Molecular dynamics of the absorption of water into the interlayers of Na-montmorillonite

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Montmorillonite is a layered swelling clay mineral that has the abilities to absorb water, causing the mineral to swell, and to exchange its structural cations, most commonly $\text{Na}^+$ and $\text{Ca}^{2+}$. These properties are applied in various fields including the nuclear waste management in Finland. Montmorillonite is the main component of bentonite clay which is planned to be used as a release barrier material in the final repository for spent nuclear fuel.

The aim of this work was to study how water is absorbed into the interlayer spaces of Na-montmorillonite. Molecular dynamics simulations were performed on a 3-layered montmorillonite particle surrounded by free water. The amount of water initially present between the layers was varied from none to 1 and 2 water molecules per unit cell. The simulations were performed at two temperatures, 298 K and 323 K, applying CLAYFF force field.

The evolution of water content showed practically no absorption at either temperature in the case of completely dry montmorillonite. For the other cases, montmorillonite with water initially present in the interlayers, absorption was observed and it was faster at the higher temperature. The evolution of interlayer thicknesses in each case showed a variation between the two interlayers of the system which was thought to result from the different placement of substitutions in the clay layers.
List of Symbols

\( \alpha \)  
lattice angle between b and c

\( \beta \)  
lattice angle between a and c

\( \epsilon_0 \)  
dielectric permittivity of vacuum

\( \epsilon_{ij} \)  
Lennard-Jones energy parameter

\( \gamma \)  
lattice angle between a and b

\( \sigma_{ij} \)  
Lennard-Jones size parameter

\( \theta_0 \)  
mean bond angle

\( a \)  
lattice parameter

\( a_i \)  
acceleration of species i

\( b \)  
lattice parameter

\( c \)  
lattice parameter

\( CEC \)  
cation exchange capacity

\( D_{0,ij} \)  
Lennard-Jones energy parameter

\( e \)  
 elemental charge

\( E_{\text{anglebend}} \)  
energy from covalent angle bending

\( E_{\text{bondstretch}} \)  
energy from covalent bond stretching

\( E_{\text{bonded}} \)  
energy from bonded interaction

\( E_{\text{Coul}} \)  
Coulombic energy

\( E_{\text{Hbond}} \)  
hydrogen bonding energy

\( E_{\text{inversion}} \)  
energy from inversion

\( E_{\text{kin}} \)  
kinetic energy

\( E_{\text{non\text{-}bonded}} \)  
energy from non-bonded interaction

\( E_{\text{torsion}} \)  
torsional energy

\( E_{\text{tot}} \)  
total energy

\( E_{\text{vdW}} \)  
vander Waals energy
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F_i$</td>
<td>total force on atom i</td>
</tr>
<tr>
<td>$k$</td>
<td>constant</td>
</tr>
<tr>
<td>$k_B$</td>
<td>Boltzmann constant</td>
</tr>
<tr>
<td>$m_i$</td>
<td>mass of species i</td>
</tr>
<tr>
<td>$N$</td>
<td>number of particles</td>
</tr>
<tr>
<td>$N_{DOF}$</td>
<td>number of degrees of freedom</td>
</tr>
<tr>
<td>$q_i$</td>
<td>(partial) charge of species i</td>
</tr>
<tr>
<td>$r_0$</td>
<td>mean bond length</td>
</tr>
<tr>
<td>$R_{0,ij}$</td>
<td>Lennard-Jones distance parameter</td>
</tr>
<tr>
<td>$r_{ij}$</td>
<td>distance between atoms i and j</td>
</tr>
<tr>
<td>$T$</td>
<td>temperature</td>
</tr>
<tr>
<td>$t$</td>
<td>time</td>
</tr>
<tr>
<td>$V$</td>
<td>volume</td>
</tr>
<tr>
<td>$v$</td>
<td>velocity</td>
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Chapter 1

Introduction

In Finland the final disposal of spent nuclear fuel is planned to be done in an underground repository, deep in the bedrock. There, release of radioactive material outside the repository can practically only happen through groundwater flow in fractured rock. To prevent or at least slow down a possible release of radionuclides into groundwater a design for release barriers is planned. Spent fuel rods are placed inside a copper canister with a cast iron core. Copper is chosen because of its ability to withstand corrosion in repository conditions. The canister is deposited into a borehole in the bedrock. The borehole is lined with compacted (i.e. dry) bentonite clay which, in contact with water, has an ability to swell and therefore slow water transport through the clay. It acts as a buffer between the canister and the bedrock preventing small rock movements from breaking the canister. The repository tunnels are filled as the canisters are placed in boreholes, and a mixture of rock and bentonite is used as the backfill material. Finally, the bedrock is intended to isolate the repository from the biosphere. It suppresses the radioactive radiation from the repository and in those depths, well below flowing groundwater, transport of species can occur only through diffusion in the bedrock’s immobile pore waters (assuming it is a non-fractured zone). An illustration of this concept is given in Figure 1.1. [19]

Bentonite clay plays an important role in the planned concept for safe disposal of spent nuclear fuel as one of the engineered barrier materials. Bentonite’s main component is montmorillonite, a swelling clay mineral, but it also contains water and some accessory minerals such as quartz, cristobalite and feldspar. Montmoril-
Figure 1.1: Bedrock and the engineered barriers in the concept for final disposal of spent nuclear fuel [19].

Ionite provides the clay with its beneficial characteristics: the ability to exchange its structural cations with surrounding material and the ability to absorb water which results in swelling of the mineral. The bulk bentonite is formed through multiple scales but the structure is not yet fully known to science. [19] It is therefore expected that the clay’s favorable properties derive from its nanolevel structure and reactions.

This work has received funding from VTT and Posiva Oy. The aim is to study wetting of montmorillonite - how water enters the mineral’s structure. We will first consider clay minerals in general and montmorillonite in a more specific fashion. Then we will explain the processes needed to perform molecular dynamics
simulations before describing the structure and steps in our simulations of montmorillonite. After this the results from simulations are presented and discussed briefly.

### 1.1 Definitions of clay minerals

Clay minerals are often products of long term weathering of rocks. Most clay minerals are sheet silicates (phyllosilicates) and the most common of them can be categorized into five different groups: kaolin (including e.g. kaolinite, halloysite), smectite (e.g. montmorillonite, beidellite), illite (e.g. illite, glauconite), chlorite (e.g. chlorite) and vermiculite (e.g. vermiculite) [23].

