Molecular Dynamics simulation of rock and clay minerals to estimate their mechanical properties

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ABSTRACT

Macroscopic analyses of rocks have produced acceptable results for many problems. These problems are simple, involving normal conditions. But a need is arising to study these rocks under extreme conditions, like high temperatures, projectile penetration and extreme pressures. Behavior of rocks under these conditions cannot be predicted using common macroscopic analyses at normal conditions. Nanostructure of the rock governs the behavior of rock under such situations. Hence, there is a need to study these materials using micro molecular mechanics.

There is also a theory that failure in a rock mass is governed by the formation and propagation of microscopic cracks. The development of these can be observed and studied using the nanoscale analyses. A new science is emerging which deals with manipulating the nanostructure of materials. It may be possible in near future to improve the properties of materials into more desirable ones, by changing their nanofabric. These prospects make the nanoscopic analyses of rocks very intriguing.

This research aims at developing methods to analyze rocks, clays and other geotechnical materials to study their nanolevel properties. Molecular Dynamics simulation is the most commonly used method in molecular mechanics. A software program TINKER was used for developing the simulation. Using this, MD simulation was performed on a (14,1) carbon nanotube for validation purposes. Later on simulations were performed on rock minerals such as quartz, albite and calcite and clays such as kaolinite and palygorskite. The simulated results are compared with published data on mechanical properties of rock and clay minerals.

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Chapter 1 Introduction

Molecular Dynamics simulation of materials can be very useful in understanding their nanoscale behavior. The study of this is important, as it is very prominent during extreme and unnatural conditions. Furthermore, using this we can delve deeper into the failure mechanism of the materials.

This chapter highlights the motivation and objectives behind this research. A brief introduction to the methods used is also given.

1.1 Motivation

Predicting physical properties of rock and clay minerals has always been one of the major geotechnical tasks. This is needed for a wide variety of civil engineering projects. There are two methods to achieve this, experimentation and modeling. Experimentation technique involves performing various standard tests over recovered rock samples and recording the data. Once sufficient amount of tests have been performed, one can statistically determine the physical parameters like compressive strength or modulus of elasticity. Once average rock strength is known, we extrapolate it, approximating the real conditions into simpler ones, and design the problem. But there are certain complex situations where simple approximation does not work. Here, a realistic modeling of the problem is needed for getting accurate results. Most of the study in this regard has involved macroscopic analysis till now.

Modeling techniques like Finite Element Method (FEM) are used to perform these macroscopic analyses. But eventually, even these analyses depend wholly on the experimental results for physical properties. Hence, this kind of analyses is very much reliable under normal conditions that involve no complexities other than non-uniform geometry or loading. But it has serious drawbacks in predicting extreme conditions such as an explosion in rock mass, a projectile penetrating a rock mass or a rock under extreme heat or pressure. Behavior of a rock under such unnatural conditions cannot be

extrapolated from these analytical methods using experimental properties. This will involve performing actual physical experiments under such conditions, which is mostly not feasible. For obtaining the properties, it is required for the rock being analyzed to be broken down to microscopic level, whereby properties of rocks can be calculated under any conditions. Such conditions are very likely to exist in reality. Storage of high temperature, radioactive nuclear wastes in a rock cavity for permanent disposal, presents such an interesting case. Behavior of rocks under high velocity impact is another phenomenon needing such analyses. Other mechanical behaviors like creep, friction, grain crushing, thermal effects and chemical effects can be better understood using nanomechanics.

Study of microstructure of materials such as rocks and clays presents another interesting possibility. Properties of such materials can be drastically changed if we are able to change the microstructure of these materials. This can be done by mixing it with another microstructure or altering the existing structure. This can be conceptualized somewhat similar to genetic engineering of biological sciences. As researchers have achieved new biological structures by engineering modified ones, a similar possibility exists here. Many such attempts have been made, and a variety of man-made materials have already been synthesized. The most fascinating one among them is the Carbon Nano Tube (CNT). This material is known to be the strongest man-made material till now, and is considered to be nearly unbreakable.

Moreover, there are issues relating to the failure prediction of the rocks. It has been proven that in all solids that crack to failure, it is the micro cracks that join together to form the failure crack. This macro cracking of the solids depends on the development of micro-cracks. Hence, failure mechanism of rocks can be really understood using a microscopic analysis. Hence, study of rocks using microscopic analysis methods is an emerging need.

Apart from the analysis of rocks using nano-level analyses, other geotechnical materials can be studied using this methodology. Clay minerals are one of the most important geotechnical materials. These materials have very interesting micro level properties. Most studies on these have been on the bulk volume. Behavior of a single clay lamella under pressure still remains fairly unexplored area in research. These have already been applied extensively in fields such as electrical, electronics and polymer sciences to astonishing and pioneering uses. Studies on these, is bound to provide some invaluable information.

1.2 Objectives

This research aims at developing the nanoscale modeling techniques to be used for modeling the response of soil and rock minerals under extreme conditions. The specific objectives of this research project are:

1. To develop a computative model to estimate rock and clay behavior at nanolevel.

Molecular mechanics methods will be developed to study rock and clay minerals at nanolevel. This will involve choosing the best available methodology, which will closely resemble the behavior of actual atomic or molecular structures and will also be simple so as to model without major difficulties. There are various methods available, Molecular Dynamics simulation being one of the most popular and accurate among them. This research will aim at developing capabilities in this method by analyzing various rock minerals, which are already simulated. After validating the methodology, more complex simulations may be proceeded with.

2. To apply Molecular Dynamics to study rock and clay minerals at extreme conditions as described above, particularly high pressures which are difficult to simulate in real life.

Molecular Dynamics can be very useful in simulating rock behavior under conditions that are not usual. This research project aims at developing molecular modeling and

simulation techniques that will help solve these issues. Micro scale properties of many minerals are still not well researched. This approach will provide an opportunity to work in this aspect. For example, palygorskite, which is commonly known as attapulgite, is one of the most peculiar naturally occurring clay minerals. The microstructure of this mineral resembles very closely, the carbon nanotubes. This can be a mineral that is one of the first known naturally occurring nanotubes in nature. The fascinating physical characteristics of carbon nanotubes are well known, hence, study of palygorskite in the same context present very interesting possibilities.

The research then will proceed towards performing some sample simulations for comparison purposes. Later on, we will move on to simulate rock and clay minerals.

1.3 Organization of Thesis

We begin by describing the theory behind Molecular Dynamics (MD) simulation. This involves the explanation of the energy minimization scheme and the algorithms applied for the calculations of molecular trajectory. Various models are also described in this section. Once the theory is clear, we move on to brief discussions on already performed Molecular Dynamics simulations on granitic rocks (quartz, albite and muscovite). Then we proceed to the description of simulations of calcite melts and montmorillonite clay lamella.

Chapter 3 deals with the description of a software program called TINKER. This is the software that was used to perform MD simulations. All the potential functions, algorithms, input and output files and modeling commands of the software are described in detail here.

Chapter 5 deals with the description of the problem. Chapter 6 mentions the results of all the MD simulations performed in our research project. These are compared with existing literature and known facts. Finally, in Chapter 7 a discussion is done regarding the results and few recommendations are made. The report is then concluded with an appendix

listing various input/output files of the simulations performed and the references are in the bibliography section.

Chapter 2 Background Theory

Berni Alder and Tom Wainwright at Lawrence Livermore National Laboratory performed the earliest molecular mechanics calculations in the 1950s. They analyzed 30 to 108 molecules, which took them 10-30 hours on the fastest computer of that time. Since then, computer power has grown manifolds, and it is thus possible to simulate millions of particles. Also, the science of molecular mechanics underwent many improvements. This chapter presents the theory behind these methods.

2.1 Introduction to Molecular Dynamics Simulation

2.1.1 Introduction

Molecular Dynamics is defined as the study of the molecular and atomic motions, obtained from the simulation of various physical, chemical and biological phenomena. Simulations are done on a theoretical system, where the molecular and atomic trajectories are studied to understand the processes affected by molecular interactions. The prediction of particle trajectory is done using classical Newtonian mechanics.

The applications of Molecular Dynamics are now not limited to any particular field. With researchers going at the elemental level of problems in every discipline, Molecular Dynamics has applications in virtually every field. In chemical and biological sciences, this analysis helps us to understand various phenomena, by looking at the atomic behavior at nanoscale level. Many chemical reactions and biological phenomena were better understood this way. In material sciences, this has huge applications. Newly synthesized materials are first tested using computer simulations and then manufactured. Behavior of materials under extreme environments is possible using Molecular Dynamics, as we can create such conditions on computer easily, as compared to actual testing. Such analyses also give us better understanding of mechanical, thermal and electrical properties of many materials.

Use of computers is essential for Molecular Dynamics simulations. This is because even for a system containing a few hundred particles, it is very difficult to keep track of each particle, manually. Thus, a program has to be developed with the help of a computer, which calculates and stores data for each particle at each time step. Also, visualizing the interacting particles is very important part of understanding different processes. Visualizing the processes helps us to actually see the behavior at nanoscale level, which is otherwise invisible to naked eye. This visualization can only be achieved by a computer, which shows trajectories of several thousands of atoms interacting with each other.

In this chapter, the theory behind Molecular mechanics will be described. Here, various models in this theory will be discussed. These models are different kinds of methods that are used to simulate system of interacting particles. Each method has its own assumptions according to which the particles are assumed to interact with each other. All of them follow one common principle, that is, the potential energy is minimized as time progresses. Steady state exists when the potential energy of the system is at its minimum.

2.1.2 Models

When we chose a model for a system, we specify the nature of interaction among the particles according to that model. Model type depends on the system, and the particles we are simulating. A model, which can depict the actual particle interaction the closest, is chosen for simulation. It is always assumed that the forces acting between the particles are conservative. This means that energy is conserved and the total force acting on a particle due to other particles is the sum of the forces between pair of particles. Hence, force acting on particle i is:

$$f_i = \sum_{j=1, j \neq i}^{n} f_{i,j} \tag{2.1}$$

where f_i is the force acting on particle i and $f_{i,j}$ is the force acting on particle i due to all other particles.

Hence, the force acting on the particle due to other particles can be seen as the interaction of particles among each other. So, the model can be described in terms of these forces of interactions. But as the forces vary according to particle properties, we need to define the model in terms of a quantity that is constant for a specific model. We are aware of a relationship between force and potential energy in a conservative system:

$$f(r) = -\nabla \phi(r) \qquad (2.2)$$

where φ is the potential energy.

As potential energy can be constant for the system for a model, it is preferred to define a model in terms of its potential energy function. Also, it is more convenient as it is a scalar quantity. At the point of equilibrium, the potential energy of a system is the minimum.

In this chapter, three of the most common models used in Molecular Dynamics are described. These are, the Hooke's Law model (HL), the Lennard-Jones model (LJ) and the hard sphere model (HS). These are the simplest and earliest of models to be used for simulation purposes. There are many more complex models that have been developed, based on these early versions. Among the three, Lennard-Jones model depicts the particle interaction at the closest distance between particles. The particles repel when they get closer to each other and attract when at a large distance. This model is the most difficult to simulate and requires a lot of computational effort. The Hooke's Law model emulates spring connections, and has more of particle attraction part. The Hard Sphere model assumes the particles to be like billiard balls, hitting and interacting with each other.

2.1.2.1 Hooke's Law Model

Hooke's Law, assumes the particles to be connected to each other with springs. Thus, the potential energy of a particle is proportional to the square of the displacement from its

equilibrium position, according to Hooke's Law. The equation of potential energy and force in this model are:

For a 1-D model, for one particle:

$$\phi(x) = \frac{k}{2}(x - x_{eq})^2 + \phi_{min} \qquad (2.3)$$

$$\text{and} \quad f(x) = -k(x - x_{eq}) \qquad (2.4)$$

where k is a constant corresponding to the spring constant according to Hooke's Law, x_{eq} is the equilibrium position of a particle and ϕ_{min} is a constant denoting the minimum potential energy.

Also, according to equation 2.2,

$$f(x) = -\frac{d\phi(x)}{dx} \qquad (2.5)$$

where $f(x)$ is the force acting on a particle.

