the unpressurized case).

The 10% difference in dipole moments at \( P = 0 \) and 800 atm can be understood from the fact that some Na\(^+\) ions are located in the mid-plane regions as shown in Figure 4-5 hence not anymore contributing to the effective system’s dipole that reflect the strength of the effective interaction between layers. Therefore, to a first approximation, one can consider that the layer to layer PMF calculated at 1 atm is not modified significantly for pressure changes up to 800 atm although more work is required to fully encompass the effect of temperature and pressure on the effective PMF interactions between clay platelets.

4.3 Meso-scale: Gay-Berne Potential

The meso-scale simulations are based on the Gay-Berne (GB) (Gay and Berne, 1981) potential as implemented (Brown et al., 2009) in LAMMPS code (Plimpton, 1995). The GB potential is a single site potential used for interaction of two rigid, aspherical, ellipsoidal particles. As we know from electron microscopy, platelets of clay are approximately equidi-
Figure 4-4: Fluctuation of dipole moments of the sodium ions between clay layers for state 12 (see Table 4.1) at two pressures (P=1 atm and P=800 atm).

Figure 4-5: Number density of sodium ions between clay layers for state 12 (see Table 4.1) at two pressures (P=1 atm and P=800 atm).

...menational in plan (Brown et al., 1978). Moreover, analysis by atomic force microscopy shows that an ellipsoidal (oblate) geometry is a reasonable approximation for describing the clay
platelets (Cadene et al., 2005). Here, we treat each platelet of clay as an effective ellipsoidal GB particle. GB was originally developed for similar ellipsoidal particles and then generalized for dissimilar biaxial particles (Berardi et al., 1995). Using the notations of Everaers and Ejtehadi (2003) the GB potential can be written as:

\[ U = 4\epsilon \left[ \left( \frac{\sigma}{h_{12} + \sigma} \right)^{12} - \left( \frac{\sigma}{h_{12} + \sigma} \right)^{6} \right] \cdot \eta_{12} \cdot \chi_{12} \]  

(4.3)

In the first term which is similar to Lennard-Jones potential, \( \epsilon = 1 \) determines the energy scale, \( \sigma \) is the atomic interaction radius and function \( h_{12} \) approximates anisotropic interparticle distance:

\[ h_{12} = r - \sigma_{12} \]  

(4.4)

And:

\[ \sigma_{12} = \left( \frac{1}{2} r_{12}^T G_{12}^{-1} r_{12} \right)^{-1/2} \]  

(4.5)

Where \( r_{12} = r_2 - r_1 = r \hat{r}_{12} \) is the center to center separation vector, \( r \) is center to center distance, \( \hat{r}_{12} \) is the unit vector and:

\[ G_{12} = A_1^T S_1^2 A_1 + A_2^T S_2^2 A_2 \]  

(4.6)

Where \( S_i = \text{diag}(a_i, b_i, c_i) \) is shape matrix which is defined by three radii \( a_i, b_i, c_i \). \( A_i \) represents rotation matrix which defines transformation of each particle from local frame to global frame. The second term characterizes anisotropic interaction of particles due to their shapes:

\[ \eta_{12} = \left[ \frac{2 s_1 s_2}{\text{det}(G_{12})} \right]^{1/2} \]  

(4.7)

And:

\[ s_i = [a_i b_i + c_i c_i] [a_i b_i]^{1/2} \]  

(4.8)

The third term characterizes anisotropic interaction of particles based on relative free energy well depths of edge-to-edge and face-to-face interactions:

\[ \chi_{12} = (2 \hat{r}_{12}^T B_{12}^{-1} \hat{r}_{12})^2 \]  

(4.9)
With:

\[
\mathbf{B}_{12} = \mathbf{A}_1^T \mathbf{E}_1 \mathbf{A}_1 + \mathbf{A}_2^T \mathbf{E}_2 \mathbf{A}_2
\]  

(4.10)

Where \( \mathbf{E}_i = \text{diag}(\epsilon_{ia}, \epsilon_{ib}, \epsilon_{ic}) \) is the energy matrix which is defined by relative well depths of edge-to-edge and face-to-face interactions. In summary, in order to define interactions between two disc-like platelets (same \( x \) and \( y \) dimensions) we need to specify five parameters: \( x = \{a(b), c, \sigma, \epsilon_a(= \epsilon_b), \epsilon_c\} \), two shape parameters \( a(= b), c \) (with length dimension), one interaction distance parameter \( \sigma \) (with length dimension) and two energy parameters per particle, \( \epsilon_a(= \epsilon_b), \epsilon_c \) which are dimensionless. These parameters are adjusted by fitting Equation (4.3) to edge-to-edge and face-to-face interactions of two platelets. Following Berardi et al. (1998), we defined a cost function and optimized characteristic features (Figure 4-6) of edge-to-edge and face-to-face energy profiles to find parameters of GB potential:

1. The well depth, \( P_{1GB}^{GB} = -\epsilon \cdot \eta_{12} \cdot \chi_{12} \)
2. The separation distance corresponding to the well minimum, \( P_{2GB}^{GB} = \sigma_{12} + \sigma(2^{1/6} - 1) \)
3. The soft contact distance, \( P_{3GB}^{GB} = \sigma_{12} \)
4. Characteristic width of the potential energy well (at half depth),
\[
P_{4GB} = \sigma \left[ \left(4 + 2\sqrt{2}\right)^{1/6} - \left(4 - 2\sqrt{2}\right)^{1/6} \right]
\]

The following cost function was used in fitting procedure:

![Figure 4-6: Fitting parameters of the GB potential.](image)
Superscript $CLAYFF$ denotes corresponding value from full atomistic simulation. $N_c$ is the number of arrangements (here $N_c=2$ as we are fitting to face-to-face and edge-to-edge interactions) and $N_i^f$ is normalizing factor.