Clay minerals consist of tetrahedral (T) and octahedral (O) sheets that stack together to form layers which are either electrically neutral or carry a net negative charge. The tetrahedral sheet is built of individual tetrahedron "blocks" that are composed of four oxygens (O$^{2-}$) surrounding one central silicon (Si$^{4+}$). Depending on the clay mineral some of the silicon atoms can be substituted with aluminums (Al$^{3+}$). These silicon tetrahedra form a sheet by each sharing 3 of the vertex oxygen atoms and arranging so that in two dimensions a hexagonal pattern is formed, as shown in Figure 1.2. The octahedral sheet is built of individual edge sharing octahedron blocks containing one central aluminum (Al$^{3+}$) and altogether six oxygens (O$^{2-}$) and hydroxyl groups (OH$^{-}$). Here some of the aluminums can be substituted with magnesium (Mg$^{2+}$) or iron (Fe$^{2+}$) depending on the mineral. In two dimensions, also these aluminum octahedra are arranged hexagonally. These sheets can be stacked into layers containing one tetrahedral and one octahedral group (a 0.7 nm thick TO layer) known as 1:1 clay (e.g. kaolinite) or alternatively two tetrahedral groups with one octahedral between them (a 1 nm thick TOT layer) which is called a 2:1 clay (e.g. smectite, illite). The crystal structure of a clay mineral is formed when layers stack together leaving an empty space between the layers, the interlayer. Substitutions in the tetra and octahedral sheets give rise to the layers’ electronegativity and, if the layers are charged, the charge is balanced by cations such as Na$^{+}$, K$^{+}$ or Ca$^{2+}$ in the interlayer. Usually water is also present in the interlayer. [23]

One very important characteristic of clay minerals is their ability to exchange
Figure 1.2: Crystal structure of montmorillonite (two ~1 nm thick layers and the interlayer space and exchangeable cations between the layers) in polyhedron rendering and the hexagonal pattern of the tetrahedral sheet.

these interlayer cations (if they are not fixed). This is described by the cation exchange capacity (CEC) which is often given as the number of positive cations in milliequivalents (1 eq refers to valence of 1) needed to neutralize 100 grams of clay i.e. in units meq/100 g clay. [23]

1.2 Montmorillonite: properties and applications

Montmorillonite is a weathering product of volcanic tuffs and ash and it belongs to the group of 2:1 layered swelling clay minerals, smectites. Montmorillonite has a layer charge of -0.2 to -0.6 e/unit cell and it is mainly due to octahedral substitutions of Al$^{3+}$ to Mg$^{2+}$. Its chemical composition in general form is written as

\[ M_i^{(x)}(Si_{4-y}Al_y)(Al,Fe^{3+})_{2-z}(Mg,Fe^{2+})_zO_{10}(OH)_2 * nH_2O \]  

(1.1)

where $M$ is the interlayer cation in exchangeable state (for example Na$^+$, Ca$^{2+}$, K$^+$ or Mg$^{2+}$). [8] The amount of cation is dependent on the amount of substitutions in the structure, $x = y + z = 0.2 - 0.6$ and $y << z$. The swelling behaviour
Table 1.1: Montmorillonite mineral properties [22, 2, 14].

<table>
<thead>
<tr>
<th>Property</th>
<th>Value/Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Class</td>
<td>Silicates</td>
</tr>
<tr>
<td>Subclass</td>
<td>Phyllosilicates</td>
</tr>
<tr>
<td>Group</td>
<td>Smectite</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic prismatic, C2/m</td>
</tr>
<tr>
<td>Cleavage</td>
<td>{001} perfect, basal</td>
</tr>
<tr>
<td>Color</td>
<td>White, gray white, yellow, brownish yellow, greenish yellow</td>
</tr>
<tr>
<td>Particle size</td>
<td>~200-400 nm wide, 1 nm thick platelets</td>
</tr>
<tr>
<td>Specific surface (m²/g)</td>
<td>800</td>
</tr>
<tr>
<td>Molecular weight (g/mol)</td>
<td>549.07</td>
</tr>
<tr>
<td>Average density (g/cm³)</td>
<td>2.35</td>
</tr>
<tr>
<td>Characteristic</td>
<td>Crystals expand to many times their volume when added to water</td>
</tr>
<tr>
<td>Field indicators</td>
<td>Softness, soapy feel</td>
</tr>
</tbody>
</table>

of the mineral is generated as the layer charge is mostly present in the octahedra and too low to fix cations and bind the layers together [23]. The most common exchangeable cations are Na⁺ and Ca²⁺ and thus the two most common montmorillonites are classified as sodium montmorillonite (Na-MMT) and calcium montmorillonite (Ca-MMT). Montmorillonite mineral properties are shown in Table 1.1 [22, 2, 14] and a photo of dried Na-montmorillonite is shown in Figure 1.3.

Calcium and sodium montmorillonites are the most studied and developed clays in the montmorillonite series and they both are in wide commercial use. Their beneficial properties are the very small sized particles that have thin, layered structure with a net negative charge and the loosely bonded exchangeable cations between the layers. Due to their hydrophilic nature they are excellent absorbents of surrounding water [3].

Calcium clay (natural and activated) has applications in various fields, for example in oil refining as a bleaching agent (sorption of colour bodies on the clay surface) and to some extent as an adsorber of impurities. It has been used as a catalyst for various chemical reactions and in the pharmaceutical industry as a
thickening and adsorptive component in creams and powders. Due to its absorption properties it has been applied to bind toxic substances (dietary, bacterial and metabolic) in the gastrointestinal system to relieve nausea, vomiting or diarrhea. [11, 27]

In water at low solid contents sodium montmorillonite forms stable suspensions and with time, gels. This property makes it possible to utilise the clay as a binding agent, a suspension aid or a plasticiser. As a binder it can be used for example in foundry molding sands and animal feed pellets. In civil engineering sodium montmorillonite is used to prevent or reduce the access of water through soils and rocks. For example in drilling muds it is used to give water greater viscosity and in excavations it supports the walls and prevents them from caving in. Due to its absorption property sodium montmorillonite is also used in such an everyday item as cat litter. It is also an additive, a plasticizer, to ceramic materials and cement. [11, 27]
Chapter 2

Theory

2.1 Introduction to molecular simulations

Atom-level computer simulations are carried out in the hope that they will provide a better understanding of the properties of molecular assemblies, their structure and microscopic interactions. In this study our interest lies in the behaviour of the swelling clay mineral montmorillonite. The simulations in this study cover the time scale of a few hundred picoseconds and the length scale of a few nanometres.