This model is illustrated in Fig. 2.1 in terms of potential energy vs. distance between particles and in Fig. 2.2 in terms of interparticle force vs. distance between particles.
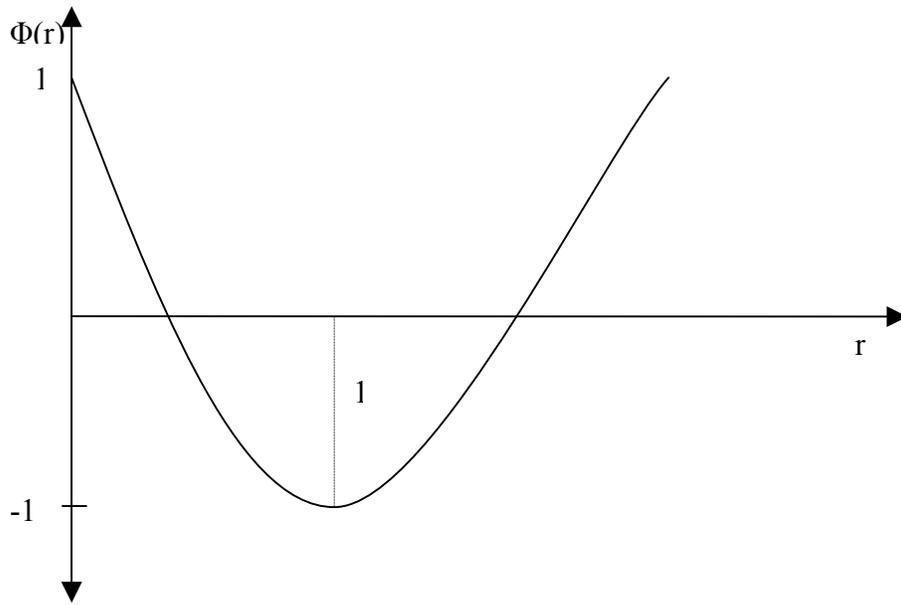
Figure 2.1 Potential energy of a particle in the Hooke's Law (HL) model
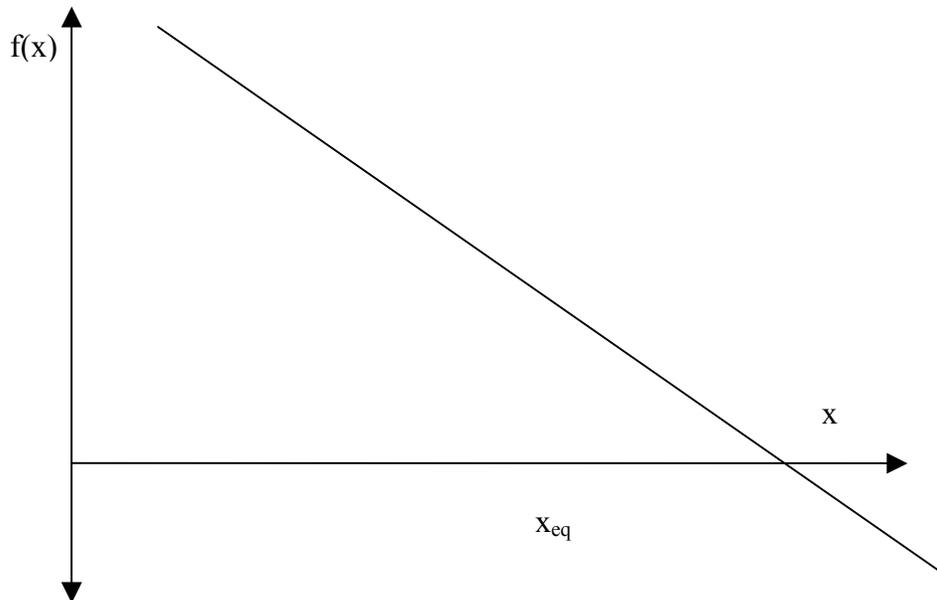
Figure 2.2 Force on a particle in the Hooke's Law (HL) model

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The generalized equation for a 3 dimensional Hooke's Law model can be depicted as:

$$\phi(r) = \frac{k}{2}\left\|r - r_{eq}\right\|^2 + \phi_{min} \tag{2.6}$$

where r is the position of the particle and, r_{eq} is the equilibrium position of a particle and φ_{min} is a constant denoting the minimum potential energy.

2.1.2.2 Lennard-Jones model

This model defines the system such as the particles have high repulsion, when too close to each other, and high attraction, when far away from each other. This model closely depicts the inter-particulate interaction of any material. For a 3 dimensional model, the Lennard Jones potential function for a pair of particles can be defined as:

$$\phi(r_1, r_2) = \left(\frac{1}{\left\|r_1 - r_2\right\|^{12}} - \frac{2}{\left\|r_1 - r_2\right\|^6} \right) \tag{2.7}$$

where r_1 and r_2 are the positions of the two particles.

There can be a multiplier term in this potential function, depending upon the material being simulated. In the above equation, units have been chosen such that the minimum of potential energy occurs at $\left\|r_1 - r_2\right\| = 1$, and the value of minimum equal to -1. The plot showing the variation of this potential with the distance is shown in Fig.2.3.
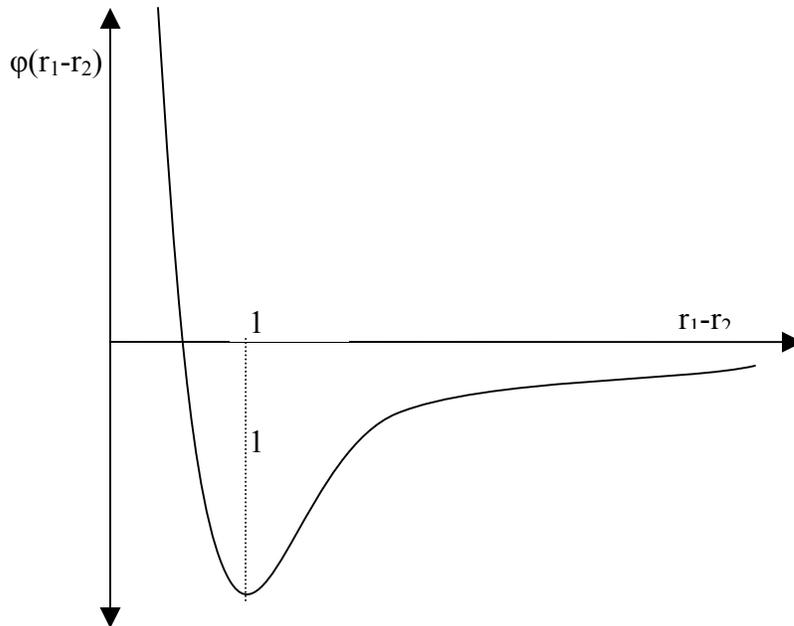
Figure 2.3 Potential Energy vs distance for LJ potential

There are a few other forms of this potential. One of the commonly used ones is:

$$\phi(r)=4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12}-\left(\frac{\sigma}{r}\right)^{6}\right]$$ (2.8)

where ε is in the units of energy, describing the strength of the interaction or the depth of the potential "well." This "well" is the depression in the curve showing variation of energy versus distance in Figure 2.3. σ describes the shape of the potential. It basically defines where the potential is zero. It is defined in the units of length.

In both forms, the positive part of the potential function controls the repulsion between particles. When the atoms are close, the value of r is lower, which makes the positive part greater. A positive potential means repulsion. Hence, when particles are close, repulsive forces will be greater than attractive. When the distance is large, the positive part

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becomes smaller compared to the negative term. This makes the potential negative and the force positive.

2.1.2.3 Hard Sphere Model

This model assumes that the particles behave as a collection of hard, perfectly elastic balls. The interaction occurs only when these particles collide with each other. These balls behave as billiard balls and collide with each other, exchange momentum and continue.

The potential energy for a pair of particles in a 3 dimensional Hard Sphere (HS) model can be described as:

$$\phi(r_1, r_2) = \begin{cases} 0, \|r_1 - r_2\| > \sigma \\ \infty, \|r_1 - r_2\| \leq \sigma \end{cases} \qquad (2.9)$$

where r_1 and r_2 are the positions of the two particles and,

σ is the distance between the centers of the two particles when they are in contact. It can also be visualized as the sum of the two radii of the two interacting particles.

According to the above equation, there is no potential acting whatsoever, when the particles are not in contact. At these times, the forces are zero too. As soon as they come in contact there is an infinite repulsive potential acting that causes them to move away from each other instantly. Hence, forces act on the two particles, only at that instant when they are at a distance σ apart from each other.

This model can be viewed as an approximation of Lennard-Jones model, only with lower attractive forces. In LJ model, particles do not move with high velocities when they are moving away from each other, this is because the attractive force is present, whereas in HS model, there is no force present at that point. Also, in LJ model, the particles never

actually collide, i.e., they never touch each other, but the repulsive forces are so high when the particles are close, that the behavior is very similar to a collision.

2.1.3 Molecular Dynamics calculations

Molecular Dynamics simulation follows the laws of classical Newtonian mechanics.

According to Newton's second law:

$$ma = f \tag{2.10}$$

where m is the mass of the body on which a force f is acting and,
a is the acceleration of the body due to the force.

Using this law, and knowing the initial position and velocity of the body, we can predict its future position and velocity, after any time t.

Force on each particle can be calculated from the relation between force and potential energy as shown in equation (2.5). Once, the forces are known, Newton's second law can be used to get acceleration for each particle. Now, if the initial velocities and positions of the particles are known, final positions and velocities can be predicted. This can be done for various time steps such that we have enough points to get a well-defined trajectory for each particle. The above explanation can be depicted in mathematical form as follows:

$$f = ma \tag{2.11}$$

$$\ddot{r} = \frac{d^2 r}{dt^2} \tag{2.12}$$

$$\dot{r} = \frac{dr}{dt} \qquad\qquad (2.13)$$

The position at any time t can be calculated from the position at a previous time step $r(0)$ and velocity $\dot{r}(0)$.

$$r(t) = r(0) + \dot{r}(0)\{t - t(0)\} \qquad\qquad (2.14)$$

Computation in Molecular Dynamics involves calculation of force on each particle according to its position, and then prediction of the positions of particles after the next time step. The equations of motions allow us to use numerical methods for these calculations.

2.1.4 Algorithms

The numerical solutions follow the procedure of calculating the values at every time step, given initial conditions. These values are mostly positions and velocities of particles. For each time step, the values are stored and other data such as momentum and energy can be calculated later on. These parameters represent the state of the system at a particular time step.

The procedure of a typical numerical algorithm can be described below. First, a system is chosen with given initial conditions, usually positions and velocities of the particles. A time step interval is chosen and the parameters are calculated at a later time step. This process is repeated till the total time interval is equal to the simulation time. The time step interval between each step has to be chosen according to the algorithm being used. If the algorithm is primitive and simple, a smaller time interval has to be chosen to reduce the error. This causes the computation time to increase considerably. Higher time step may be chosen for a sophisticated algorithm, which has lower error per time step. But then, in this case, the computation time per time step increases. Hence, the algorithm to be chosen really depends on the problem. If there is a need of greater accuracy, we will

have to sacrifice computation time for the sake of accuracy. Otherwise, computation can be really fast for low accuracy algorithms. Here we describe three of the simpler algorithms, which are the most commonly used, and are the basis of various other algorithms.

2.1.4.1 Euler's method

Here we describe Euler's algorithm in brief.

We know that

$$f = m\ddot{r}, \tag{2.15}$$

$$\ddot{r} = \frac{d^2 r}{dt^2} \tag{2.16}$$

$$\dot{r} = \frac{dr}{dt} = v \tag{2.17}$$

Position and velocity after time step h can be given as below:

$$r(t+h) = r(t) + hv(t), \tag{2.18}$$

$$v(t+h) = v(t) + \frac{h}{m} f(x(t)) \tag{2.19}$$

where $r(t)$ and $v(t)$ is the particle position and velocity at time t, $f(x(t))$ is the force acting on the particle at time t and m is the mass of the particle. A pseudo-code for the above calculation is shown below:

for i=1 to nstep

```
        x(t+1) = x(t) + h*u(t)
        u(t+1) = u(t) + (h/m)*f(x(t))
end
```

This method has an error in the computed solution of O(*h*), where *h* is the chosen time step interval. This algorithm is virtually simple that's why the error in the solution is a little higher. The next method we are going to discuss is still relatively simple but still has lower error.

2.1.4.2 Verlet's method

This algorithm is the most commonly used one in Molecular Dynamics. It is known as Stormer's method in mathematical community. The error in this method is of O(h^2), and thus, the method is more accurate than the previous one.

In this method, the second derivative is approximated with a central difference,

$$\ddot{r} \approx \frac{r(t+h) - 2r(t) + r(t-h)}{h^2}$$

(2.20)

Using the equation (2.15) we can approximate the above equation as,

$$r(t+h) = 2r(t) - r(t-h) + h^2 f(x(t))$$

(2.21)

The pseudo code for the above calculation may be written as,


```
for i = 1 to nsteps
        r(t+1) = 2*r(t) – r(t-1) +(h^2)*f(r(t))
end
```

The above equation forms the basis of all calculations for this method. But, as we can see, evaluation of any term needs the values of last two time steps. So, there is a problem for evaluating the term after the first time step. Here, we use Taylor's series expansion,

$$r(h) = r(0) + h\,\dot{r}\,(0) + \frac{h^2}{2} f(x(0)) \qquad (2.22)$$

The pseudo code for this is:

for i = 1 to nsteps
     dr(t) = dr(t-h) + h*f(r(t))
     r(t+h) = r(t) +h*dr(t)
end

The velocity can be calculated as shown below,

$$\dot{r} = \frac{r(t+h) - r(t-h)}{2h} \qquad (2.23)$$

The difference in the error between Euler's and Verlet's algorithm is due to the h^2 term in latter. It causes the error in the solution to be of $O(h^2)$.