For $i = 1$, $N_1^f = p_{CLAYFF}^{1}$, well depth for face-to-face interaction. For $i = 2, 3, 4$, $N_i^f = p_{CLAYFF}^{2}$, distance of well minimum for edge-to-edge interaction.

We parametrized the GB potential for three different platelet sizes: 100 Å, 500 Å and 1000 Å.

In all those the GB potential was fitted to the main (first) free energy minimum ($X_1$, Figures 4-2(b) and 4-3(b)) denoted by 'v' (P=1 atm), 'v' (P=10 atm), 'v' (P=50 atm), 'v' (P=300 atm) and 'v' (P=800 atm). A second set of GB parameters was chosen for the 1000 Å platelet by fitting to the second free energy minimum of the face-to-face interaction ($X_2$, Figure 4-3(b)) denoted by 'vv' and the main (first) minimum of edge-to-edge interaction ($X_1$, Figure 4-2(b)). Figures 4-7(a), (b), (c) and (d) show fitted GB to full atomistic simulations for D= 100, 500, 1000(1000,1000,1000,1000), and 1000 Å. The GB parameters for different cases are listed in Table 4.2. By increasing diameter of the platelet, potential wells become deeper due to larger edge and surface. Moreover, difference between face-to-face and edge-to-edge interaction increases since face-to-face free energy scales with (length)$^2$ while edge-to-edge interaction scales with (length). This is reflected in the change of energy parameters ($\epsilon_a(\epsilon_b)$ and $\epsilon_c$ Table 4.2).

For each case, ten different samples were prepared with initial random orientation of particles by putting 1000 platelets in a simple cubic lattice with interatomic spacing of $(r_0)$ larger than diameter of a platelet. For each sample, an NPT simulation was performed at constant temperature, $T=300$ K to find the final ‘jamming state’ configuration which is characterized by no further change in potential energy of the system. Figure 4-8 shows step function of applied pressure in those simulations. Table 4.3 lists details of the simulations for each size of platelets. The Nosé–Hoover thermostat (Nosé, 1984; Hoover, 1985) is used to control temperature and the Parrinello–Rahman barostat (Parrinello and Rahman, 1981) to control temperature.
Table 4.2: Parameter values of the GB potential.

<table>
<thead>
<tr>
<th>GB calibration case</th>
<th>100</th>
<th>500</th>
<th>1000,1000</th>
<th>1000,1000</th>
<th>1000</th>
<th>1000</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a,2b(Å)</td>
<td>104.12</td>
<td>504.12</td>
<td>1004.12</td>
<td>1000.05</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2c(Å)</td>
<td>9.62</td>
<td>9.62</td>
<td>9.62</td>
<td>12.25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>σ(Å)</td>
<td>11.00</td>
<td>11.00</td>
<td>11.00</td>
<td>14.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ε_a,ε_b</td>
<td>12.37</td>
<td>12.88</td>
<td>12.94</td>
<td>16.47</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ε_c</td>
<td>105.99</td>
<td>551.81</td>
<td>1108.46</td>
<td>1252.60</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| v: P=1 atm, v: P=10 atm , v: P=50 atm , v: P=300 atm , v: P=800 atm , vv: P=1 atm and GB fitted to the second minimum of face-to-face interaction |

Table 4.3: Details of simulations performed in NPT (T=300 K) ensemble for different systems at meso-scale. dt: time step, r_a: initial interatomic spacing, r_c: cutoff radius. Symbols as in Table 4.2.

<table>
<thead>
<tr>
<th>GB calibration case</th>
<th>100</th>
<th>500</th>
<th>1000</th>
<th>1000</th>
<th>1000</th>
<th>1000</th>
</tr>
</thead>
<tbody>
<tr>
<td>dt(fs)</td>
<td>40</td>
<td>40</td>
<td>40</td>
<td>40</td>
<td>40</td>
<td>40</td>
</tr>
<tr>
<td>r_a, r_c(Å)</td>
<td>120</td>
<td>520</td>
<td>1020</td>
<td>1020</td>
<td>1020</td>
<td>1020</td>
</tr>
<tr>
<td>po(atm)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>p1(atm)</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>10</td>
<td>50</td>
</tr>
<tr>
<td>t1(ns)</td>
<td>40</td>
<td>40</td>
<td>40</td>
<td>40</td>
<td>120</td>
<td>120</td>
</tr>
<tr>
<td>tf(ns)</td>
<td>5000</td>
<td>1200</td>
<td>1200</td>
<td>1200</td>
<td>360</td>
<td>320</td>
</tr>
</tbody>
</table>

pressure in the system. The pressure and temperature damping parameters were 1 ns and 0.001 ns, respectively. For each column, ten simulations were performed to sample phase space and report average properties of the final state. Initial state of each sample with P > 1 was taken from the end of 1000 simulations (with P=1 atm).

### 4.4 Meso-scale: Aggregation

The meso-scale aggregation of clay platelets can be examined by considering snapshots of the simulation at selected timesteps using QMGA (Gabriel et al., 2008) molecular graphics software. Each simulation, uses a total number of 1000 equal-sized clay platelets with random orientations in a unit cell with different GB calibrations for different particle sizes and...
Figure 4-7: Fitting GB potential to face to face and edge to edge interactions for different platelet diameters, D=100 Å (b) D=500 Å (continued on next page)
(Figure 4-7 continued) (c) $D=1000(1000,1000,1000,1000,1000) \text{ Å}$, fitted to the first well of face to face interaction. (d) $D=1000 \text{ Å}$, fitted to the second well of face to face interaction ("\dots" denotes contraction of the x scale).
confining pressures (Table 4.3). Geometrical and mechanical properties are averaged over ten samples for each type of simulation. A qualitative picture of the evolution of the system of particles during MD simulations for a typical sample can be seen in Figure 4-9. This example shows snapshots of a sample 1000 GB case (i.e., platelets of diameter 1000 Å at P=1 atm and T=300 K). Platelets are color coded based on the orientation of their normal vector with respect to the Z axis (φ angle). When platelets become clustered into aggregates, their normal vectors point in the same direction and the spectrum of colors decreases with time as the sample compresses to the fully jammed configuration (t=1200 ns, Figure 4-9(c)).