Molecular modelling as a tool makes it possible to compare properties of an experimental system with those calculated in a model system. If the model agrees with the experiment, we have an adequate estimate of the intermolecular interactions in the system, otherwise further improvement of the model is needed. On the other hand, we may consider computer simulations as experiments to test theories before they are applied in the real world, as computer experiments. In a computer experiment we perform simulations in a model system and compare the results with the theoretical predictions of an approximate analytical theory that is applied to the same model system. If the simulation results disagree with the theory’s predictions, the theory is flawed. Molecular modelling also compliments experimental work enabling one to see what happens in the microscopical level instead of just the macroscopical changes. Testing new theories and systems is fairly uncomplicated, especially those difficult to produce in laboratory conditions, e.g. high temperature or pressure experiments. In addition, computer simulations can
be used to predict properties of new materials and aid in their development. [9]

There are two main classes of molecular simulation methods for classical many-body systems: molecular dynamics (MD) and Monte Carlo (MC). Simulations provide us with microscopic level information that is used to calculate thermodynamic properties of molecular systems. Monte Carlo method is used to calculate equilibrium properties of molecular assemblies and it gives them as ensemble averages. Molecular dynamics offer these properties as well, but they are calculated as time averages. Additionally, MD gives out the time evolution of the system, i.e. atoms’ trajectories. [9] Another way to do simulations is by quantum mechanical approach which doesn’t rely as much on approximations as the classical methods, but it has limitations concerning e.g. the system’s size. [6]

2.2 Molecular dynamics

The molecular dynamics method is used to study complex systems, e.g. to evaluate equilibrium and transport properties that cannot be calculated analytically. While these properties are determined in the microscopic i.e. atomistic level, they are linked to the macroscopic properties of the bulk system through thermodynamics and statistical mechanics.

MD produces time evolution of a system, the trajectory, by solving Newton’s equation of motion

$$m_i a(t)_i = F(x)_i = -\nabla E(x(t))_i$$

(2.1)

for the N-body system under the influence of specified forces. These equations are numerically integrated at given time intervals (∼ 1 fs). At every interval, a new set of particle positions and velocities is generated and used in the next set of integration. A schematic view of this loop is shown in Figure 2.1. The total force acting on an atom is calculated from the first derivative of the atom’s potential energy, as is shown on the right hand side of equation (2.1). The forces and energies are evaluated either using classical potential energy functions that describe interactions between atoms in the system, so called force fields, or using quantum mechanical methods to calculate the potential energy of the system “on the fly”. The final output of these calculations contains the information on positions,
velocities and accelerations for each particle in the system at each time step, the trajectory, which is then used to determine (time averaged) values of the desired properties. [24, 4]

In practice a basic molecular dynamics simulation consists of the following steps: initialization, equilibration and dynamics run. The simulation is initiated by assigning atoms with initial positions (compatible with the structure one wishes to simulate) and velocities (usually set according to the desired system temperature). The next step is equilibrating the system i.e. finding the system in its free energy minimum. This can be done by simply performing a preliminary molecular dynamics run long enough so the system’s thermodynamic quantities (e.g. temperature and potential energy) fluctuate around constant average values. When this is achieved the actual calculation run can be done. [9] The time scale of these simulations generally ranges from a few picoseconds to dozens of nanoseconds.

2.2.1 Force fields i.e. potentials

A molecular mechanics force field is a simplified yet accurate enough model to describe the intramolecular and intermolecular interactions in a system. It contains the functional form of the potential energy that best describes a system’s molecular structure and for each atom type a set of fitted parameters that are used in the energy and force calculation. [4] Hence, a force field contains the following information:

![Diagram](image-url)
• A list of atom types (differentiates an element according to its placement e.g. oxygen in water and oxygen in mineral structure) and charges assigned to each type

• Atom typing rules linking an atom type to its element type and chemical microenvironment (e.g. number and nature of connected atoms)

• Functional forms of the potential energy components and parameters for the components

• Rules for generating parameters that were not explicitly defined

The functional form of the energy expression takes into account both bonded i.e. atoms linked by covalent bonds \( (E_{\text{bonded}}) \) and non-bonded interaction terms \( (E_{\text{non–bonded}}) \). The total energy in general form can then be written as

\[
E_{\text{tot}} = E_{\text{bonded}} + E_{\text{non–bonded}}
\]  \hspace{1cm} (2.2)

where the bonded term takes into account interactions such as [24] (see Figure 2.2):

• **Bond stretching** describes the change in energy which occurs due to the change in bond length from its equilibrium value

• **Angle bending** describes the change in energy due to change in the angle between two sequential covalent bonds from the equilibrium value

• **Torsion** describes the change in energy of three bonds connected as IJ, JK and KL due to change in the dihedral (or torsional) angle between the planes IJK and JKL from the equilibrium value

• **Inversion** describes the energy of three atoms bonded to one central atom in the same plane due to an out of plane configuration

and can then be expressed as a sum of these interactions

\[
E_{\text{bonded}} = E_{\text{bond stretch}} + E_{\text{angle bend}} + E_{\text{torsion}} + E_{\text{inversion}}
\]  \hspace{1cm} (2.3)

The non-bonded energy takes into account the electrostatic (coulombic) and van
der Waals interactions and sometimes also the effect of hydrogen bonding

\[ E_{\text{non-bonded}} = E_{\text{Coul}} + E_{\text{vdW}} + E_{\text{Hbond}} \]  

Each force field has a set of parameters that are predetermined for all atom combinations in a specific (target) system to mimic with reasonable accuracy the results of experiments or quantum chemical calculations. The more general the target system is, i.e. covering a larger set of elements, the more simplifications these parameters contain and thus the accuracy of the force field is lower. On the other hand, the more accurate the force field is, the more computational resources are needed in the simulation. Therefore the choice of force field has a great impact on the validity of results from a molecular dynamics simulation. [4]