2.1.4.3 Beeman's method

Beeman algorithm is one of the many algorithms similar to Verlet algorithm. This is one of the algorithms available in the software TINKER, which is described in Chapter 3.

This method uses following equations for position and velocity calculations,

$$r(t+h) = r(t) + \dot{r}(t)h + \frac{2}{3}\ddot{r}(t)h^2 - \frac{1}{6}\ddot{r}(t-h)h^2 \qquad (2.24)$$

$$\dot{r}(t+h) = \dot{r}(t) + \ddot{r}(t)h + \frac{1}{3}\dddot{r}(t)h + \frac{5}{6}\dddot{r}(t)h - \frac{1}{6}\dddot{r}(t-h)h \qquad (2.25)$$

This algorithm provides a more accurate expression for the velocities and better energy conservation, as compared to the Verlet algorithm. The error in the calculation of particle position in this method is $O(h^4)$ and for velocity calculations, it is $O(h^3)$. The disadvantage of this method is that the complex expression increases the computation time greatly.

2.1.5 Periodic Boundary Conditions

It is necessary here to give a brief explanation of periodic boundary conditions, what they are and why they are needed. Whenever we simulate a group of particles, we are assuming that they are just a few particles that represent the whole material. But that is not true. In reality, if we are simulating a few particles inside a material, it means that those particles are surrounded by many more of the same, in all directions. Thus the particles we are simulating are in fact interacting with the surrounding atoms and the surrounding atoms with their own surrounding atoms and so on. The interaction is assumed to be limited to only one surrounding layer because of the short range of interatomic potentials. If we do not consider this effect, then we are inducing a large surface effect on our simulation, meaning, it will seem as if the particles are on the surface of the material.

To eliminate or reduce this effect, we have to devise a technique to incorporate the surrounding particle effect. This can be done by assuming a fixed layer of surrounding atoms, encompassing our system. It is assumed here that those fixed atoms do not interact in turn with their own surrounding atoms, thereby making them fixed. This kind of approach is known as *fixed boundary condition* approach. As we can see, this method makes a huge approximation about atoms being fixed. This approximation still causes a significant error to remain in the solution.

There is another method that is more powerful and more accurate than the above mentioned. It is *periodic boundary condition* (PBC) approach. In this method, we assume that the original cell containing the particles we are simulating is surrounded on all sides by cells that are replicas of the original cell. Those surrounding cells are in turn surrounded by the same replicas, and so on. This makes the system virtually infinite without making any significantly wrong approximations.
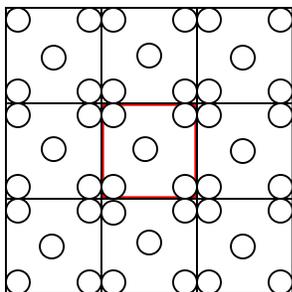
Figure 2.4 Original periodic cell surrounded by its replicas in a Periodic Boundary Condition case

In TINKER, such *periodic boundary condition* may be produced by connecting the topmost atom of the periodic cell to the bottom most one, left most to the right most and so on. This way, we can simulate behavior of a chosen number of particles in a cell, surrounded by infinite number of similar particles.

2.1.6 Calculation and analyses of results

NPT (constant number of particles, pressure, and temperature) and NVT (constant number of particles, volume, and temperature) ensembles are used for analyses purposes. In NPT ensemble calculations, a constant external pressure is applied and molecular dynamics calculation is performed. The strain is measured as an ensemble average after steady state is achieved, and we get the stress from the pressure applied. Thus, we get the stress-strain curves, and the elastic properties.

In the NVT ensemble a known amount of strain is applied and the stress undergone by the structure is measured. Stress can thus be calculated from force, and we get the stress-strain curve hence.

For calculation of pressure using ensemble average, the virial theorem is used,

$$P = \frac{Nk_B T}{V} - \frac{1}{3V}\left\langle \sum\sum_{i<j}(-F_{ij}).r_{ij} \right\rangle \tag{2.32}$$

Where N is the no. of particles in the system, V is the system volume, k_B is the Boltzmann constant and F_{ij} is the force between particles i and j.

The atomic level stress tensor is defined as:

$$\sigma_{\alpha\beta} = \frac{1}{V}(Nk_B T_{\alpha\beta} - \left\langle \sum\sum_{i<j}(-F_{ij\alpha}).r_{ij\beta} \right\rangle) \tag{2.33}$$

where $T_{\alpha\beta}$ is the temperature tensor defined as,

$$T_{\alpha\beta} = \frac{\sum_i m_i v_{i\alpha} v_{i\beta}}{Nk_B} \tag{2.34}$$

Once we have the stress tensor and the strain tensor for a material, elastic coefficients for that material can be calculated using Hooke's law. According to the Hooke's law, stress and strain are proportional for an elastic material.

Chapter 3 Literature Review

In this chapter, Molecular Dynamics simulation studies will be discussed over various materials. We will start with the most commonly simulated material, Carbon Nanotube, and then proceed to other rock and clay minerals. Methodology followed and results obtained from these studies are also discussed for each material. These studies form the guidelines for our methodology and the comparison for our results.

3.1 Carbon Nanotube Simulation

3.1.1 Carbon Nanotubes:Introduction

Carbon Nanotubes (CNTs), as the name suggests, are long tubes made up of just carbon atoms. They do not occur naturally, and were first discovered by Ijima in 1991. They are the strongest man-made material ever. Although it has only been a decade since their discovery, still they enjoy a lot of attention from researchers. They have ultra high elastic moduli, strength and low mass density. Due to their structure and form, they seem to tolerate extreme distortion without fracture. This opens a whole new window for possible structures that were impossible due to material strength restriction earlier. Apart from their use in material sciences, they have large applications in other fields. For example they demonstrate unique coupling between their electrical property and mechanical deformations. This gives them the potential to be used as conductors or transistors in electronical devices, as they are 500 times smaller than the current devices. In this chapter previous researches for calculating elastic properties of carbon nanotubes will be explained. Many references will be made to the journal papers by Zhang et al (2002) and Greibel et al (2004).

Carbon nanotubes are cylinders of graphine with diameters from 1 to 2 nm. They have single or multiple layers of carbon, in the direction of thickness of the tube. This makes

them either SWNTs (Single Walled carbon Nano Tubes) or MWNTs (Multiple Walled carbon Nano Tubes). Carbon nanotubes are fullerene-related structures, which may or may not be closed at either end by hemispherical graphene. They are composed entirely of sp^2 bonds, like graphite, which is stronger than the sp^3 bonds of diamond.

The structure of SWNTs may be conceptualized by wrapping a one-atom thick layer of graphite sheet (called graphene) into a seamless cylinder. The sheet is arranged in a hexagonal network of carbon atoms, known as honeycomb structure. The way this sheet is wrapped is given by two numbers, (n,m), which constitute the chiral vector of the nanotube. The integers n and m denote the number of unit vectors along two directions in the honeycomb lattice structure of graphite. If m is zero, the nanotube is "zigzag" and if n is equal to m, the nanotubes are called "armchair." If neither case exists, they are just called "chiral".

3.1.2 Potentials

As mentioned before, there is sp^2 bond present between the carbon atoms. This happens when one of the electrons in the s orbital of carbon is transferred to p orbital. For bonding, one electron of s orbital and two electrons of p orbitals are used. This type of carbon-carbon bonding is usually represented by Brenner's potential. This term, obviously, accounts for the short distance carbon − carbon atom interactions. For the long-range interactions, van der Waal's interaction between atoms is considered. This is the most commonly used model for simulating carbon nanotubes and has been fairly accurate in predicting the elastic parameters. This potential can be shown as below:

The short-range Brenner potential is:

$$V(r_{ij}) = V_R(r_{ij}) - B_{ij}V_A(r_{ij}) \tag{3.1}$$

where r_{ij} is the distance between atoms i and j , V_R is the repulsive potential term and V_A is the attractive potential term.

These terms are given by,

$$V_R = \frac{D^{(e)}}{S-1} e^{-\sqrt{2S}\beta(r-R^{(e)})} f_c(r) \tag{3.2}$$

$$V_A = \frac{D^{(e)}S}{S-1} e^{-\sqrt{2S}\beta(r-R^{(e)})} f_c(r) \tag{3.3}$$

Parameters $D^{(e)}$, S, β and $R^{(e)}$ are material constants for carbon nanotubes which are derived from known properties of graphite and diamond. The function $f_c(r)$ is given as:

$$f_c(r) = \begin{cases} 1 \rightarrow r < R^{(1)} \\ \frac{1}{2}\{1+\cos[\frac{\Pi(r-R^{(1)})}{R^{(2)}-R^{(1)}}]\} \rightarrow R^{(1)} < r < R^{(2)} \\ 0 \rightarrow r > R^{(2)} \end{cases} \tag{3.4}$$

This function is just a smooth cutoff function with $R^{(1)} = 0.17$ nm and $R^{(2)} = 0.2$ nm. The other term in the expression (3.1) are :

$$Bij = [1+ \sum_{k(\neq i,j)} G(\theta_{ijk}) f_c(r_{ijk})] \tag{3.5}$$

where r_{ijk} is the distance between between atoms k and i. And f_c is the cutoff function in (4), θ_{ijk} is the angle between atoms k,j and i. The function G is given by

$$G(\theta) = a_o\left[1+ \frac{c^2_a}{d^2_o} - \frac{c^2_a}{d^2_o + (1+\cos\theta)^2}\right] \tag{3.6}$$

$D^{(e)} = 6.000$ eV, S $= 1.22$, $\beta = 21$ nm^{-1}, $R^{(e)} = 0.1390$ nm, $\delta = 0.50000$, $a_o = 0.00020813$, $c_o = 330$, $d_o = 3.5$. These potentials were taken from Zhang et al (2002).

The Lennard-Jones potential term is added to the above mentioned Brenner's potential to get the full potential function for the simulation. It is of the form

$$\phi(r) = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r}\right)^{12} - \left(\frac{\sigma_{ij}}{r}\right)^{6}\right] \tag{3.7}$$

where ε is in the units of energy, describing the strength of the interaction or the depth of the potential "well." This "well" is the depression in the curve showing variation of energy versus distance in Figure 2.3. Sigma (σ) describes the shape of the potential. It basically defines where the potential is zero. It is defined in the units of length. Following Lennard Jones parameters were used,

Table 3-1 LJ paramters for CNT

	ε_{ij}[eV]	σ_{ij}[A^o]	R_{ij}
C – C	6.2040512e-3	3.9230	10.0

3.1.3 Results from Previous Researches

From the various researches on the above analysis, following range of physical parameters were calculated (Krishnan et al):

Table 3-2 Results

Density (g./c.c.)	E_{SWNT} (TPa)	E_{MWNT} (TPa)	Tensile strength (GPa)
1.3 – 1.4 g./c.c.	1	1.28	30

Modulus of Carbon Nanotubes is known to be around 1 TPa. Hence, we can see that molecular mechanics simulation of carbon nanotubes is a widely used method giving fairly accurate results. Data regarding these analyses is readily available. These reasons make the simulation of carbon nanotubes a testing ground for our techniques.

3.2 Molecular Dynamics Simulations of Granitic Rocks

3.2.1 Introduction

Granitic rocks are composed of discrete elements of rock forming minerals, and thus are non homogenous to their very microstructure. There is a lot of interaction going on at the micro level. Because of this, micro level interactions affect the macro properties of these minerals to a great extent. Hence, the study of micro level interactions is needed in this regard. There are various techniques which can be used for the above mentioned study. We can observe rock samples in 3-D, under different conditions, using a technique known as X-ray computerized tomography. We perform actual relaxation tests that allow us to observe the micro crack development and how they propagate to form macro cracks. But the best method for this is Molecular Dynamics (MD) simulation. This allows us to observe atomic motion in great detail and can be done sitting on a computer. Such analysis can be used to calculate stress-strain properties of various rock forming minerals. Many tests can be performed and behavior can be predicted. It can also be used to predict the thermo elastic properties. This study is presented in Ichikawa et al (2001). These researchers belonged to Nagoya University, Japan, Tokyo Institute of Technology, Japan and Korea Institute of Construction Technology, Republic of Korea.