In this case, Figure 4-10(a) shows that there are no further changes in the total energy of the system for t≥1000 ns (1000 case). Figure 4-11 shows that systems with smaller platelets have larger kinetic energy compared to the total energy scale (Ke/Te). For instance, the percentage of kinetic energy to total energy decreases from 0.25% to 0.0026% as the size of the platelet increases from 100 Å to 1000 Å. In other words, temperature becomes irrelevant which is characteristic of the jamming state. In Figure 4-11, the transition to the jamming state can be identified from the sudden removal of the scatter in the Ke/Te function which occurs around 20 ns, 500 ns and 1000 ns for 100Å, 500Å and 1000Å platelets, respectively. Below the jamming transition, ergodicity is broken. This is demonstrated by the change in rotational relaxation time (area under the autocorrelation function of the normal vector of platelets, see Appendix A) from a finite value to an infinite time as we can see in Figures 4-12,4-13 and 4-14.

These figures show the rotational autocorrelation functions of the normal vectors of platelets.
before and after jamming points. As we can see, after jamming the autocorrelation function becomes 1 (relaxation time becomes infinite) which is another indication of the jamming state. Smaller particles need longer simulation times to reach to their final jammed state as seen in Figure 4-10(b) for a 100 Å simulation case. In this example the final state is attained at t~5000 ns. Moreover, for 1000 Å platelets (Figure 4-10(a)) the energy decays smoothly with time while for the 100 Å platelets (Figure 4-10(b)) the changes are stepwise. This is an evidence of passing into a glassy regime, where stepwise reduction of energy is indicative of crossing of barriers on the rugged free energy surface. Larger platelets are stuck in a single well, unable to cross any barriers.

Figure 4-9: Snapshots showing aggregation of 1000 Å simulation at: (a) t=40 ns (b) t=200 ns (c) t=1200 ns. The particles orientations are color coded according to the $\phi$ angle, orientation of their normal vector with respect to the Z axis (colorbar A).

4.4.1 Geometrical analysis

Following Chen et al. (2013), we used two criteria to determine whether two platelets are stacked on top of each other. Figure 4-15 shows the two criteria used for the analysis of platelets stacking. Two platelets are assumed to belong to the same clay aggregate (stack) if:

\[ C 9-59)1- \]
Figure 4-10: Total energy of the system of platelets for typical samples from simulations (see Table 4.3) (a) 1000 Å  (b) 100 Å.
Figure 4-11: Percentage of kinetic energy to total energy for typical samples (see Table 4.3).

Figure 4-12: Autocorrelation function of the normal vector of 100 Å platelets.

(a) their interlayer distance, \( r \), is less than an upper limit, \( r_u \). The current analysis assumes that \( r_u \) is 25% larger than the equilibrium distance for face-to-face interactions to allow for offsetting of platelets. For seven of the GB calibration cases (100, 500, 1000, 1000, 1000, 1000, 1000
and 1000 Å, \( r_u = 13.75 \) Å; while \( r_u = 17.5 \) Å for 1000 Å.

(b) the absolute value of scalar product of the two normal vectors of the platelets is greater than 0.95 (\( n_1 \cdot n_2 > 0.95 \)).
Figures 4-16 and 4-17 illustrate probability distribution of aggregate stack sizes averaged over ten simulations and fitted to log-normal distribution functions for GB cases with P=1 atm and P >1 atm, respectively. Log-normal distribution of stack sizes was reported in X-ray diffraction (XRD) and transmission electron microscopy (TEM) of Na-smectite (Mystkowski et al., 2000). In each case the goodness of fit is assessed using the chi-squared $\chi^2$ test (see Table 4.4), at $\chi^2_{0.05} = 0.05$ significance level. The histograms of stack sizes were grouped into $n_{\text{bins}}=10-14$ centered on integer number of stacks. The last bins in the right tail of the distribution were merged together until the count in the extreme bin is at least 5. Degrees of freedom of the test, $\text{dof} = n_{\text{bins}}-3$ to take into account the two estimated parameters of the test, $(\mu, \sigma)$. In all cases $\chi^2 < \chi^2_{0.05}$ which confirms that the log-normal distribution is able to represent the distribution of stack sizes at $\alpha = 0.05$ significance level. The average stack size ($n$) increases from 3.05 to 5.01 for platelets with size increasing from 100 Å to 1000 Å (Table 4.4). This is in agreement with small angle X-ray scattering (SAXS) experiments of Segad et al. (2012) who reported an increase in size of aggregates with increase in the platelet size for Ca-montmorillonite. As the surface area of a platelet increases the number of platelets subtended in its solid angle also increases. This means that each platelet would
Table 4.4: Results of geometrical analysis of aggregates. Symbols as in Table 4.2.