### 2.2.1.1 Types of force field for clay systems

There are many different force fields in use to simulate clay systems. Depending on the structure of the system to be modelled, one chooses the force field that is best suited to describe the target system. As an example of available force fields one could mention AMBER, CHARMM and REAXFF, of which we shall give brief descriptions here, or CLAYFF which we have used in the simulations.
AMBER (Assisted Model Building with Energy Refinement) force field is used in the simulation of proteins, nucleic acids and organic molecules [5]. The functional form of the AMBER force field is

\[
E_{\text{tot}} = \sum_{\text{bonds}} k_r (r - r_0)^2 + \sum_{\text{angles}} k_\theta (\theta - \theta_0)^2 + \sum_{\text{dihedrals}} \frac{V_n}{2} [1 + \cos(n\phi - \gamma)] \\
+ \sum_{i<j} \left\{ \epsilon_{ij} \left[ \left( \frac{R_{0,ij}}{r_{ij}} \right)^{12} - 2 \left( \frac{R_{0,ij}}{r_{ij}} \right)^6 \right] + k \frac{q_i q_j}{r_{ij}} \right\} \quad (2.5)
\]

where the first three terms represent the bonded interaction and the last two represent the non-bonded interaction. The first and second terms describe the energies between covalently bonded atoms and their angles given in harmonic form. The third term represents the energy due to torsions. The fourth term gives the energy due to short range van der Waals interaction represented by a Lennard-Jones 12-6 potential and the last term gives the electrostatic energy modelled by Coulombic interaction for atom centered point charges.

CHARMM (Chemistry at HARvard Macromolecular Mechanics) is a program and a force field used in the simulation of proteins, nucleic acids and lipids [15] with parameters developed for clay systems [16]. The functional form of the force field is

\[
E_{\text{tot}} = \sum_{\text{bonds}} k_r (r - r_0)^2 + \sum_{\text{angles}} k_\theta (\theta - \theta_0)^2 + \sum_{\text{dihedrals}} k_\phi [1 + \cos(n\phi - \gamma)] \\
+ \sum_{i<j} \left\{ 4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + k \frac{q_i q_j}{r_{ij}} \right\} \quad (2.6)
\]

where the first three terms represent the bonded interaction (covalently bonded atoms with their angles and torsions) and the last two represent the non-bonded interaction (van der Waals and electrostatic energies).

REAXFF [28] is a so called reactive force field that combines a bond-order concept with polarizable charges which makes it possible to model the breaking and formation of bonds together with the associated charge rearrangements. However, the limitations of this force field include a limited set of available parameters, a need for short time steps (0.25 fs used in [20]) and long computation times.
2.2.1.2 CLAYFF force field

CLAYFF [7] is a general force field for hydrated and multicomponent mineral systems and their interfaces with aqueous solutions. It was chosen for this study because in the past it has been successfully used in montmorillonite mineral simulations (e.g. [25]). Its advantages include the use of partial atomic charges instead of full formal charges in order to not produce too large electrostatic potentials. CLAYFF also differentiates an element into different types depending on its structural position. For example aluminum has different properties whether it occurs in tetrahedra or octahedra.

The total energy in CLAYFF takes into account the Coulombic interaction, the short-range interactions and the bonded interactions as follows:

\[ E = E_{\text{Coul}} + E_{\text{vdW}} + E_{\text{bond stretch}} + E_{\text{angle bend}} \]  

(2.7)

where \( E_{\text{Coul}} \) is the energy due to the electrostatic interaction, \( E_{\text{vdW}} \) the energy due to van der Waals interaction, \( E_{\text{bond stretch}} \) represents energy due to (two body) bond stretching and \( E_{\text{angle bend}} \) the energy due to (three body) angle bending. The first two terms describe the nonbonded interaction in the system and the last two describe the bonded interaction.

Coulombic energy is calculated from

\[ E_{\text{Coul}} = \frac{e^2}{4 \pi \epsilon_0} \sum_{i \neq j} q_i q_j \frac{1}{r_{ij}} \]  

(2.8)

where \( q_i \) and \( q_j \) are partial charges of the atoms, \( r_{ij} \) is the distance between atoms, \( e \) is the electron charge and \( \epsilon_0 \) is the dielectric permittivity of vacuum. Van der Waals energy is calculated from the Lennard-Jones (12-6) equation

\[ E_{\text{vdW}} = \sum_{i \neq j} D_{0,ij} \left[ \left( \frac{R_{0,ij}}{r_{ij}} \right)^{12} - 2 \left( \frac{R_{0,ij}}{r_{ij}} \right)^{6} \right] \]  

(2.9)

where

\[ D_{0,ij} = \sqrt{D_{0,i}D_{0,j}} \]  

(2.10)

is the energy parameter and

\[ R_{0,ij} = \frac{1}{2}(R_{0,i} + R_{0,j}) \]  

(2.11)
is the distance parameter. The partial charges and per atom type energy and distance parameters are given in Table 2.1. Bond stretching is described by a harmonic oscillator

\[ E_{\text{bond stretch } ij} = k_1 (r_{ij} - r_0)^2 \]  

(2.12)

where \( k_1 \) is a force constant and \( r_0 \) is the equilibrium bond length. Angle bending is also given in harmonic form

\[ E_{\text{angle bend } ijk} = k_2 (\theta_{ijk} - \theta_0)^2 \]  

(2.13)

where \( k_2 \) is a force constant, \( \theta_{ijk} \) represents the bond angle for metal-oxygen-

<table>
<thead>
<tr>
<th>species</th>
<th>charge (e)</th>
<th>( D_0 ) (kcal/mol)</th>
<th>( R_0 ) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>water H</td>
<td>0.4100</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>hydroxyl H</td>
<td>0.4250</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>water O</td>
<td>-0.8200</td>
<td>0.1554</td>
<td>3.5532</td>
</tr>
<tr>
<td>bridging O</td>
<td>-1.0500</td>
<td>0.1554</td>
<td>3.5532</td>
</tr>
<tr>
<td>bridging O with octahedral substitution</td>
<td>-1.1808</td>
<td>0.1554</td>
<td>3.5532</td>
</tr>
<tr>
<td>hydroxyl O with substitution</td>
<td>-1.0808</td>
<td>0.1554</td>
<td>3.5532</td>
</tr>
<tr>
<td>tertaehedral Si</td>
<td>2.1000</td>
<td>1.8405e-6</td>
<td>3.7064</td>
</tr>
<tr>
<td>octahedral Al</td>
<td>1.5750</td>
<td>1.3298e-6</td>
<td>4.7943</td>
</tr>
<tr>
<td>octahedral Mg</td>
<td>1.3600</td>
<td>9.0298e-7</td>
<td>5.9090</td>
</tr>
<tr>
<td>aqueous Na ion</td>
<td>1.0000</td>
<td>0.1301</td>
<td>2.6378</td>
</tr>
</tbody>
</table>

Table 2.1: A set of nonbond parameters for the CLAYFF force field [7].