3.2.2 Methodology

Molecular Dynamics simulation has been used many times to calculate physical properties of materials. For example, physical properties of a Lennard-Jones solid with

fcc crystals was calculated by Quesnel et. al. Mizayaki and Shiozaki calculated elastic constants using NVT ensemble (constant volume, number of particles and temperature) and thermal properties using NPT (constant volume, number of particles and pressure). Similarly, in the above mentioned paper, MD simulations were carried out on granitic rock minerals, under NPT and NVT ensembles to get their stress-strain properties.

For MD simulation of the minerals, each system was chosen having several thousands of atoms inside a basic cell. The atomic structure depended on the periodic lattice structure of the mineral. The trajectories of atoms were calculated according to the potential function governing the interaction between atoms. Once the positions and velocities of particles at each time step are known, elastic properties of the system can be easily calculated. The rock minerals that were simulated were quartz, muscovite and albite.

3.2.3 Potential used

The interatomic potential used in this study is as shown below:

$$U_{ij}(r_{ij}) = \frac{z_i z_j e^2}{r_{ij}} + f_o(b_i + b_j)\exp(\frac{a_i + a_j - r_{ij}}{b_i + b_j}) - \frac{c_i c_j}{r^6_{ij}} + D_{ij}[\exp\{-2\beta_{ij}(r_{ij} - r^*_{ij})\} - 2\exp\{-\beta_{ij}((r_{ij} - r^*_{ij})\}]$$

(3.8)

where r_{ij} is the distance between the atom i and the atom j,

The first term in this potential function is the coulomb's charge interaction term. This term takes into account any charge interactions between two charged atoms.
z_i and z_j are the respective atomic partial charges
The second term in the expression takes into account the van der Waal's potential. The positive term accounts for the repulsive force between atoms when they are close to each other. When they are farther away, the attractive forces come into play, depicted by the negative term. Here,

f_o is the appropriate force unit,

a, *b* and *c* are material constants

The third and the last term here is the Morse bonding potential term. This term accounts for the interatomic interactions due to the covalent bonding between the atoms.
In this term,

D_{ij} denotes the depth of the potential of the Morse term,

β_{ij} denotes the shape of the potential and

r_{ij}^* is the equilibrium distance between atoms for the covalent bonding part.

The initial coordinates of each atom were determined from the theory. The structure was determined using the periodic lattice of the mineral. Following lattice parameters were used for the minerals:

Table 3-3 Lattice parameters for quartz, albite and muscovite

	a(nm)	b(nm)	c(nm)	γ(degrees)
quartz	0.4913	0.4913	0.5405	120.00
albite	0.8152	1.2784	0.7165	87.74
muscovite	0.5200	0.9021	2.0070	95.71

The basic cell for MD simulation consisted of 100 lattice unit cells (5*a* X 5*b* X 4*c*, 900 atoms) for quartz (SiO_2, triagonal), 18 unit cells (3*a* X 2*b* X 3*c*, 936 atoms) for albite ($NaAlSi_3O_8$, triclinic) and 18 unit cells (6*a* X 3*b* X 1*c*, 1512 atoms) for muscovite ($KAl_2(Si_3Al)O_{10}(OH)_2$, monoclinic, respectively.

The potential parameters used for MD simulations, for the minerals are given below:

Table 3-4 Potential parameters for quartz and albite

	w^a	z	a	b	c
O	16.00	-1.2	0.1926	0.0160	0.0409
Si	28.09	2.4	0.0945	0.0090	0.0000

Morse	D(KJ/mol)	β(1/nm)	r^*(nm)
Si-O	310	20.00	0.151

	w^a	z	a	b	c
O	16.00	-1.3025	0.1907	0.0150	0.0450
Si	28.09	2.4000	0.0890	0.0080	0.0000
K	39.10	1.0000	0.1573	0.0120	0.0327
H	1.01	0.3400	0.0053	0.0044	0.0000

Morse Term	D(KJ/mol)	β(1/nm)	r^*(nm)
Si-O	310	20.00	0.151
Al-O	147	20.00	0.164
H-O	314	27.6	0.082

3.2.4 Discussion of Results

First, MD calculation was done for first 20,000 time steps under 300K temperature and 0 GPa pressure, to determine the steady state configuration of each structure. For the next 5000 steps, initial relaxation is carried out for each steady state. Then the next 20,000 steps are used for calculations under different conditions, and parameters are calculated as ensemble averages.

Using the MD simulations under NPT and NVT ensembles, stress-strain properties of the above mentioned rock minerals were calculated and compared with actual tests. In the

NPT ensemble, constant pressure was applied on the system and resulting strains were measured. On the other hand, in an NVT ensemble, strains were applied to the system by changing its axes lengths or lattice angles, and the energy difference was measured, and thus force needed to bring such change was calculated. The stress-strain curves for the simulations can be seen in the referenced journal paper.

Granitic Rock	Elasticity modulus calculated
Quartz	$E = 120$ GPa
Albite	$E = 175$ GPa

Comparing the elastic constants got from the above curves with those got by experiments; it was observed that they are in good agreement. This comparison can be also seen in the referenced paper.

MD calculations done for these analyses were computationally very expensive and time consuming. For these calculations, a Pentium II processor, 350 MHz with 128 MB RAM was used. It took 420 minutes for calculations for quartz, 1048 minutes for muscovite and 386 minutes for albite, to calculate 20,000 time steps.

This study forms the basis of this research project. There can be many more rock minerals that can be analyzed using the given approach. This project aims at analyzing various such minerals for the objectives as described in Chapter 4. MD simulation can be very helpful in doing such analyses. The aim in our study is to develop capabilities to perform MD simulations for various rock and clay minerals, which are generally used in the field of Geotechnical Engineering. Such analyses help us to delve into the nanostructure of many materials, which if modified, can significantly alter the physical properties. Such an event may revolutionize the engineering fields involving materials and their physical properties.

3.3 Molecular Dynamics Simulation of Clays

3.3.1 Introduction

Molecular Dynamics simulations have been performed previously for solving mechanical and thermal properties of clays. There has been a lot of research on the properties of clays, but not enough on the properties of a single clay lamella, or a single layer of clay. These have specific applications in manufacturing of a variety of polymer-clay nanocomposites, which have interesting mechanical, thermal and electrical properties. They have special applications in various ongoing researches. For this analysis of a nanoscale structure, Molecular Dynamics simulation is a very good approach for analysis. There has been some work done already in this area. For example, Sato et. al. performed Molecular Dynamics simulation of a single layer of beidellite under compression. The results showed that clay sheets might bend under compressive strains upto 40% before failure, with stresses upto 0.7 GPa. But, the elastic constants were not reported. In this chapter, we will look into a journal paper by Manevitch et al (2004) which describes MD simulation performed on a single lamella of montmorillonite (MMT) clay, to evaluate its elastic coefficients.

3.3.2 Methodology

The model simulated here was a single clay sheet of MMT, which is a clay lamella made of one crystallographic unit cell in the thickness direction. Montmorillonite has the formula $(Na,Ca)_{0.33}(Al_{2-y},Mg_y)Si_4O_{10}(OH)_2.nH_2O$. The unit cell parameters are as follows:

$a = 0.53$ nm $b = 0.92$ nm $\beta = 97^o$ and the value of c varies for clays a lot. The structure was monoclinic. A 288-atom model was chosen for the analysis.

3.3.3 Potential Function

The potential function, along with the parameters used for the simulation, is listed below in Table 1. This potential function includes harmonic bond-stretching and bond-angle-bending terms, a Lennard-Jones term for non-bonded interactions and a Coulombic potential term to account for interaction between charged atoms.

Table 3-5 Potential function and force field parameters used for MD simulation of MMT lamella

	l_o, θ_o	k_b, k_θ	mass(g/mol)	ε	σ	z
Si-O[b,d]	0.1665	39 280	na	0.0952	0.3822	na
Al-O[b,d]	0.1775	39 280	na	1.436	0.3072	na
Si-Si[d]	Na	Na	28.086	0.040	0.4550	+4
O-O[d]	Na	Na	16.000	0.2280	0.3210	+3
Si-Al[d]	Na	Na	na	0.6016	0.3658	na
Si-O-Si[c]	149.8	31.1	na	Na	na	na
O-Si-O[c]	113.1	42.3	na	Na	na	na
O-Al-O[c]	113.1	42.3	na	Na	na	na
Al-O-Al[c]	149.8	31.1	na	Na	na	na
Si-O-Al[c]	149.8	31.1	na	Na	na	na
Al-Al[d]	Na	Na	26.982	9.043	0.2941	na

Where b denotes bond stretch potential, c denotes angle bending potential and d denotes vander Waals potential. These potentials have the same form as described below:

Bond stretch potential: $E = k_b (l - l_o)^2$

Angle bending potential: $E = k_\theta (\theta - \theta_o)^2$

Van der Waals functions is as defined in Chapter 2. Above parameters are taken from Manevitch et al (2004).

3.3.4 Simulation and Results

For the MD calculations, time step was chosen to be 0.001 ps and the machine used had a Pentium III processor of 1 GHz processor speed. The system was first allowed to stabilize at 300K with zero pressure. Calculations were done for elastic constants of the simulated single MMT lamella. These had no previously calculated or experimentally reported values to compare or validate with. But, these followed the expected trend. The elastic constants of the single lamella were observed to be greater than that known to be for bulk clay. This may be explained due to the presence of a compressible inter-lamellar separation in the bulk calculations. This allows more strain to occur in bulk clays for the same pressure as compared to that for a single lamella, which causes the elastic coefficient to go down for the bulk case. Apart from this, the equilibrium structure of the clay sheet was seen to be in good agreement with the available X-ray diffraction data for MMT clay.

Hence, we see that Molecular Dynamics simulation is helpful in the field of material sciences and geotechnical engineering, for analysis of those structures which are very minute in size and whose experimental analysis is almost impossible in physical reality. This has motivated us to perform MD simulations of a Kaolinite clay lamella, for evaluation of stress-strain properties. This will enable us to enhance as well as validate our MD simulation capabilities, and will also provide valuable insights towards elastic properties of single clay layers.

3.4 Molecular Dynamics Simulation of Calcite

3.4.1 Introduction

Calcite, or calcium carbonate, is one of the most fascinating of minerals. It comprises of about 4% by weight of total minerals occurring on the face of earth. Calcite is present abundantly and in different forms, occurring in different geological conditions. It occurs as igneous, sedimentary as well as metamorphic rocks. It is a major component in the

igneous rock *carbonatite*, forms *limestone* that is a sedimentary rock and is also present in *marble* that is a metamorphic rock. There are around 300 different crystal forms that calcite can take and their combinations make several thousand others. So, calcite is one of the most studied and important minerals in the field of material sciences and geotechnical engineering.

There have been many occasions where calcite has been simulated using Molecular Dynamics for various reasons and objectives. Being, one of the most abundant minerals in geology, it has a large impact in the filed of geological and material sciences. Molecular Dynamics simulation of calcium carbonate melts was performed to better understand the process of metasomatism of the lithospheric mantle as described in Genge et al (1995). Metasomatism is a process by which chemical composition of a rock is changed without the rock being melted. This process occurs naturally, by interaction of the rocks with fluids, which replace one mineral with another. For this study, it was necessary to understand the physical and structural behavior of calcite at mantle pressures and temperatures. Performing actual tests on calite at such high temperatures and pressures is not feasible; hence Molecular Dynamics simulation method was chosen to perform the analysis.

3.4.2 Potential Function used

This study was performed using pairwise interatomic potentials containing only coulombic interactions and short-range Born-type repulsive potentials.

$$\phi_{ij} = \frac{q_i q_j}{4\pi\varepsilon_o r_{ij}} + A_{ij}\exp\left(\frac{-r_{ij}}{B_{ij}}\right) \tag{3.9}$$

where q_i and q_j are the partial atomic charges of atoms i and j,

r_{ij} is the distance between the two atoms,

A_{ij} and B_{ij} are two pairwise iteraction constants, which are given below:

Table 3-6 Potential parameters for calcite potential function

	A_{ij}(eV)	B_{ij}(nm)
O-O	2879.1262	0.0252525
O-C	1.7411309e11	0.0038700
O-Ca	3943.6977	0.0251570
Ca – charge	1.64203e	
O – charge	-0.89429e	
C – charge	1.04085e	

This potential function is not totally realistic as the two-body potential provides only a poor approximation of the covalent, directional bonding of CO_3^{2-} group since they cannot constrain molecular geometry, and hence do not provide realistic molecular vibrations. This potential was taken from Dove et al (1999).

3.4.3 Simulation and Results

Simulations were performed on a system containing 540 atoms (108 formula units of Calcium Carbonate). Normal periodic boundary conditions were adopted. Verlet algorithm was chosen for the molecular dynamics calculations, which is described earlier in this chapter. The simulations were performed at temperatures of 1600-2000°K and 0.01 – 11.5 GPa pressures.