interact with many more other platelets. Moreover, since the interaction energy scales with the surface area, the attraction force between platelets increases which results in larger stack sizes. Increasing pressure from 1 atm to 10 atm (1000 vs 1000, see Table 4.4) has similar effect with the average size of the aggregates increasing from 5.01 to 7.07. Figures 4-18 and 4-19 show typical equilibrated systems of platelets for samples with P=1 atm and P >1 atm, respectively. The effect of increase in pressure can be seen by comparing Figures 4-18(c) and 4-19(a) (1000 vs 1000). However, fitting GB to the first or second potential energy well for face-to-face interaction, has no effect on the size of the aggregates (1000 vs 1000, see Table 4.4). By increasing pressure to 50 atm, average stack size increases to 8.33. More increase in pressure results in decrease of the stack size (from 8.33 to 6.68 and 4.46 as pressure increases from 50 atm to 300 atm and 800 atm, respectively). This is due to the sliding of the platelets (more than rω). We can see sliding of platelets from Figure 4-19(a) to Figure 4-19(d). The same effect is reflected in the stack size distributions in Figure 4-17. By increasing pressure, distribution is skewed more to the left and number of isolated platelets increases. As a result, average number of platelets per stack decreases. Using transmission electron microscopy, scanning electron microscopy, SAXS and X-ray diffraction experiments (Tessier and Pedro, 1981; Pons et al., 1981; Rhaiem, 1985; Hetzel et al., 1994; Mystkowski et al., 2000) on different types of Na-smectites have found that particles typically comprise three to ten layers of platelets, consistent with our numerical simulations.

In order to study the degree of orientation of particles, we use a scalar measure of the
Figure 4-16: Probability distributions and fitted log-normal distributions to the stack size analysis for different types of simulations (P=1 atm, see Table 4.3): (a) 100 Å (b) 500 Å
average over ten samples
-log-normal fit

(Figure 4-16 continued) (c) 1000 Å (d) 1000 Å
Figure 4-17: Probability distributions and fitted log-normal distributions to the stack size analysis for different types of simulations (P >1atm, see Table 4.3): (a) 1000 Å (b) 1000 Å

(continued on next page)
(Figure 4-17 continued) (c) 1000 Å (d) 1000 Å
Figure 4-18: Equilibrated system from different types of simulations (P=1 atm, see Table 4.3): (a) 100 Å (b) 500 Å (c) 1000 Å (d) 1000 Å. The particles orientations are color coded according to the $\phi$ angle, orientation of their normal vector with respect to the Z axis (colorbar A).

orientation as an order parameter:

$$S = \left\langle \frac{3 \cos^2 \theta - 1}{2} \right\rangle$$

(4.12)

Where $\theta$ is the angle of normal vector of a platelet (u) with director of the system (n). The brackets denote average over all the particles. The director vector of a system of particles, (n), is a measure of the average orientation of the particles in the system. Director is the
Figure 4-19: Equilibrated system from different types of simulations (P > 1 atm, see Table 4.3): (a) 1000 Å (b) 1000 Å (c) 1000 Å (d) 100 Å. The particles orientations are color coded according to the $\phi$ angle, orientation of their normal vector with respect to the Z axis (colorbar A).

The eigenvector corresponding to biggest absolute eigenvalue of the order tensor, $q_{ij}$:

$$ q_{ij} = \frac{1}{N} \sum_{m=1}^{N} \left( u_i u_j - \frac{1}{3} \delta_{ij} \right) $$

(4.13)

Where $N$ is the number of particles and $\delta_{ij}$ is the Kronecker delta function. For completely isotropic and randomly oriented system $S=0$, while perfectly aligned systems have $S=1$. Results of the calculated order parameter are listed in the Table 4.4. As the size of the platelets increases from 100 Å to 500 Å there is little change in the order parameter of
the particles (from 0.11 to 0.10 for 100 and 500, respectively). Similarly, fitting to the first or second potential energy well of the face-to-face interaction has little effect on S (from 0.23 to 0.21 for 1000 and 1000, respectively). However, there is a more pronounced change in S for 1000/1000 simulations vs 1000/500 cases (0.23/0.21 vs 0.10/0.11). In other words, as size of the platelets decreases the system becomes more isotropic since smaller particles have more freedom to move around due to their sizes. This is in agreement with experiments done by Hetzel et al. (1994) who showed that lateral extension of particles decreases disorder in the geometrical arrangements of particles and the system becomes more anisotropic. Increasing the confining pressure has a significant effect on ordering of particles reflected in an increase in the order parameter from S=0.23 to 0.46 for P=1 to 10 atm (1000 vs 1000 Table 4.4) then to 0.65 for P=50 atm (case 1000). More increase in pressure has small effect on the order parameter. The effect of pressure can be seen by comparing Figures 4-18(c) and 4-19. In summary, as pressure increases system becomes more ordered and the number of platelets per stack increases until reaching to the maximum ordered state (here at P=50 atm, case 1000, where we have S=0.65). More increase of the pressure decreases the average stack size due to sliding of platelets at fixed orientation (constant S). This result shows much smaller deviations in particle orientations at high confining pressure such that platelets can cross energy barriers, and as a result, become more aligned. Increasing pressure results in increasing concentration of particles due to decrease in volume. This result is in agreement with isotropic (orientationally disordered) to nematic (orientationally ordered) phase transition for nonspherical charged objects known as the Onsager transition (Onsager, 1949). According to Onsager theory at low concentration the system of particles is isotropic and orientational entropy of particles are maximum. As the density of particles increases, nonspherical objects start to align to maximize the free volume in which they can move leading to the nematic phase.