<table>
<thead>
<tr>
<th>bond stretch species</th>
<th>( k_1 ) (kcal/mol Å²)</th>
<th>( r_0 ) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>water O - water H</td>
<td>554.1349</td>
<td>1.0000</td>
</tr>
<tr>
<td>hydroxyl O - hydroxyl H</td>
<td>554.1349</td>
<td>1.0000</td>
</tr>
<tr>
<td>hydroxyl O with substitution - hydroxyl H</td>
<td>554.1349</td>
<td>1.0000</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>angle bend species</th>
<th>( k_2 ) (kcal/mol rad²)</th>
<th>( \theta_0 ) (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>water H-water O-water H</td>
<td>45.7696</td>
<td>109.47</td>
</tr>
<tr>
<td>metal-hydroxyl O-hydroxyl H</td>
<td>30.0000</td>
<td>109.47</td>
</tr>
<tr>
<td>metal-hydroxyl O with substitution-hydroxyl H</td>
<td>30.0000</td>
<td>109.47</td>
</tr>
</tbody>
</table>

Table 2.2: Bond parameters for the CLAYFF force field [7].
hydrogen bond and $\theta_0$ is the equilibrium bond angle. Parameters for the bonded interaction are given in Table 2.2.

### 2.2.2 Simplifications in MD calculations

When the size of a system under study grows, the number of particles in it and the number of interactions that need to be calculated grows also. This means that more and more computational resources are needed. One way to restrict the effects due to a very large set of particles is to apply periodic boundary conditions on the system. A model set-up is bound into a box which is surrounded by exact copies of it. The simulation is then done in the original restricted box where a particle leaving the box on one side enters it on the opposite side which is illustrated in Figure 2.3. [1]

One basic method for restricting the number of non-bonded interactions calculated in the system is to use a cut-off radius. For interactions that weaken fast enough with increasing atom distance (for example for the electrostatic interaction $E_{\text{Coul}} \propto r_{ij}^{-1}$ and for the van der Waals interaction $E_{\text{vdW}} \propto r_{ij}^{-6}$), the effects are assumed negligible beyond a certain distance and interactions are only calculated within this "cut-off". Also, when calculating pairwise interactions, some computational economy can result from listing atom pairs that are in range of the cut-off and a bit of extra "skin" distance. Over the next few time steps only pairs that appear in this neighbour list are checked in the force calculation in stead of going through the complete set of atoms each time step. [1]

![Figure 2.3: Periodic boundary condition.](image-url)
2.2.3 **Ensembles in molecular dynamics**

An ensemble is a term used in mathematical physics meaning a collection of numerous mental copies of a system, each copy representing a microscopic state the real system could be in. All the possible states are covered and all are considered the same time. Ensemble covers the notion of a physical experiment being repeated over and over again under the same macroscopic condition but uncontrolled microscopic specifics leading to a range of different observable outcomes.

An ensemble can have an infinite number of elements, microstates, which in the phase space of the system define a probability measure for realizing each element. However complex the dynamical evolution of a real system may be, the average statistical properties over the whole thermodynamic ensemble may remain well-defined. A partition function which is the normalizing factor of the probability measure is used together with various thermodynamic relations to determine statistical thermodynamic properties of the system.

The range of ensembles used in molecular dynamics include [9, 6]:

- **Microcanonical (NVE) ensemble** - The number of particles $N$, volume $V$ and total energy $E$ are fixed in this ensemble. By checking the conservation of total energy, this ensemble can be used to evaluate the correctness of an algorithm or the time step of the simulation.

- **Canonical (NVT) ensemble** - While the energy is allowed to fluctuate, a fixed temperature is imposed on the system by bringing it in contact with a heat bath using a thermostat.

- **Isothermal-isobaric (NPT) ensemble** - Pressure and temperature are conserved while volume of the system is allowed to vary. In addition to a thermostat, a barostat is used to impose an external pressure on the system as if it were in contact with a pressure bath. This allows the system to reach the density determined in the force field.

The properties of these ensembles are given in Table 2.3.
<table>
<thead>
<tr>
<th>Ensemble</th>
<th>All states of</th>
<th>Probability distribution</th>
<th>Schematic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microcanonical (NVE)</td>
<td>given NVE</td>
<td>$\pi_i = \frac{1}{\Omega}$</td>
<td><img src="image1" alt="Diagram" /></td>
</tr>
<tr>
<td>Canonical (NVT)</td>
<td>all energies</td>
<td>$\pi(E_i) = \frac{1}{Q} e^{-\beta E_i}$</td>
<td><img src="image2" alt="Diagram" /></td>
</tr>
<tr>
<td>Isothermal-isobaric (NPT)</td>
<td>all energies and volumes</td>
<td>$\pi(E_i, V_i) = \frac{1}{\Delta} e^{-\beta(E_i + PV_i)}$</td>
<td><img src="image3" alt="Diagram" /></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ensemble</th>
<th>Thermodynamic potential</th>
<th>Partition function</th>
<th>Bridge equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microcanonical (NVE)</td>
<td>Entropy, S</td>
<td>$\Omega = \sum 1$</td>
<td>$S/k = \ln \Omega(E, V, N)$</td>
</tr>
<tr>
<td>Canonical (NVT)</td>
<td>Helmholtz free energy, F</td>
<td>$Q = \sum e^{-\beta E_i}$</td>
<td>$-\beta F = \ln Q(T, V, N)$</td>
</tr>
<tr>
<td>Isothermal-isobaric (NPT)</td>
<td>Gibbs free energy, G</td>
<td>$\Delta = \sum e^{-\beta(E_i + PV_i)}$</td>
<td>$-\beta G = \ln \Delta(T, P, N)$</td>
</tr>
</tbody>
</table>

Table 2.3: Ensembles used in molecular dynamics and their properties.
Chapter 3

Model set-up

3.1 Montmorillonite structure

A simple method to produce a crystal structure for a simulation is to define its unit cell, then replicate and translate it along each lattice vector as many times as needed. However, in nature the structure is rarely homogenous i.e. substitutions are randomly located so we have defined a three-fold unit cell (1x1x3) where the substitutions are not all in the same position. This, when replicated and translated, produces 3 layers with different configurations. For further simplicity we have defined just one substitution type in the mineral structure, magnesium, and it is present only in the octahedral sheets of the layers. We defined one substitution per unit cell in order to have some in each layer but not too much to prevent swelling [20]. The chemical composition of our Na-montmorillonite is now Si$_{24}$Al$_9$Mg$_3$O$_{60}$(OH)$_{12}$.3Na.