The results obtained from the simulations agree quite well with the expected ones. The paper mentions that molecular dynamics provides a useful approach for the study of their kind. It also suggests that as molecular dynamics simulations have produced physically reasonable estimates of the values they were calculating, they may be treated as individual experiment runs. This is because, these experiments also have inherent various experimental errors.

In this study, we have tried to simulate calcite using molecular dynamics method. The aim was to calculate the stress-strain properties of the mineral. The potential function used was similar to the one used in above mentioned paper, as it yielded fairly accurate results. This simulation will allow us to test our capability of molecular dynamics simulation, as well as give us insights on the micro scale behavior of calcite mineral.

Chapter 4 TINKER: Introduction and modifications

4.1 Introduction

As mentioned before, TINKER was used for performing molecular dynamics calculations in this research project. This is a software package that can perform molecular mechanics computations of various kinds. It was developed by Dr. Jay Ponder, Department of Biochemistry and Molecular Biophysics, Washington University School of Medicine, Missouri. It is an assembly of separate small programs which interact with each other to perform molecular computations. The core TINKER system consists of nearly 135,000 lines of source code, composing 482 files, written in FORTRAN77 with some part in C. The software also has a Graphic User Interphase (GUI), called Force Field Explorer (FFE), which is in Java. This has been developed by Mr. Michael Schneiders, Department of Biochemistry and Molecular Biophysics, Washington University School of Medicine, Missouri. Force Field Explorer also provides basic visualization for various molecules, as well as their simulations. There is a 213 page user's guide provided along with the package.

The functions performed by TINKER can be listed as:

1. Energy minimization of a given structure over Cartesian coordinates, torsional angles or rigid bodies via conjugate gradient, variable metric or truncated Newton method.
2. Molecular dynamics with periodic/non-periodic boundary conditions with control over temperature and pressure.
3. Normal mode vibration analysis.
4. Building protein and nucleic acid structures.
5. Simulated annealing with various cooling protocols.
6. Analysis and breakdown of single point potential energies.
7. Verification of analytical derivatives of standard and user defined potentials.

8. Location of transition state between two minima.

9. Searching of full energy surface via Conformation Scanning method.

10. Performing free energy calculations via free energy perturbation or weighted histogram analysis.

11. Fitting of intermolecular potential parameters to structural and thermodynamic data

12. Performing global optimization via energy surface smoothing.

13. Performing distance geometry analysis using random pairwise metrization

In this research, the second function was used for Molecular Dynamics calculations. Given the potential function, TINKER performed MD calculations as per the principles mentioned in Chapter 1.

The heart of TINKER is a set of 54 callable routines that perform trajectory calculations and energy minimization calculations. This software readily allows the user to make any changes in the source code or to add any other subroutine according to the job. Also, separate programs can be added by the user for user-defined potential functions. A detailed description is provided in user's manual for compiling and linking the modified source code to the executables and GUI respectively.

TINKER can be installed in any machine by downloading a self-extracting kit from the World Wide Web URL http://dasher.wustl.edu/tinker/. Separate packages are available for MS Windows, Linux or Macintosh OS X 10.3. Distributors provide full right to use and modify the software, but not to distribute it further. Much of the software is well tested but many modules are still in the early stages of inception. The software is still unstable in many areas and is very sensitive to small errors. It is certainly not for a person having no background in the field of computational mechanics. Thus, it can be made more user-friendly. This package was developed mainly for biological structures such as proteins and nucleic acids. Hence, performing analyses on structural materials required a lot of software modification and manipulation. These modifications have been described in detail under section 4.7. The adjacent page shows a typical input screen of TINKER.
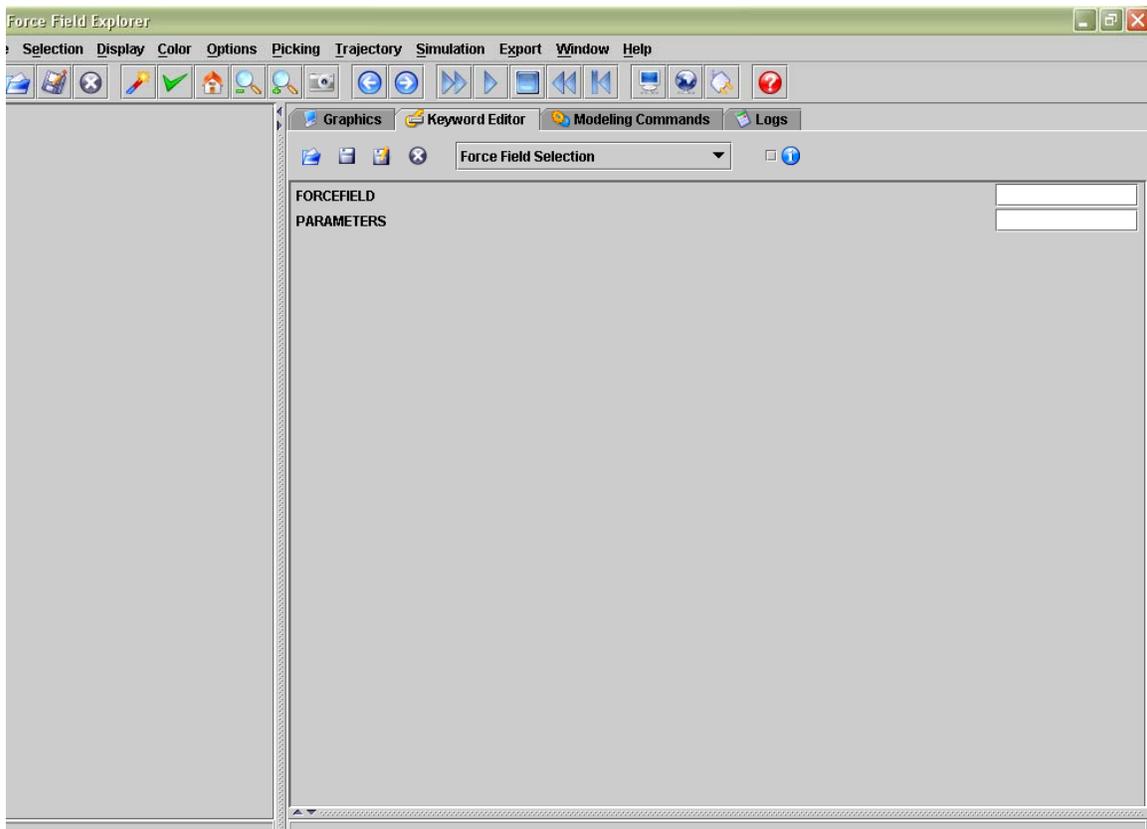
Figure 4.1 A typical TINKER input screen
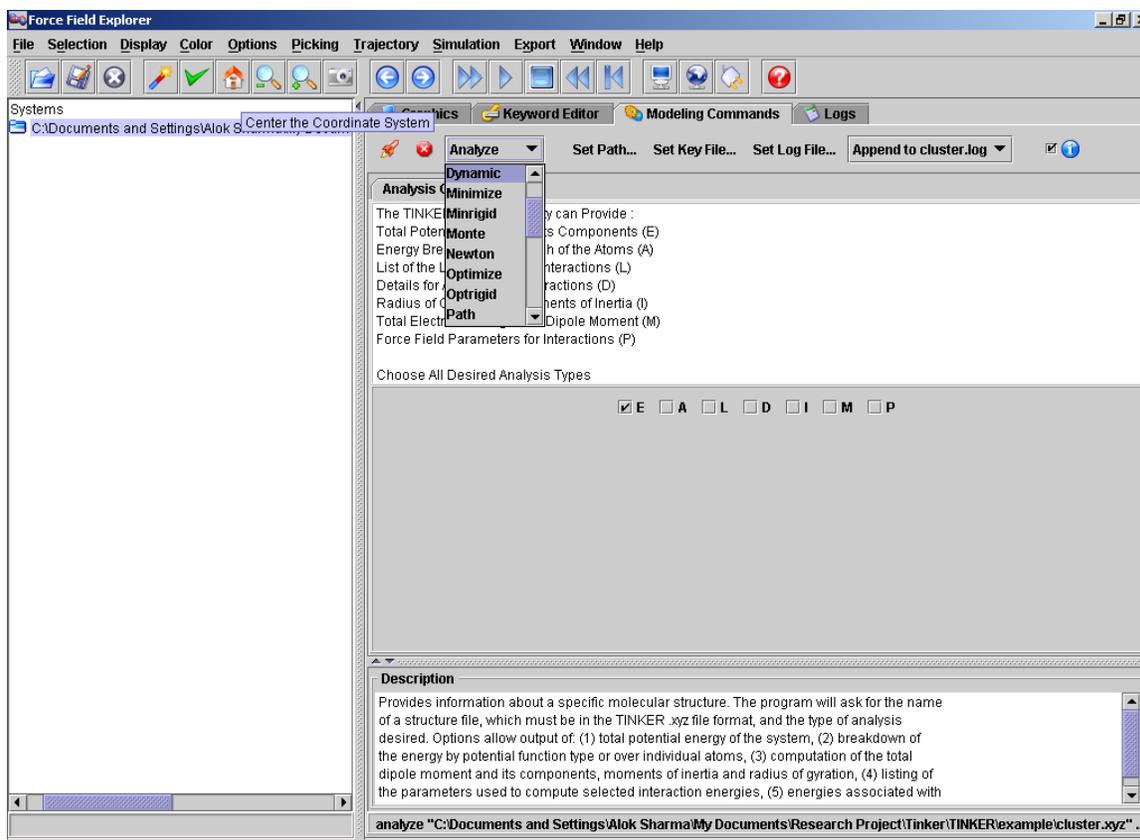
Figure 4.2 Force Field Explorer showing various modeling commands

4.2 Input Files

There are mainly two kinds of files that TINKER needs to perform the analyses. One file has to describe the initial position and bonding of the structure to be simulated, and the second one defines the simulation process. Once this information is input, the temperature and pressure data has to be provided before performing the simulation. The software calculates atomic trajectories and stores them in the output file along with various other variables.

The two input files can be described as follows:

40

1. .XYZ file

This is the input structure file for any molecule to be simulated. It provides initial positions of atoms in the structure in Cartesian coordinates. The first line in this file lists the number of atoms in the structure and name of the structure. Any extra atom description which has the serial number greater than the number provided in the first line is disregarded. From the second line onwards, each atom is describes individually. The serial number is followed by the symbol for the atom, which is followed by the x, y and z coordinates. After that, atom class number is provided. This number describes the type of atom. The same number is related to the atomic properties in the .KEY file. All the numbers that follow the atom class number provide data regarding the atoms to which the atom is connected with. Thus, each line defines one atom each. For each .XYZ file a corresponding .KEY file has to be there to function. Below, a sample .XYZ file is shown, depicting a cluster of Argon atoms.

```
13  Cluster of Argon Atoms
 1 Ar   -2.662398    4.100169    1.166503   175
 2 Ar    0.000000    1.631968    0.965153   175
 3 Ar    2.662397   -0.836234    0.763804   175
 4 Ar    0.917809    5.076113    0.246536   175
 5 Ar    1.184428    0.257049    4.115971   175
 6 Ar   -3.295278    0.563002   -0.139099   175
 7 Ar   -1.184427    3.006886   -2.185664   175
 8 Ar   -0.917810   -1.812177    1.683773   175
 9 Ar    2.497619    2.142111   -1.627639   175
10 Ar   -0.106213   -0.647145   -1.865974   175
11 Ar    0.106212    3.911079    3.796282   175
12 Ar   -2.497618    1.121825    3.557947   175
13 Ar    3.295278    2.700934    2.069407   175
```

2. .KEY file

As described before, this file provides all the information about the atoms in the structure file and other input data needed for simulation. This file has following parts:

(a) Output Control: This mentions the format in which output is desired.

(b) Forcefield Selection: This option allows to give the path of a predefined parameter file in which all simulation parameters are predefined for some of the structures/

(c) Potential Function Selection: TINKER has almost all kinds of potential functions already built in. Using this tab, we can select or deselect any type pf potential function according to our simulation. These are described in detail in the next section.

(d) Potential Function Parameters: Here we list the values of all the variables in the potential function terms as chosen in previous tab.

(e) Energy Unit Conversion: In this option, conversion factor may be provided if the output for energy calculations is desired in a different unit. The default unit in TINKER is in kcal.

(f) Local Geometry Functional Form: Coefficients of Taylor series to be used for potential function may be listed here for angle and bond type.

(g) Van der Waals Functional Form: In this tab, van der Waals functional form can be chosen. It can be Lennard-Jones, Buckingham, Gaussian or any other specific type of potential format. Values of variables to be used for these are also provided under this tab.