4.4.2 Calculation of elastic properties

We have used quasi-static algorithm to construct stress-strain behaviors and interpret elastic stiffness properties of the particle assemblies with 500 Å and 1000 Å platelets. This algorithm
consists of two steps: (1) application of a small homogeneous strain to the system (2) relaxing strain step over a relation time period using an NVT ensemble (T= 0.01 K). The procedure was used previously to build stress-strain curves for gold crystal structure (Aghaei et al., 2009). We applied six different strains on the system and computed stress components. The elastic constants are determined from Hooke’s law:

$$\sigma_{ij} = \sum_{k,l} C_{ijkl} \epsilon_{kl}$$

(4.14)

Where $C_{ijkl}$ represents fourth order elasticity tensor and $\epsilon_{kl}$ is the kl element of the second order strain tensor. We use the Voigt notation in representing components of the $C_{ijkl}$ with indices: 11→1, 22→2, 33→3, 23→4, 13→5 and 12→6. In this notation, fourth order elasticity tensor can be represented by a symmetrical matrix with components $C_{ij}$. In the Cartesian coordinate indices $1, 2$ and $3$ map to $x, y$ and $z$, respectively. The internal stress tensor of the system are given by (Vitek and Egami, 1987):

$$\sigma_{ij} = \frac{1}{V} \sum_{\alpha} \left( m^\alpha v^\alpha_i v^\alpha_j + \sum_{\beta} f^\alpha_{i \beta} r^\alpha_{j \beta} \right)$$

(4.15)

Where $V$ is the volume of the system, $m^\alpha$ and $v^\alpha$ are mass and velocity of platelet $\alpha$, respectively. $f^\alpha_{i \beta}$ is the force acting on platelet $\alpha$ by platelet $\beta$ in the i direction and $r^\alpha_{j \beta}$ is the Cartesian component of the vector from platelet $\beta$ to platelet $\alpha$ in the j direction. Compressive and shear strain steps applied using an (NVT) ensemble (T=0.01 K). Each strain step was relaxed over a relaxation time period. The stress values were averaged over the last ten percent of the relaxation time. Simulation details for calculation of elastic properties are summarized in Table 4.5. Elastic constants were obtained from a linear fit over the initial part of the stress strain curve representing values from $\epsilon$ =0 to 0.01% for 500 Å platelets and $\epsilon$ =0 to 0.03% for 1000 Å platelets. Figure 4-20 shows typical stress-strain curves used to calculate elasticity for a sample comprised of 500 Å platelets. Values of elastic properties are averaged over ten samples for each type of simulation (i.e., each GB calibration case). Table 4.6 summarizes the mean and standard deviation of the elastic constants.

It can be seen that diagonal terms can be approximated with two parameters: $C_{11} =$
Table 4.5: Details of simulations to calculate elastic properties. dt: time step, dc: strain step, n_s: number of steps, t_r and t_s: relaxation time and sampling period for each strain step. Symbols as in Table 4.2.

| GB calibration case | 500 | 1000 & 1000 & 1000 & 1000 & 1000 |
|---------------------|-----|-----------------|-----------------|-----------------|-----------------|
| dt(fs)              | 5   | 5               | 5               | 5               | 5               |
| dc                  | 2.5x10^{-5} | 5x10^{-5}      | 5x10^{-5}      | 5x10^{-5}      | 5x10^{-5}      |
| n_s                 | 25  | 50              | 50              | 50              | 50              |
| t_r(ps)             | 800 | 100             | 100             | 100             | 100             |
| t_s(ps)             | 80  | 10              | 10              | 10              | 10              |

1/3 (C_{11} + C_{22} + C_{33}) and \(\bar{C}_{44} = \frac{1}{3} (C_{44} + C_{55} + C_{66})\). For instance, in the case of 500 Å the normal stiffness values are 0.51, 0.50 and 0.52 GPa (\(\sim 0.51\) GPa) and shear stiffness values are 0.1, 0.1 and 0.09 GPa (\(\sim 0.1\) GPa). In the off diagonal terms, \(C_{12}, C_{13}\) and \(C_{23}\) are close together and one order of magnitude larger than the rest of the off diagonal terms. For example, in the case of 500 Å the values of these terms are 0.12, 0.14 and 0.12 GPa (\(\sim 0.13\) GPa), respectively, and the absolute values of the remaining off-diagonal terms are between 0.00-0.03 GPa. This suggests that the particle assemblies approximate cubic symmetry of the full elasticity tensor with three independent elastic constants: \(C_{11}, C_{12}\) and \(C_{44}\). Table 4.7 summarizes the cubic average of the elastic properties calculated via simple averaging over the three directions, [100], [010] and [001]: \(\bar{C}_{11}, \bar{C}_{44}\) and \(\bar{C}_{12} = \frac{1}{3} (C_{12} + C_{13} + C_{23})\). By increasing the size of the platelets, \(\bar{C}_{11}\) increases from 0.51 GPa to 0.98 GPa. The increase in compressive stiffness is expected for larger platelets as the cohesion between the platelets increases due to the larger surface area. The value of \(\bar{C}_{12}\) is related to the lateral Poisson's ratio connecting deformation between orthogonal axes. There is a negligible change in this elastic constant (from 0.13 to 0.14 GPa). Similarly the shear stiffness, \(\bar{C}_{44}\), has a small change with changing size of the platelet (from 0.10 to 0.08 GPa). For a system equilibrated at larger pressures (cases 1000, 1000, 1000 and 1000), all elastic constants increase as expected. Comparing 1000 and 1000 cases shows decrease in all stiffness values for the case we have larger face-to-face distance at equilibrium condition. Shear stiffness decreases by 38% (from 0.08 to 0.05 GPa), normal stiffness decreases by 23% (from 0.98 to 0.75 GPa) and the
Figure 4-20: Stress-strain curves for a typical sample of 500 Å platelets. By applying strain in the z direction, $\epsilon_3$, associated column in the stiffness matrix can be determined. (a) $\sigma_{ii}-\epsilon_3$ curves. $m=1,2,3$ (b) $\sigma_{ij}-\epsilon_3$ curves. $m=4,5,6$

stiffness related to Poisson's effect, $C_{12}$, decreases by 21% (from 0.14 to 0.11 GPa). This change can be explained by difference in the width of the second energy well compared to
the first (Figure 4-3(b)). As $c<d$ the second derivative of the energy with respect to strain (i.e., elastic properties) are larger for GB calibrated to the first potential well.