The general structure coordinates of montmorillonite were obtained from the work of Tsipursky and Drits [26]. It was used as a base to find the optimized three-fold unit cell structure for Na-montmorillonite with substitutions. The optimized structure was used in this work to reduce the amount of fitting and guesswork. The structure optimization was performed by Eini Puhakka at VTT, Technical Research Centre of Finland, using density functional code CASTEP (Cambridge Serial Total Energy Package) implemented into Materials Studio version 6.0 [13]. The optimized structure is shown in Figure 3.1 and its lattice parameters (defini-
Table 3.1: Lattice parameters of the optimized three-fold unit cell of MMT. Explanation of the parameters is given in Appendix A.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>0.5012 nm</td>
<td>$\alpha = 90^\circ$</td>
</tr>
<tr>
<td>b</td>
<td>0.8752 nm</td>
<td>$\beta = 114.2^\circ$</td>
</tr>
<tr>
<td>c</td>
<td>3.4839 nm</td>
<td>$\gamma = 90^\circ$</td>
</tr>
</tbody>
</table>

3.2 Simulation cell

The aim of this work is to study wetting of montmorillonite which is to say how water enters the interlayer space. To model this we created a three layered montmorillonite particle by replicating the three fold unit cell 10x6x1. Then a c-code was written to generate water molecules into the empty space around the particle. Given bounding box coordinates, this code excluded the volume with montmorillonite. Then, using a density of 55.5 mol/l, it created water into the remaining space inside the box. This generated $\sim$6500 water molecules around the montmorillonite as shown in Figure 3.2. Altogether the simulation cell contains approximately 27000 atoms and the simulation cell is a rectangular "box" sized 8.7 nm x 7.8 nm x 4.5 nm. We built three separate systems with the difference between them being that one contains montmorillonite with no water in the interlayer and the other two have 90 or 180 water molecules randomly generated into both interlayers (i.e. 1 or 2 water molecules per unit cell). An illustration of these set-ups is shown in Figure 3.3. The aim in varying the interlayer water content in the initial set-ups is to be able to compare the wetting behaviour of a completely dry clay to that of a clay with a very low water content.

3.3 Computational details

All the molecular dynamics simulations in this work were performed using LAMMPS (Large-Scale Atomic/Molecular Massively Parallel Simulator) software [21] and the CLAYFF force field and the computations were done on a cluster computer.
Figure 3.1: The CASTEP optimized three-fold unit cell structure of Na-montmorillonite without interlayer water, Si=yellow, Al=purple, Mg=green, O=red, H=white and Na=blue. Lattice parameters are given in pm. The thickness of one layer is $\sim 0.64$ nm, measured using atom center coordinates.
using 8 CPUs. Visualizations were done with VMD (Visual Molecular Dynamics) software [12].

In the CLAYFF force field the short range interactions are calculated from the Lennard-Jones equation and electrostatic interactions are defined as long range Coulomb interactions. The short range van der Waals forces were applied with a 12.5 Å cut-off radius (in [18] a 12 Å cut-off was used). To calculate the long range electrostatics the Ewald summation method [9] (that takes advantage of the periodicity of the system) is used. Periodic boundary conditions were inforced on the system.

The kinetic energy of a system is related to its temperature as

\[
\frac{1}{2} k_B T = \frac{\langle E_{\text{kin}} \rangle}{N_{\text{DOF}}}
\]  

(3.1)

where \( k_B \) is Boltzman constant, \( E_{\text{kin}} \) the kinetic energy of the system and \( N_{\text{DOF}} \) is the number of degrees of freedom in the system [9]. So to produce a specific temperature in the system, atoms were given initial velocities. The velocities were generated using a random number generator to give a a gaussian velocity distribution that would corresponds the requested temperature.
A molecular dynamics simulation consists of three stages: a minimization, an equilibration and a production run. Minimization is performed in order to relax a system with overlapping atoms i.e. to get rid of huge forces and energies present in the initial set-up. This can be done in two ways: iteratively adjusting atom coordinates or running dynamics with a very small time step. [17] The montmorillonite structure used in our simulations was already optimized for the case of no interlayer water, however, in order to keep the simulation conditions as unvaried as possible each system went through the same minimization process. First
an initial iterative minimization was performed after which the whole system was
minimized by running dynamics with a 0.001 fs time step for 10 fs. Equilibration
in each case was performed in the NVE ensemble. Calculations were performed
in the NPT ensemble applying a Nose-Hoover thermostat [9] at 298 K and 323 K
temperatures and barostat at 1 atm pressure. The systems were equilibrated for
50 ps with a 0.5 fs time step after which the production run in the NPT ensemble
took place for 500 ps with a time step of 1 fs. The details of the system were
recorded every 100th time step. An example LAMMPS code used to model our
clay system is given in Appendix B.

3.4 Data processing

In order to determine the amount of water in the interlayers of our montmoril-
lonite particle we first defined two rectangular volumes Layer1 and Layer2 to
contain the two interlayer spaces as shown in Figure 3.4. The volume coordinates
were defined at each outputted time step and taken as the coordinates from central
aluminums in the near-left corner of the bottom clay layer and the far-right corner
of the layer on top of it. This definition of interlayers doesn’t cover the whole
interlayer space so, in order to find the amount of water per unit cell of clay, a
correction to the total number of system unit cells (10x6x3) must be made. In the
x-direction about 9 of 10 cells are taken into account and in y-direction about 5.4
of 6 cells giving a total of (9x5.4x3) 145.8 cells which we round down to 145 unit
cells in the calculation area.