(h) Electrostatic Functional Form: Here we provided values for various kinds of charge and dipole interactions. Dielectric constant for the medium is also to be inputted here.

(i) Non-bonded Cutoff Keywords: Under this section, we provide cutoff lengths for various potentials. Interactions are disregarded between atoms separated by lengths greater than the mentioned.

(j) <u>Crystal Lattice and Periodic Boundary</u>: Here we provide the dimensions of the periodic box for a periodic boundary condition simulation. For some crystals, specific spacegroups can also be provided.

Apart from these, other inputs such as random number to be used for calculation, algorithm to be used for trajectory calculation and kind of thermostat model to be used can be provided. This can be done by using the Force Field Explorer.

The .KEY file can be generated by using TINKER or can be done manually. Also, many structures already have all the parameters defined in parameter file. Their .key files can be generated using those parameter (.PRM) files. The .key file has to have the same filename as the corresponding .xyz file. Below, a .key file depicting the simulation properties of the cluster of Argon atoms is shown:

```
-------------------------------------------------------------------------------------------------

parameters    ../params/smooth


randomseed        123456789


basin      2.600     0.0001


atom        175      Ar   "Argon Atom"    18   39.948  0
vdw         175      3.361     0.2824
charge      175       0.000

-------------------------------------------------------------------------------------------------
```

There are a few other auxiliary input files other than .XYZ and .KEY files. These include the parameter or .PRM files. These files provide force field parameters for a specific group of molecules. These files are already provided with the software package. MM2/MM3/MM3PRO.PRM files can be used for the simulation of Carbon Nanotubes. For rock and clay simulation, there was no parameter file available, and parameters were to be provided separately in the .KEY file.

Also, many output file in TINKER can be used as input files for simulating the molecule further. If a simulation is performed in breaks, the output file of first simulation can be used as input for the second and so on. In addition to this, TINKER gives an option to provide the input files in different formats. These are the popular formats in molecular simulations. Structure files such as <filename>.pdb, <filename>.int and <filename>.xmol are supported and can be readily converted into the .xyz format.

4.3 Potential Functions

As mentioned before, there are various types and forms of potential functions already built into TINKER. We can choose the potential function terms from a list, which depends on the structure and the model we are simulating. Below is a list of some of the major potential terms along with their format:

1. Angle term - This switches on a built-in angle bending potential function of the form

$$E_a = k_\theta(\theta - \theta_o)^2 \tag{4.1}$$

where k_θ is the force constant in kcal/mol/deg^2 and θ_o is the equilibrium angle in degrees.

2. Bond term - This controls use of the bond stretching potential.

$$E_b = k_b(l - l_o)^2 \tag{4.2}$$

where k_b is the force constant value in kcal/mol and l_o is the ideal bond length in Angstroms.

We can also change the bond term form to Morse potential format. This kind of potential is generally used for covalent bonding. Morse potential form is depicted as:

$$E_{b(\text{morse})} = D_{ij}[\ \exp\{-2\beta_{ij}(r_{ij} - r^*_{ij})\}]$$ (4.3)

where D_{ij} denotes the depth of the potential, β_{ij} determines the shape of the potential and r_{ij} is the distance between the pair

3. Charge Term - This activates the use of charge-charge interaction potential energy term between pairs of atoms with partial atomic charges.

$$E_c = \sum_{i=1}^{n}\sum_{j=1}^{n} \frac{z_i z_j e^2}{r_{ij}}$$ (4.4)

where z_i and z_j are partial atomic charges between a pair and r_{ij} is the distance between the pair.

4. Dipole term: This adds the dipole-dipole interaction potential energy term to the total potential energy for the system.

$$E_{\text{dipole}} = \sum_{i=1}^{n}\sum_{j=1}^{n} \frac{z_i P}{r_{ij}}$$ (4.5)

where z_i is the charge on the atom, P is the dipole moment in Debeyes and r_{ij} is the distance between the pair

5. Torsion energy term: Due to the torsion angle in a bond, a potential can be developed. This term controls use of the potential energy term.

$$E_{\text{torsion}} = \sum_{\text{torsional interactions}} A[1 + \cos(n\tau - \phi)]$$ (4.6)

where A is the half-amplitude of the potential function in kcal/mol, n is the periodicity of the function and ϕ is the phase offset in degrees.

6. van der Waals term: This turns on the use of van der Waals potential energy term in the total function. This potential energy function can have different forms. There are various options available to choose the function and the variable format. The major two forms of the potential are:

(a) Lennard Jones:

$$E_{lj} = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right] \tag{4.7}$$

where ε is the homo-atomic well depth in kcal/mol, σ is the atomic radius in Angstroms and r is the distance between atoms

(b) Buckingham:

$$E_{buckingham} = e \left\{ A \exp \left[-B \left(\frac{R_o}{R} \right) \right] - C \left(\frac{R_o}{R} \right)^{6} \right\} \tag{4.8}$$

where A, B and C are the three premultiplier terms .i.e., exponential terms in the above equation, R_o is the atomic radius in Angstroms and R is the distance between atoms.
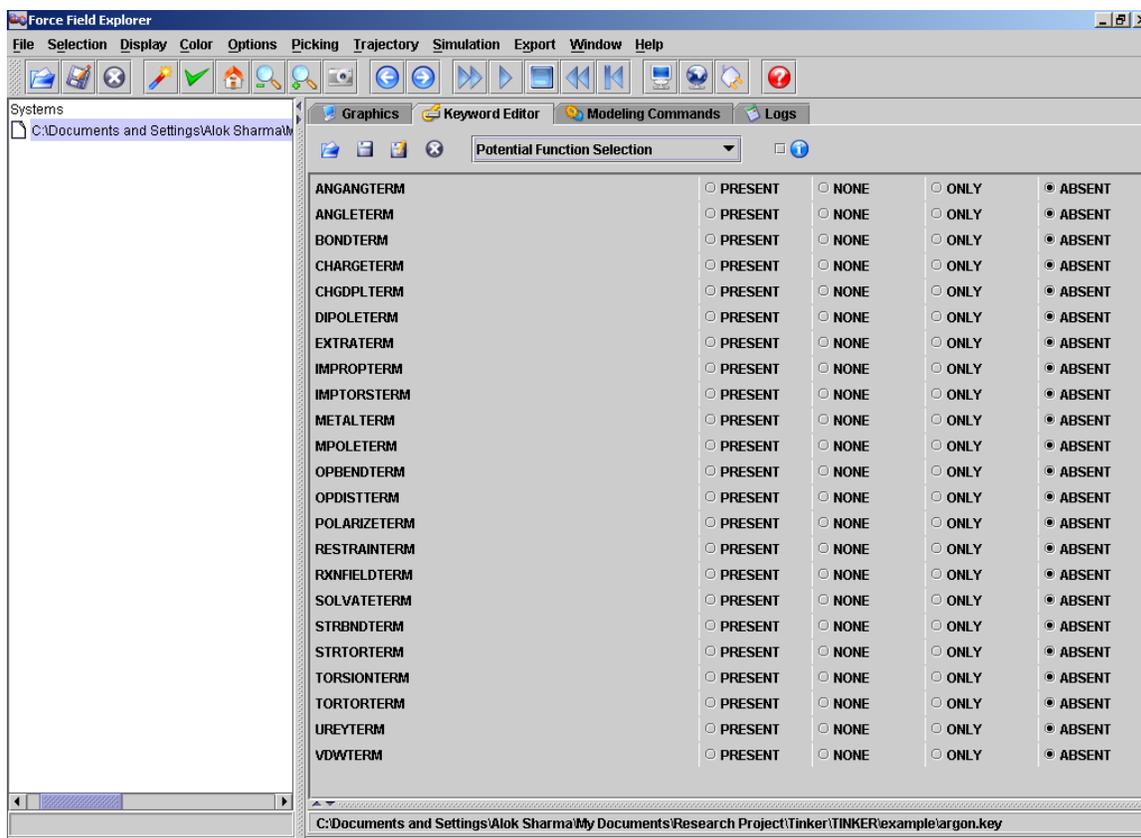
Figure 4.3 Force Field Explorer showing potential function selection tab for a .KEY file
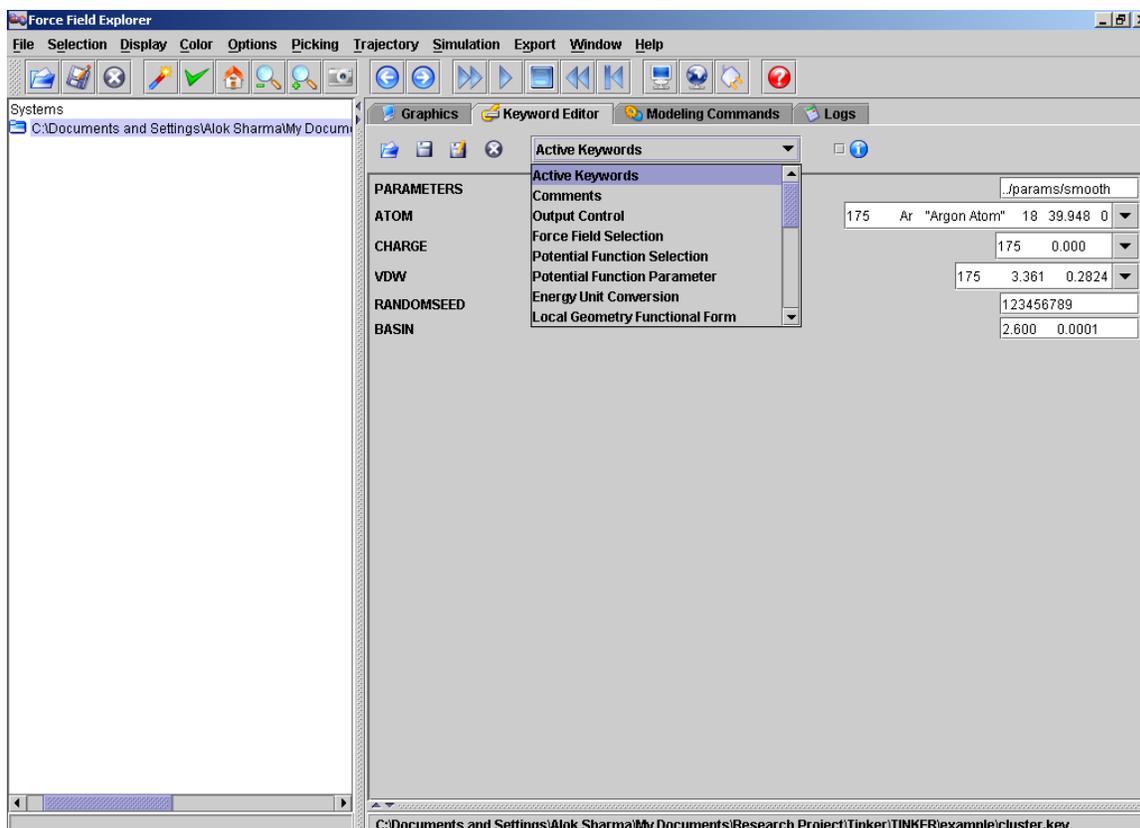
Figure 4.4 Force Field Explorer showing various options for creating .key file using FFE

4.4 Algorithms

As mentioned before, there are various integration algorithms for molecular dynamics calculations. These algorithms are needed to calculate the position of atoms as function of time. For this we have to integrate the acceleration got for the time step to get the displacement for that time step. There are various numerical integration methods that approximate the integration procedure for lower computational times. In TINKER, we have the following methods available:

(i)   Verlet algorithm

(ii)   Beeman algorithm

(iii)   Stochastic algorithm

(iv)   Rigidbody algorithm

These algorithms are described in Chapter 2. Similar algorithms are available for maintaining a constant temperature. This is done by bringing the system in contact with a large heat bath. For such calculations, following algorithms are available in TINKER:

(i)   Berendsen thermostat – The instantaneous temperature is pushed towards the desired temperature by scaling the velocities at each timestep. This scaling factor for two dimensional system is,

$$\chi = \left[1 + \frac{\Delta t}{\tau_T} \left(\frac{T_{ext}}{\tau} - 1 \right) \right]^{1/2} \tag{4.9}$$

where τ_T is the temperature at time t, T_{ext} is the external temperature and τ is the desired temperature.

(ii)   Andersen thermostat – The initial set of positions and velocities are integrated with time. After each time step, some of the particles are chosen to go in contact with the heat bath, for maintaining a constant system temperature. These particles will be assigned new velocities according to Maxwell-Boltzmann distribution corresponding to the desired temperature T.

4.5 Output Files

When a simulation is run in TINKER, a lot of output data is generated. Specifying type of output files can control the type and format of output data. These files vary according to the type of simulation run and by user preference. These files are describes below:

(a) .DYN file: This file stores the values needed to restart a molecular or stochastic dynamics computation. It stores the current velocity, current position and current and previous acceleration for each atom, as well as the size and shape of any periodic box or crystal unit cell.