The accuracy of the cubic-averaged elastic constants ($\bar{C}_{ij}$) in representing the full elastic stiffness matrix was evaluated using Euclidean distance metric. This metric has been used previously to assess similarity between full elastic constant matrix and averaged symmetric one (Shahsavari et al., 2010). The Euclidean distance between two square matrices, $A_1$ and $A_2$, is calculated as follows:

$$d_E(A_1, A_2) = \|A_1 - A_2\|_E$$

(4.16)

and the associated norm is defined by:

$$\|A\|_E = \sqrt{\text{tr}(A^T A)}$$

(4.17)

where $\text{tr}(\cdot)$ stands for the trace and the superscript $T$ denotes the transpose. Smaller values of the metric mean more similarity between matrices. Smaller values of this metric indicate better approximation of the full elastic matrix using cubic-averaged values. In other words, when there is no preferred direction in the microstructure, elastic constant values over three directions become close together and can be cubic-averaged to represent full elastic matrix.

For each sample, the dimensionless Euclidean distance metric (divided by norm of the cubic averaged elastic matrix) was calculated. By averaging over ten samples, the mean and standard deviation of the metrics are reported in Table 4.7. By increasing platelet size, distance metric increases from 0.18 to 0.22. By applying confining pressure up to 10 atm we see a more pronounced increase to 0.43. Increasing pressure to 50 atm shows decrease in distance metric to 0.38 (case 1000) and metric starts to increase again as pressure increases (to 0.42 and 0.47 for $P=300$ atm and 800 atm, respectively). In general distance metric increases with pressure with an exception at $P=50$ atm. The exception occurs at the onset of the maximum ordering ($S=0.65$, case 1000). More increase of the pressure slides platelets against each other leading to more anisotropic system (compare Figures 4-19(a) and 4-19(b) with 4-19(c) and 4-19(d)). This is consistent with the change of microstructure. Figure 4-19 shows that there is less variation in particle orientation at higher pressure and hence, greater discrepancy from cubic symmetry approximation. Moreover a decrease in the order
GB calibration case

<table>
<thead>
<tr>
<th>Parameter</th>
<th>500 Å</th>
<th>1000 Å</th>
<th>1000 Å</th>
<th>1000 Å</th>
<th>1000 Å</th>
<th>1000 Å</th>
<th>1000 Å</th>
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<td>0.96</td>
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<td>0.05</td>
<td>0.03</td>
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</tr>
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<td>0.04</td>
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<td>0.03</td>
<td>0.33</td>
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<td>0.02</td>
<td>-0.15</td>
</tr>
<tr>
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<td>0.01</td>
<td>0.03</td>
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<td>0.02</td>
<td>0.01</td>
<td>0.02</td>
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</tr>
<tr>
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<td>0.01</td>
<td>0.03</td>
<td>0.00</td>
</tr>
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<td>0.01</td>
<td>0.03</td>
<td>-0.01</td>
</tr>
<tr>
<td>$C_{56}$</td>
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<td>-0.01</td>
<td>0.03</td>
<td>-0.01</td>
<td>0.02</td>
<td>-0.04</td>
</tr>
</tbody>
</table>

Table 4.6: Elastic constant properties (in GPa) calculated for 500 Å and 1000 Å platelets. Symbols as in Table 4.2.

Parameter $S$ with decreasing platelet size (Table 4.4) indicates more randomness in orientation distribution for smaller platelets. This leads to better approximation of the elasticity matrix with cubic symmetry. Mechanical properties at the meso-scale should be validated against experimental data.

Nanoindentation is a submicrometer experiment used to measure material stiffness parameters. So far, we scaled up our simulations to submicron length scale, the scale accessible by indentation tests. We compared our meso-scale mechanical properties with the nanoindentation experiments performed by Bobko and Ulm (2008) on different shale (highly compacted...
<table>
<thead>
<tr>
<th>GB calibration case</th>
<th>500</th>
<th>1000</th>
<th>2000</th>
<th>3000</th>
<th>4000</th>
<th>5000</th>
<th>6000</th>
<th>7000</th>
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<td>$\bar{C}_{11}$</td>
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<td>0.75</td>
<td>4.07</td>
<td>6.42</td>
<td>14.17</td>
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<tr>
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<td>0.11</td>
<td>0.53</td>
<td>1.24</td>
<td>4.12</td>
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</tr>
<tr>
<td>$\bar{C}_{44}$</td>
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<td>0.44</td>
<td>0.66</td>
<td>1.91</td>
<td>4.68</td>
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</tr>
<tr>
<td>$\frac{d_E}{\parallel C_{ij} \parallel}$</td>
<td>0.18±0.05</td>
<td>0.22±0.08</td>
<td>0.17±0.07</td>
<td>0.43±0.11</td>
<td>0.38±0.12</td>
<td>0.42±0.12</td>
<td>0.47±0.10</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.7: Cubic averaged elastic properties (in GPa) and Euclidean distance between averaged and full elasticity tensors. Symbols as in Table 4.2.

...clay) samples. To compare our results, we calculated values of indentation modulus from elasticity components ($C_{ij}$) using the derivation by Delafargue and Ulm (2004) for an orthotropic solid (see Appendix B). Each value of packing density (one minus porosity) at the final state is calculated using 11 Å as the thickness of a platelet which corresponds to the minimum favorable face-to-face distance (Figure 4-3). Table 4.8 summarizes average packing density and indentation modulus for different types of simulations. In our upscaled model, values of indentation modulus show no preferential direction (almost identical) which is consistent with cubic symmetry assumption for the elasticity tensor. The mean indentation modulus is used to compare with experiment. Figure 4-21 shows indentation modulus versus packing density from experiment and simulations. Three simulation points (associated with $P=1$ atm) lie on the left side of the graph (around packing density of 0.2) which correspond to colloidal clay system. The other indentation values from simulations of confined clay ($P > 1$ atm) show a good agreement with experiment with similar trend.