To determine the thickness of an interlayer we took advantage of some basic
trigonometry and vector algebra. For each interlayer we defined two vectors (in
xz-direction and approximately the same y-position) along its bottom and top clay
surfaces (let’s call these vectors \( \mathbf{A} \) and \( \mathbf{B} \)).

\[
\mathbf{A} = A_x \mathbf{e}_x + A_z \mathbf{e}_z = (x_{Afin} - x_{Ainit}) \mathbf{e}_x + (z_{Afin} - z_{Ainit}) \mathbf{e}_z \quad (3.2)
\]

\[
\mathbf{B} = B_x \mathbf{e}_x + B_z \mathbf{e}_z = (x_{Bfin} - x_{Binit}) \mathbf{e}_x + (z_{Bfin} - z_{Binit}) \mathbf{e}_z \quad (3.3)
\]

The interlayer thickness was then taken as the distance \( d \) of a chosen point \( P \) (in
Figure 3.4: Volumes where interlayer waters are calculated: Layer1 (blue) and Layer2 (magenta).

Figure 3.5: The distance $d$ of point $P$ from vector $B$.

From the middle of vector $A$)

$$P = \left( \frac{x_{A_{init}} + x_{A_{fin}}}{2}, \frac{z_{A_{init}} + z_{A_{fin}}}{2} \right)$$ (3.4)

from a line that goes along vector $B$, as shown in Figure 3.5.

From vector algebra and trigonometry we can deduce a relation for the distance $d$

$$\mathbf{B} \cdot \mathbf{e}_x = B \cos \alpha$$ (3.5)

$$\cos \alpha = \frac{d}{z_0}$$ (3.6)

$$\Rightarrow d = \frac{z_0 B_x}{B}$$ (3.7)
The line that goes through B can be written as

\[
    z_B(x) = \frac{B_z}{B_x} x + C1
\]

\[
    z_B(x_{\text{Binit}}) = z_{\text{Binit}} \Rightarrow C1 = \frac{x_{\text{Bfin}} z_{\text{Binit}} - x_{\text{Binit}} z_{\text{Bfin}}}{B_x}
\]

(3.8)

(3.9)

On this line we can now determine a point with the same x-coordinate as P,

\[
    Q = (P_x, z_B(P_x))
\]

(3.10)

which leads us to the final component of equation 3.7

\[
    z_0 = Q_z - P_z
\]

(3.11)

To reduce error in the calculation this procedure was performed in three different positions for each interlayer and the three d-values obtained were then averaged to give the interlayer thickness presented in our results. Using this method requires that the clay layers are small enough so they don’t bend or twist during the simulation.

### 3.5 Error estimation

In order to determine the amount of interlayer water at the end of a simulation we average over the last ten data points. The mean (average) value is obtained from

\[
    \bar{x} = \frac{1}{N} \sum_{i=1}^{N} x_i
\]

(3.12)

where \(x_i\) is the value of data point \(i\) and \(N\) is the total number of data points. The standard error of the mean is given as

\[
    s_{\bar{x}} = \frac{s}{\sqrt{N}}
\]

(3.13)

where \(s\) is the standard deviation

\[
    s = \sqrt{\frac{1}{N-1} \sum_{i=1}^{N} (x_i - \bar{x})^2}
\]

(3.14)
Chapter 4

Result and discussion

4.1 Results

Evolution of the total energy in each simulation is given in Figure 4.1. The energy data was recorded every 2000 timesteps. The energy in each system drops at the beginning because of the iterative minimization. Then the equilibration process in NVE ensemble takes place for 50 ps during which the total energy slowly decreases to stable ranges. Simulations are separated by their structure into three cases according to the initial water intake (case 0: no interlayer water, case 1: 1 water molecule/unit cell and case 2: 2 water molecules/unit cell).

Figures 4.2-4.4 present the intake of water into the interlayers of montmorillonite (layer1 refers to the bottom interlayer and layer2 to the one on top of layer1, see Figure 3.4) as a function of time and the corresponding interlayer thicknesses obtained from simulations at two temperatures (298 K and 323 K). Each of these figures represents one simulation case. Results of both the equilibration (NVE) and production (NPT) runs are plotted with the two interlayer spaces treated separately but also the total amount of interlayer water is given. The interlayer thickness does not take into account the effect of atomic radius since the particles in the system are treated as point charges. Figure 4.5 illustrates the final configurations of the simulations at 298 K temperature and Figure 4.6 at 323 K. Table 4.1 shows the amount of interlayer water per unit cell at the beginning and end (averaged and error given as the standard error of the mean) of each simulation.
Figure 4.1: Evolution of total energy in each simulation. Equilibration takes place in the first 50 ps. Note the fast decline at t=0, a result of the iterative minimization.

Figures 4.7-4.9 show the basal spacings (i.e. layer ~0.64 nm + interlayer thickness) of montmorillonite with the corresponding water intake from the NPT calculations at different temperatures. The two interlayers are treated separately.
Figure 4.2: Simulation case 0: initial interlayer water 0 molecules/unit cell. The amount of water in the interlayers of montmorillonite (top two) and thickness of the interlayers (bottom two) at temperatures of 298 K and 323 K. Explanation of layer1 and layer2 is given in Figure 3.4.
Figure 4.3: Simulation case 1: initial interlayer water 1 molecule/unit cell. The amount of water in the interlayers of montmorillonite (top two) and thickness of the interlayers (bottom two) at temperatures of 298 K and 323 K.
Figure 4.4: Simulation case 2: initial interlayer water 2 molecules/unit cell. The amount of water in the interlayers of montmorillonite (top two) and thickness of the interlayers (bottom two) at temperatures of 298 K and 323 K.
Figure 4.5: Snapshots from the middle of the simulation box at the end (550ps) of each simulation at 298 K temperature (from top to bottom: cases 0, 1 and 2).
Figure 4.6: Snapshots from the middle of the simulation box at the end (550ps) of each simulation at 323 K temperature (from top to bottom: cases 0, 1 and 2).
Table 4.1: Amount of water (molecules per unit cell) at the beginning and end of each simulation.

<table>
<thead>
<tr>
<th>Case</th>
<th>Init 298 K</th>
<th>Final 298 K</th>
<th>Init 323 K</th>
<th>Final 323 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0.10 ± 0.01</td>
<td>0</td>
<td>0.11 ± 0.01</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>1.36 ± 0.01</td>
<td>1</td>
<td>2.30 ± 0.01</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>2.63 ± 0.02</td>
<td>2</td>
<td>2.89 ± 0.01</td>
</tr>
</tbody>
</table>

Figure 4.7: Simulation case 0: Basal spacings of the clay layers as a function of their water content at 298 K and 323 K temperatures.
Figure 4.8: Simulation case 1: Basal spacings of the clay layers as a function of their water content at 298 K and 323 K temperatures.