(b) .END file: The .end file provides a mechanism to end a running simulation without any errors.

(c) .001,.002,… files: These files are referred to as cycle files. These files store various types of structures in a single file. For a molecular dynamics simulation, one cycle file is saved for each time step.

(d) .LOG file: The results of all calculation that were launched, is stored in this file. Data such as total energy, pressure, temperature etc, for each time step is stored in this file.

(e) .ARC file: This file stores the position of all atoms during the whole simulation for each time step in a sequential order. This file can be used for viewing the trajectory of the atoms for a given simulation.

4.6 Force Field Explorer's Graphic Viewer

The Graphic User Interphase of TINKER also includes a graphic viewer for visualization of static molecules as well as their simulations. The graphic viewer provides a 3-D view and has a simple but elegant rendering mechanism. Molecules can be visualized by rotating along any axis in the 3-D. Animation of a Molecular Dynamics simulation can be visualized too. Molecules can be visualized in various forms, such as:

1. Wireframe: Only bonds are visible as wires.
2. Spacefill: Atoms fill the space and bonds are not visible.
3. Ball and stick: Atoms are represented as balls and bonds as wires.
4. Tube: Only bonds are visible as tubes.

Also, multiple molecules can also be viewed on a single FFE screen.
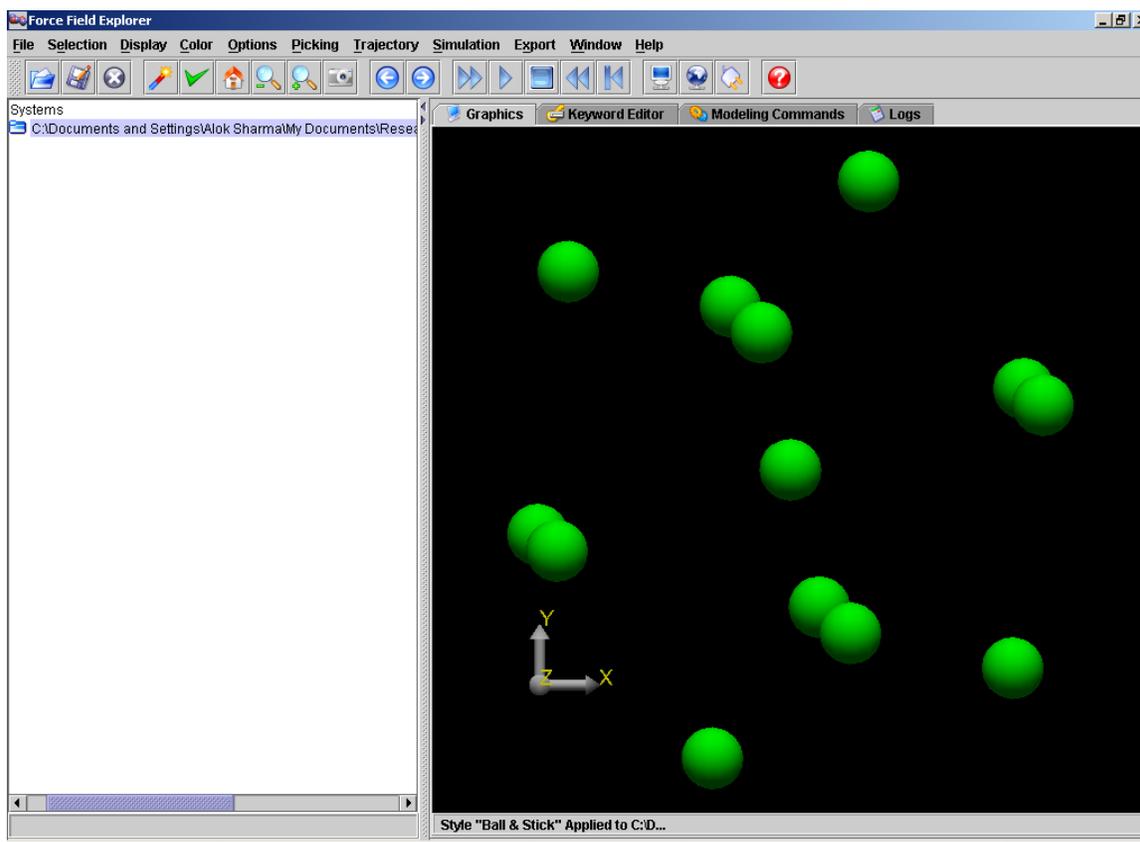
Figure 4.5 Force Field Explorer graphic viewer showing an Argon cluster

4.7 Interpreting the results from output files

Output files do not provide data in the desired format every time. Hence, we have to interpret the output to get the desired results. For a typical Molecular Dynamics simulation, the two major output files are .ARC and .LOG files.

As we know, .LOG file provides the following data for each 100 time-steps, averaged over the whole time period:

1. Pressure
2. Temperature
3. Potential Energy

From this data we can determine whether the desired pressure and temperature have been achieved by the system after the specified number of time steps. Also, we can check that the minimization of potential energy is taking place. This data can also be used for providing auxiliary information.

THE .ARC file provides the position of all atoms at every time step. This data can be used to calculate the strains in a structure. The initial position of atoms can be known using the .XYZ file. The final position of an atom can be calculated by averaging the positions for a certain number of time steps in the end. This has to be done because the molecule vibrates even in the equilibrium position. Once the final position of atoms is known, we can calculate the final dimensions of the molecule or structure. Once we have this data we can calculate the axial strain by using the following equation:

Axial Strain = (Final length-Initial length)/Initial length

The average pressure can be calculated by averaging the pressure for the last few time steps. From the pressure and the strain data, we can draw a stress-strain curve and then calculate the elastic modulus of materials.

4.8 Modifications done on TINKER for this project

TINKER program was developed originally for biological molecular simulations. Hence, for simulating structural materials such as rocks, modifications had to be done in this software. For instance, there was absolutely no provision in the program to perform a uniaxial compression of the materials. The pressure that was inputted was an all-round

pressure. Hence a scheme had to be developed to analyze a problem where we have to simulate a uniaxial pressure application.

For this a study of the source code was done. It was realized that the periodic box was changed in all three directions as per the pressure modification. This was done so that the pressure in all 3 directions remains the same. This procedure was changed so that only the pressure in one direction was maintained constant and was zero in other directions. This allowed the program to analyze a problem with pressure applied in a single direction.

This was done by reducing the stress tensor by setting all other terms except the z-direction stress to be zero. This element of the stress tensor was made equal to the value given by the user as input.

```
pres = (stress(1,1)+stress(2,2)+stress(3,3)) / 3.0d0
```

```
Above code was changed to:
```

```
pres = stress(3,3)
```

A scaling factor was applied to the periodic box of the structure being simulated. This altered the x,y and z dimensions of the structure.

```
scale = (1.0d0 + (dt*compress/taupres)*(pres-atmsph))**third
```

The third power in this factor was removed. Now this scale factor had to be applied only to z direction of the periodic box. Hence,

```
xbox = scale * xbox
ybox = scale * ybox
zbox = scale * zbox
```

the above code was changed to the following one:

```
zbox = scale * zbox
```

Once the source code was altered, the code had to be compiled and run again to create a new set of executable files. For this, a copy of Intel Fortran Compiler and Intel C++ compiler each, was installed. A copy of MS Visual Studio .NET was also required. The compile command was run on Intel Fortran Compiler using the batch file provided in the TINKER package. This created a sockets.lib file, which was to be executed again using lib command in Visual Studio .NET. Once this was done, another set of command was run in Intel C++ Compiler to create the executables. Now, the new executable files had to be linked with GUI of the software. For this a copy of JAVA had to be installed on the machine. The command was run using the batch file provided and the new executables were linked with the GUI.

Another method for uniaxial pressure simulation would have been to use energy minimization function rather than using molecular dynamics simulation. In this method, we will provide a periodic molecular structure as input and provide an equilibrium periodic cell dimension according to the molecule. In this technique, we will provide a certain strain to the system by increasing/decreasing the periodic cell dimensions in the direction where pressure application is desired. Then we proceed with energy minimization using the MINIMIZE command on TINKER GUI. Once the program finishes the function, results are displayed on log file indicating the energy difference in each step and the total atomic movement. From this data the total change in energy and the average displacement of atoms can be calculated. Then, force can be calculated as change in energy divided by the atomic displacement. Hence, in this method, we control strain instead of stress.

 A guide for performing MD simulations on rock and clay minerals is provided in the Appendix of this thesis.

Chapter 5 Problem Description

In this research, we aim to develop a methodology to analyze rock and clay minerals using molecular mechanics. For this problem, few calculations have been done for verifying our methods and validating our results. This can be done by comparison with published results. Once the methodology is validated, we can proceed to analyze other rock minerals.

The problem can be divided into the following parts:

1. Modification of TINKER software for uniaxial loading

TINKER software was developed mainly for the molecular mechanics calculations for biological systems. An all round pressure, given by the user, is applied on the system and there is no provision for application of uniaxial stress. The structural materials we are simulating are mostly tested for their strengths using uniaxial loading. TINKER source code will have to be modified so that such an analysis can be performed using the software.

2. Simulation of Carbon Nanotube for verification

Carbon nanotubes (CNTs) are the most researched nanomaterial of recent times. These are well known in the field of nanotechnology for their fascinating physical properties, i.e., high strength without breaking. Hence, carbon nanotubes present us with an opportunity to verify our method. The methodology of MD simulation of CNTs is described in Chapter 2.

Our next part of the problem is then to simulate a chosen carbon nanotube using MD simulation. After calculating the stress-strain curve for the CNT, the results are to be compared with the published ones. In our analysis, we have chosen a (14,1) "chiral"

carbon nanotube. Generation of stress-strain curve for the nanotube was proposed using Molecular Dynamics simulation. The results will be compared with the published data.

3. Performing MD simulation on rock and clay minerals

The next step in the project will be to simulate some rock minerals. For this analysis we chose granitic rocks such as quartz, albite and muscovite. Methodology followed by Ichikawa et. al. (2004) is described in Chapter 2. Here, we try to simulate the same minerals under similar conditions and try to generate stress-strain curves. This way, we can once again verify our two methods against each other, as well as compare the results with already existing values. This will once again validate our procedure as well as give us the capability to simulate rock minerals at nanoscale. Apart from granitic rocks, calcite was another rock mineral chosen to be simulated.

Clay minerals are the other important set of geotechnical materials apart from rocks. Their microbehavior has always been less researched and mysterious. The behavior of a clay lamella under stresses is a very intriguing problem. Here, we try to simulate the single clay lamella of Kaolinite clay mineral and analyze under different stresses. A stress-strain curve was to be generated using the two simulation methods. Another clay mineral that is proposed for analysis is palygorskite. This mineral has interesting properties as described in Chapter 2. It is often referred to as "naturally occurring nanotubes." A structure of Palygorskite mineral was also proposed to be analyzed in this project.

4. Comparing the results with published data

After getting the results of our simulations, we will be in a position to assess Molecular Dynamics as a method for analyzing geotechnical materials. Appropriate comments and suggestions will be provided once we compare the results among the two methods as well as comparing them with already published data.

Prior to all these steps, an exhaustive study of Molecular Dynamics theory shall be done. TINKER software will be studied in detail using examples and user's guide. A huge database of 135,000 lines of source code for TINKER will also be studied for the modification. Also, for each simulation, a structure of the mineral to be analyzed will be prepared. Hence, some knowledge of lattice theory will be essential. Literature regarding this has also to be reviewed.

Chapter 6 Simulations and Results

This chapter describes the methods followed for performing the Molecular Dynamics (MD) simulations, obtained using TINKER with modified source code. The results that were got are presented here.

6.1 Carbon Nanotube Simulation

Molecular Dynamics of carbon nanotube has been a well-researched area. Our task here was to reanalyze Carbon Nanotube using Molecular Dynamics (MD) simulations. The idea is to choose a specific carbon nanotube and simulate it under similar temperatures and pressures to get stress-strain curve. If the results from both methods agree, then we proceed to the simulation of other rock minerals.

6.1.1 Model

For the analyses, a (14,1) nanotube was chosen. The coordinates were generated from a program called TubeGen3.3 (http://turin.nss.udel.edu/research/tubegenonline.html). Many fellow researchers, who have performed similar analyses on carbon nanotubes, recommended the program. J.T. Frey and D.J. Doren, University of Delaware, as a part of their PhD. thesis, developed the program. The program has many options to choose the shape and form of the nanotube. These are described below:

1. Chirality of the carbon nanotube can be chosen by entering chiral vectors for the tube.
2. The type of atoms forming nanotube can be entered, which in this case, is carbon.
3. Bond length between the atoms forming the tube can be chosen, which in the case of a carbon nanotube is 1.4210 A$^{\text{o}}$.