### 4.5 Conclusion

Meso-scale aggregates of clay were studied using Gay-Berne potential calibrated from full atomistic simulations. The free energy of face-to-face and edge-to-edge interactions of clay platelets were calculated as the elementary configurations for calibration. Minima of the free energy are separated with $\sim 3$ Å distance which corresponds to the diameter of a water molecule. The meso-scale simulations show that structural and mechanical properties of the
GB calibration case

<table>
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<tr>
<th></th>
<th>500</th>
<th>1000</th>
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<th>1000</th>
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<tr>
<td>2</td>
<td>&lt;.&gt;</td>
<td>±</td>
<td>&lt;.&gt;</td>
<td>±</td>
<td>&lt;.&gt;</td>
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<tr>
<td>η</td>
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<td>0.02</td>
<td>0.21</td>
<td>0.02</td>
<td>0.20</td>
<td>0.02</td>
<td>0.43</td>
<td>0.07</td>
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<td>0.11</td>
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<td>0.15</td>
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<td>0.61</td>
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<tr>
<td>M_2</td>
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<td>2.40</td>
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<td>M</td>
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<td>0.05</td>
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<td>0.17</td>
<td>0.36</td>
<td>0.11</td>
<td>2.26</td>
<td>0.92</td>
</tr>
</tbody>
</table>

Table 4.8: Average packing density and indentation modulus (in GPa). Symbols as in Table 4.2.

Figure 4-21: Indentation modulus versus clay packing density, η. The experimental data in the normal ($x_3$ direction) and parallel ($x_1(x_2)$ directions) to the bedding plane are taken from Bobko and Ulm (2008).

Aggregates are related to the clay platelet size and external applied pressure. Simulations for Wyoming Na-montmorillonite have shown that aggregate size distributions are well described by log-normal functions with mean stack size that increases from 3 to 8 platelets per aggregate. Smaller platelets have less order (more isotropic) structures while confining pressure generates more ordered structures (more anisotropic).
The microstructure of the system of particles plays an important role in their mechanical properties. We found that larger aggregates produce more anisotropic structure with higher compressive and shear stiffness due to higher attraction between larger platelets. These features become more pronounced by increasing external pressure on the system until reaching to the maximum ordered state. More increase of the pressure, reduces aggregate size due to sliding of platelets against each other whereas mechanical properties are still increasing. While the size of the aggregates remains constant by their formation in the second energy minimum of face-to-face interaction, the mechanical properties of the microstructure decreases due to wider width of the second energy well.
Chapter 5

Conclusion and future works

5.1 Summary

The goal of this research was to develop a multiscale bottom-up framework for modeling clay properties in order to understand the physics governing macroscopic properties. This was accomplished through molecular modeling of clay-water system and interactions between two clay platelets. Atomistic modeling was carried out using CLAYFF (Cygan et al., 2004) force field and variety of MD and MC methods. The research has focused on a reference clay mineral, Wyoming montmorillonite (Na-smectite) which has isomorphous substitutions in both tetrahedral and octahedral layers with Cation Exchange Capacity of 102 meq/100g. At the atomistic scale we studied clay swelling mechanism by modeling clay-water systems with different amount of water between clay layers. The analyses of the distributions of water molecules showed formation of quantized layers of water as clay adsorbs more amount of water. The density and number of hydrogen bonds of confined water is smaller than the corresponding values of bulk water due to its strong interaction with the clay surface. The mechanical properties of the system was calculated from the second derivative of potential energy density with respect to strain. Mechanical properties of clay-water system change upon water adsorption. Atomistic simulations showed the in-plane stiffness decreases by increasing amount of adsorbed water while the change of elastic properties perpendicular to the clay layers has an oscillatory behavior with maximum stiffness values occurring at formation of one and two layers of interlayer water. The in-plane stiffness is more affected
by the iono-covalent bonding inside clay crystal while the stiffness perpendicular to the layers is governed by the screened electrostatic interactions between layers. As a result, planar stiffness is 5 to 8 times larger than the stiffness perpendicular to the clay layers. The Poisson’s ratio around 0.5 for the in-plane stiffness indicates rigidity of the system in the planar direction. The shear stiffness normal to the basal plane and Poisson’s ratio connecting deformation between the vertical and horizontal axes show a decrease upon moving from dry state followed by an increase during formation of the first layer of water which has strong bonds with the clay surface. Values of these stiffness parameters decrease with further adsorption of water until reaching to a constant value. For a layered system we expect to have transverse isotropy. Transverse isotropic assumption of the mechanical properties is a good assumption after formation of the first layer of water in between clay platelets while is less reliable for the dry state.

In order to study formation of clay aggregates, we calculated Potential of Mean Force (PMF) (e.g. free energy) for edge-to-edge and face-to-face interactions of two clay platelets in water from full atomistic simulations. The free energy perturbation technique along with simple overlap sampling (Lee and Scott, 1980; Chipot and Pohorille, 2007) were used to compute PMF for two modes of clay interactions (edge-to edge and face-to-face). Results of the PMF indicate one main minima for the edge-to-edge interaction and two comparable minima for the face-to-face interaction. The two PMF then used to calibrate Gay-Berne (GB) (Gay and Berne, 1981) potentials for different platelet sizes for meso-scale modeling of clay aggregation. The GB potential generalize the interaction between platelets with arbitrary orientation. The results of modeling various single size platelets of clay at different confining pressures showed the importance of microstructure and external pressure on the formation of clay particles and resulted mechanical properties of the system. The number of platelets per aggregate, anisotropy of the system of aggregates and ordering of the platelets increases with increasing platelet plan area. Aggregate size distributions are well described with log-normal function with mean stack size ranging from 3-8 platelets. Larger external pressure has similar effect in terms of anisotropy of the structure while the size of the aggregates increases until system reaches to its maximum ordered state. After this point further increase of pressure slides platelets relative to each other leading to decrease in the number of platelets per aggregate.
The microstructure of the system of aggregates is not affected by their formation around the first or second minimum of face-to-face interaction but the mechanical properties decreases for aggregation in the second energy well.