Figure 4.9: Simulation case 2: Basal spacings of the clay layers as a function of their water content at 298 K and 323 K temperatures.
4.2 Discussion

During equilibration the total energy in cases 1 and 2 has reached stable levels, but in case 0 it is still slowly decreasing at the end of the process. The change of ensembles from NVE to NPT is demonstrated by a drop in the total energy at t=50 ps. The change in energy is in the order of 0.1%.

Looking at the total water intake in Figures 4.2-4.4 we can see in case 0 (no initial interlayer water) rapid fluctuation at both simulation temperatures. Cases 1 and 2 present a much smoother increase in the amount of interlayer water (though case 1 presents some fluctuation at 323 K) and in both cases this increase is steeper at 323 K compared to 298 K. This, along with the entries in Table 4.1 for the two cases, suggests that a system’s temperature affects the rate water is absorbed into montmorillonite’s interlayers i.e. that a higher temperature results in faster absorption, as would be expected based on increased motion of atoms at increased temperatures. However, determining the dependence between this rate and temperature would require further study (at several temperatures). The fluctuations in cases 0 and 1 are most likely due to the clay particle having rotated in a way that our definition for interlayer volumes contained some "outside" water. This could be corrected by choosing the volumes within the clay particle more carefully.

On a case by case basis the interlayer thicknesses in Figures 4.2-4.4 look to be in the same ballpark. Comparing the two interlayers of a system at one temperature, the difference between their thicknesses varies only up to about 0.1 nm. This variation is possibly the result of substitution placement in the montmorillonite layers (bottom and middle: different, middle and top: identical). We noted also that case 0 presents a fast decline in interlayer space thickness during the equilibration process. The clay structure was originally optimized for this particular case and should have been in equilibrium to start with. It is clearly a feature of the chosen force field to move clay layers closer together in this instance.

Illustrations of the end of simulation configurations in Figures 4.5 and 4.6 demonstrate the rotation montmorillonite particles have undergone in the xz-plane. We can also see that with little or no water in the interlayers sodium cations tend to move closer to the clay layer surfaces. Case 0 in these figures shows no visible water in the interlayers. This suggests further that some outside water was
included in the calculation of interlayer water (for the case of completely dry montmorillonite) and that in this case no absorption of water took place in the 0.5 fs simulation time.

Figures 4.7-4.9 resemble Rorschach’s inkblots and for case 0 they represent not much more because of the "extra" (i.e. outside water) in our water content data, though they give a rough estimate of the basal thickness of (completely) dry montmorillonite. In cases 1 and 2 however, the figures give an estimation of how much water can be confined into the volume between montmorillonite layers. This is more clearly demonstrated by the bottom layer (presented by the blue data points in a slowly rising fashion).
Chapter 5

Conclusions

In this work we have studied the absorption of water molecules into the interlayers of Na-montmorillonite and the resulting swelling through molecular dynamics simulations. We chose the CLAYFF force field to describe our system, a three-layered montmorillonite particle in free water. The simulations were performed under NPT conditions for 0.5 ns.

We plotted the time evolution of the interlayer water content and the interlayer space thickness in this system for different initial water contents at two temperatures. Additionally, we plotted the interlayer water content as a function of the basal thickness. We detected no absorption of water into the interlayers of completely dry montmorillonite during the simulation time interval. For montmorillonite with low initial water content we were able to determine that at the higher temperature water is absorbed faster into the interlayers. We concluded also that the placement of substitutions in montmorillonite layers could affect the interlayer thicknesses in the montmorillonite particle.

Future work on this subject could include performing the same simulations with different cations, namely calcium and potassium, and study how the choice of cation affects montmorillonite’s ability to absorb water and whether there is any significant change in the mineral’s swelling properties. Also, the initial water content could be increased and simulations could be performed at a few different temperatures.
Bibliography


[7] Randall T. Cygan, Jian-Jie Liang, and Andrey G. Kalinichev. Molecular models of hydroxide, oxyhydroxide, and clay phases and the development


Appendix A

Lattice parameter definition
Appendix B

A LAMMPS input file

An example code file used in LAMMPS to simulate montmorillonite. Comment line begins with the symbol #

# define units used in simulation
units real
# allow use of charges and bonds in the system
atom_style full
# define dimensionality of the simulation cell
dimension 3
# use periodic boundary conditions
boundary p p p

# bonded interactions: bond stretching and angle bending in harmonic form
bond_style harmonic
angle_style harmonic
# neighbor list skin distance 3Å
neighbor 3.0 bin
# neighbor list build:
neigh_modify every 2 delay 0 check yes one 3000
# nonbonded interactions: Lennard-Jones with 12.5Å cut-off and long range Coulomb
pair_style lj/cut/coul/long 12.5
pair_modify mix arithmetic
# ewald summation method for long range Coulomb
kspace_style ewald 1.0e-4

# read in structural information: atom coordinates, types and charges and the
# bonded information
read_data data.MMT_1water
# group together elements in clay
group clay type 2 4 5 6 7 8 9 10 11 13

# generate initial velocities for atoms using gaussian distribution,
# target temperature 298K
velocity all create 298.0 105112 dist gaussian
# initial minimization
minimize 1.0e-4 1.0e-6 100 1000

# use NVE ensemble in first equilibration
fix 1 all nve
# system temperature 298K
fix 2 all langevin 298.0 298.0 100 123345
# fix the center of mass for MMT
fix COM clay recenter INIT INIT INIT units box
# output (every 100 time steps) file: atom info, coordinates and velocities
dump NVE all custom 100 dump.MMT_w1_NVE id mol type q mass x y z vx vy vz

# info echoed every 2000 time steps including temperature and pressure of system
thermo 2000
thermo_style custom step dt spcpu temp press
# set timestep: 0.001fs
timestep 0.001
# run for 10000 time steps= 10fs
run 10000
# run with 0.5fs time step for 100 000 steps= 50ps
timestep 0.5
run 100000
# end equilibration run
undump NVE
unfix 1
unfix 2

# use NPT ensemble in production run, system temperature 298K and
# pressure 1atm
fix 1 all npt temp 298 298 100 aniso 1 1 1000
# output (every 100 time steps) file: atom info, coordinates and velocities
dump NPT all custom 100 dump.MMT_w1_NPT id mol type q mass x y z vx vy vz
# run with 1fs time step for 500 000 steps= 500ps
timestep 1.0
run 500000