The microstructure of the system affects its mechanical properties. Mechanical properties of the system increases with increasing platelets plan area and external applied pressure.

5.2 Future work

The modeling scheme proposed in this research can be extended to more general cases to include the following factors:

- The amount of adsorbed water depends on the isomorphous substitution and counter-ions of the clay. Isomorphous substitution can take place in tetrahedral and/or octahedral sheets of the clay layer. Different types of counter-ions like Na\(^+1\), Ca\(^+2\), Li\(^+1\), K\(^+1\) were found in clay. We started with Wyoming Na-montmorillonite, Na\(_{0.75}\)H\(_2\)O[Si\(_{7.75}\)Al\(_{0.25}\)][Al\(_{3.5}\)Mg\(_{0.5}\)]O\(_{20}\)(OH)\(_4\), which carries IS in both tetrahedral and octahedral sheets. The work can be expanded to explore effect of different isomorphous substitutions and different counter-ions on the elastic mechanical properties of clay.

- The intensity of the platelet charge which is controlled by the amount of isomorphous substitution influences the attraction or repulsion of platelets towards each other. The substitutions in Wyoming Na-montmorillonite used in this research corresponds to Cation Exchange Capacity (CEC) of 102 (mequiv/100 g). According to Mitchell and Soga (1976), CEC of montmorillonite varies between 80-150 (mequiv/100 g). The methodology used in this research might be used to explore the effect of the amount of substitution on the formation of clay particles and their mechanical properties.

- All the studied models in this research were charged platelets in water. The only ions in the solution were counter ions to neutralize the systems. It is common to have clay platelets in solutions containing electrolyte ions such as NaCl, KCl, MgCl\(_2\) and CaCl\(_2\). The existence of electrolyte ions has significant effect on the interaction between clay
layers (Israelachvili, 2011). The study can be extended to include this effect.

- At the meso-scale we studied interaction of single size (monodisperse or uniform) platelets. The heterogeneity of the platelet sizes at the meso-scale can change the distribution of aggregate sizes. The research can be extended to study effects of the polydispersity of clay platelets.

- The GB potential can be calibrated to one minimum for the face-to-face interaction. The study can be extended to include both minima of the face-to-face interactions in the proposed potential to allow crossing from energy barriers leading to the first or second minimum. The resulted microstructure can have aggregates formed in one or both energy wells. At high pressure or low relative humidity we expect the system to be formed at the main (first) energy well. At high relative humidity or low pressure system can exist in the second potential well. The mixed condition may occur inbetween.

- In order to close the loop between atomistic behavior and macroscopic behavior, the future research should be done at the Micro-scale using the results of the current research at the Meso-scale (see Figure 1-4). At that scale, clay aggregates, silt inclusions and voids are homogenized using micromechanical methods (Nemat-Nasser and Hori, 1999) to calculate soil material properties to be used in continuum models.
Appendix A

Collective behavior of a material property can be analyzed using correlation functions (Rapaport, 2004). The autocorrelation function (ACF), \( C(t) \), for a property \( A(t) \) is (Allen and Tildesley, 1989; Haile, 1992):

\[
C(t) = \langle A(t_0) \cdot A(t_0 + t) \rangle_{t_0}
\]  

(A.1)

The bracket represents an average accumulated over many time origins, \( t_0 \). The property \( A \) is sampled at the time origin \( t_0 \) and after a delay time \( t \). The integral of the autocorrelation function over time is the relaxation or correlation time:

\[
\tau = \int_0^\infty C(t)dt
\]  

(A.2)
Appendix B

The equations relating elastic constants \((C_{ij})\) to indentation modulus \((M_1, M_2, M_3)\) for an orthotropic solid are summarized in this appendix (Delafargue and Ulm, 2004):

\[
M_1 \approx \sqrt{M_{12}M_{13}}
\]

\[
M_2 \approx \sqrt{M_{21}M_{23}}
\]

\[
M_3 \approx \sqrt{M_{31}M_{32}}
\]

where

\[
M_{21} = 2\sqrt{\frac{C_{11}C_{22} - C_{12}^2}{C_{11}}} \left( \frac{1}{C_{66}} + \frac{2}{C_{11}C_{22} + C_{12}} \right)^{-1}
\]

\[
M_{31} = 2\sqrt{\frac{C_{11}C_{33} - C_{13}^2}{C_{11}}} \left( \frac{1}{C_{55}} + \frac{2}{C_{11}C_{33} + C_{13}} \right)^{-1}
\]

and

\[
M_{32} = 2\sqrt{\frac{C_{22}C_{33} - C_{23}^2}{C_{22}}} \left( \frac{1}{C_{44}} + \frac{2}{C_{22}C_{33} + C_{23}} \right)^{-1}
\]

and

\[
M_{12} = M_{21} \sqrt{\frac{C_{11}}{C_{22}}}
\]

\[
M_{13} = M_{31} \sqrt{\frac{C_{11}}{C_{33}}}
\]

\[
M_{23} = M_{32} \sqrt{\frac{C_{22}}{C_{33}}}
\]
Bibliography