4. Format of the output file can be chosen. Output file can be got in different formats for different molecular modeling programs. We used the PDB (Protein Data Bank) file with periodic boundary conditions. This file was then converted to .XYZ format, to be used in TINKER.

5. Length unit can be chosen, it can either be in Angstroms or nanometers. In our case, Angstrom unit was chosen, as is default for TINKER.

Once the carbon nanotube was chosen and coordinates defined, the file was then converted to the .XYZ file format manually. This was done to make it run in TINKER. It was a 845-atom (14,1) chiral carbon nanotube. Periodic boundary conditions were also applied to the system.
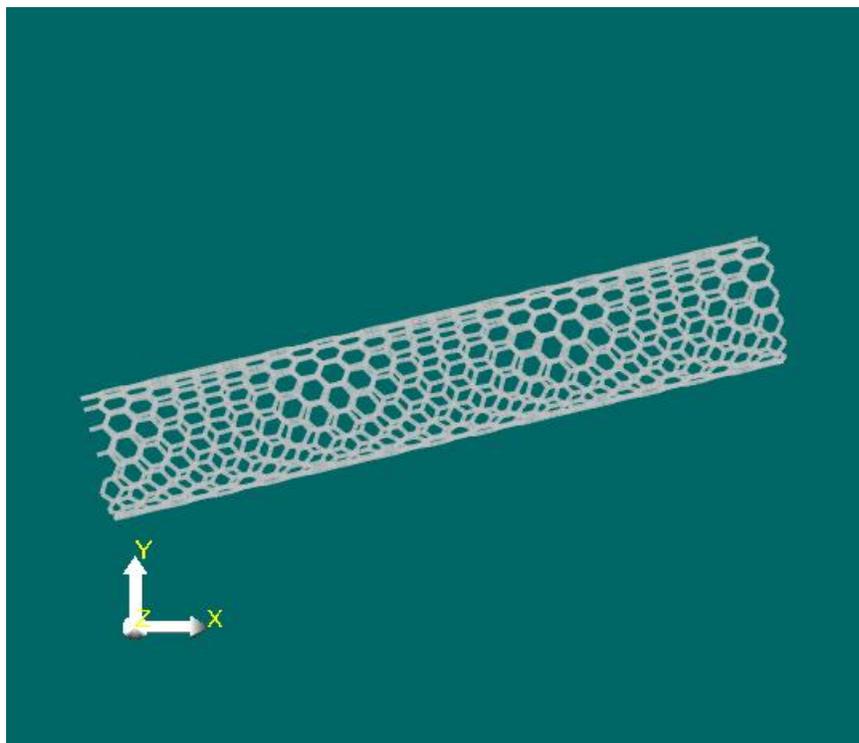
Figure 6.1 845-atom Single-Walled uncapped CNT as seen in TINKER

6.1.2 Potential Function

For the analysis of carbon nanotubes, MM2 potential parameters were used. These potential parameters depict the sp2-sp2 interactions between carbon atoms. Also, it takes into consideration van der Waals forces acting during the interaction. Hence, this potential function is same as the Brenner's potential described previously. MM2 paramters were developed in Allinger et al (1997) and have been widely used for the simulation of carbon nanotubes. This parameter file is provided with TINKER installation package.

The potential can be depicted as follows:

1. A valence of 3 for all carbon atoms
2. For the Lennard-Jones van der Waals potential as shown in equation 3.7, ε = 0.044 kcal/mol and σ = 1.94 Angstroms.
3. For bond stretching potential as shown in equation 3.2, k_b = 1.337 kcal/mole/A^{o2} and l_o = 9.6 A^o.
4. For the angle bending potential as shown in equation 3.1, k_θ = 0.43 kcal/mol/radians^2 and θ_o = 120.0^o.
5. For the torsion potential as shown in equation 3.6, A = -0.930 kcal/mol, φ = 180.0^o and n =0.0.

No charge or dipole interactions were present.

6.1.3 Methodology

MD simulation was performed then, to observe the strain of the nanotube under different pressures. The nanotube was first allowed to relax under no pressure and 300K temperature. This was done for 20,000 timesteps. After that a range of uniaxial pressures

were applied to the nanotube along the z-axis, i.e., along the length of the nanotube. This was done for 450,000 timesteps, with each timestep measuring 0.1 ps. All calculations were done under 300K temperature using Beeman integration algorithm, as described in chapter 2. Using this data, a .key file for TINKER was created. Values of the last 20,000 time steps were used for calculating average strains for the simulation. Once the strains corresponding to the stresses were calculated, stress strain curve was generated for the tube. The behavior of the tube under applied pressures could be seen using the visualization scheme of TINKER. Thus, buckling load of the tube could be determined with reasonable accuracy. The average time for performing one MD simulation of 450000 timesteps (45 ps) was 120 minutes. This was done using a machine with Pentium IV processor, 1.4 GHz processor speed and 228 MB RAM.
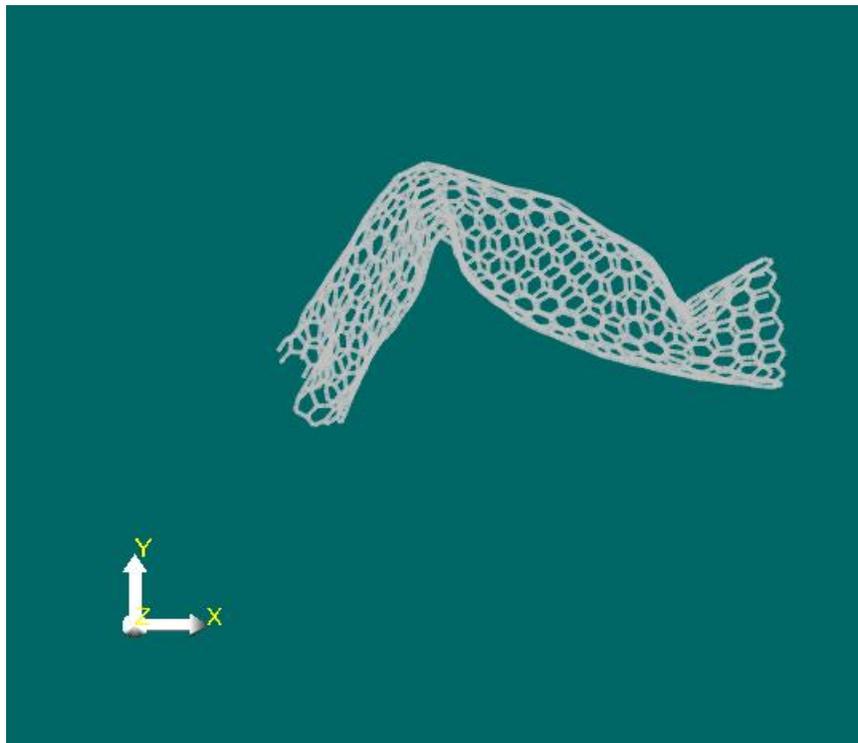
Figure 6.2 A buckled CNT, 25 ps after the application of 50 GPa pressure and 300K temperature

6.1.4 Results

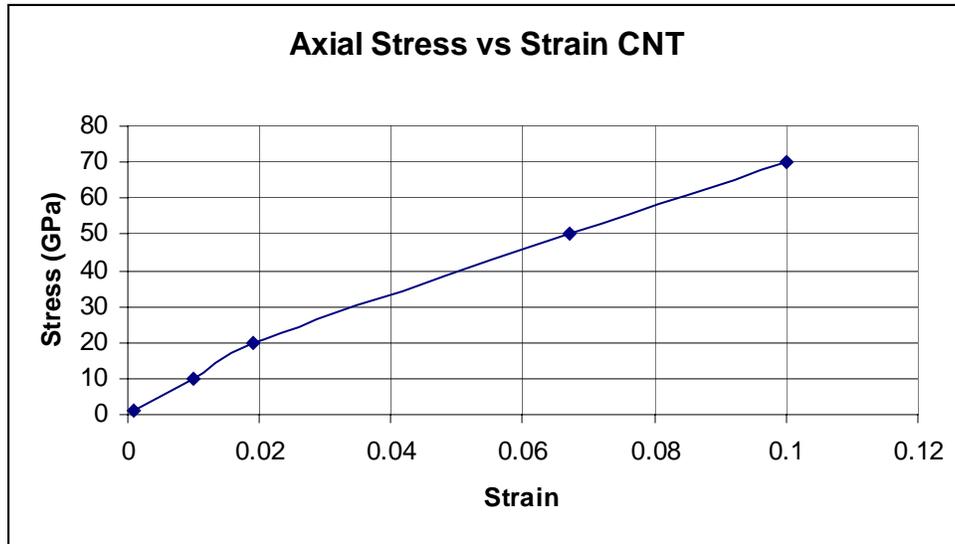Following results were obtained from MD simulation of the (14,1) CNT:

Figure 6.3 Axial stress-strain curve for (14,1) CNT in uniaxial compression

Table 6-1 Axial stress strain data for CNT in tabular form

| Stress(GPa)	Strain
1	0.001
10	0.01
20	0.019
50	0.067
70	0.1

6.2 Simulation of Quartz

The first mineral chosen for analyses was quartz. It is the most abundant mineral on the surface of the earth. Quartz is one of the many minerals composed of silicon-di-oxide (SiO_2). Almost every rock has quartz as its constituent mineral. It is present in nature in a

wide variety of forms and in much abundance. This abundance makes quartz one of the most important materials in the field of civil engineering and material science. Hence, quartz is one of the natural choices for our nanoscale molecular dynamics analysis. Also, we have a journal paper which already provides us with data to validate our results. The analysis was done on alpha-quartz form on quartz mineral. This is the stable form of quartz under normal room conditions.

6.2.1 Model

The next step was to get the quartz structure of few hundreds of atoms. This was attained using software, CrystalMaker1.3. This is available at the webpage www.crystalmaker.com, and a demonstration version is available for free download at the webpage. This program is a product of Crystal Maker Software Ltd. It provides the capabilities for analyzing and visualization of crystal and molecular structures. There are a few examples of molecular structures available with the software package, which also includes quartz. Below, we show a screenshot of the software, showing a quartz molecule.
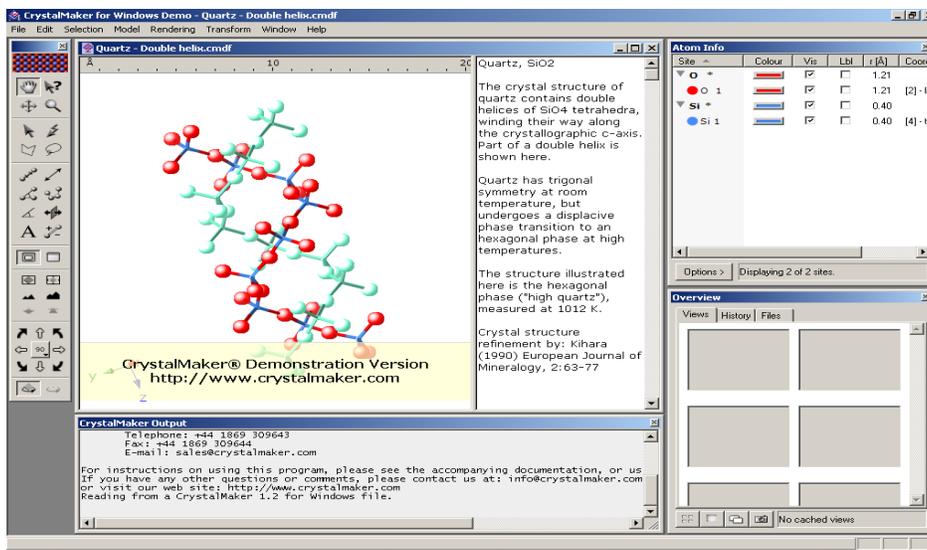
Figure 6.4 A screenshot of CrystalMaker showing a quartz molecule

Using this demo-version of CrystalMaker1.3, we can ascertain the Cartesian coordinates of several hundreds of quartz molecule. A model of 955 atoms was chosen for quartz. Atomic coordinate data for this available by changing the cell dimensions for above figure to accommodate 955 atoms. But this version does not provide us with the atom connectivities. Hence, though we have the coordinates of quartz molecule, we still do not know which atom is connected to which others. This problem was solved by creating a small program in MATLAB. We are aware of the bond lengths of all the bonds in Quartz. Hence, if the distance between any silicon atom and oxygen atom is very close to that bond length, then those two atoms were assumed to be connected. This approach was used to create the program, and thus, the connectivity data among the atoms was achieved. Once the coordinates and connections were known, the .xyz input structure file for quartz was created manually.
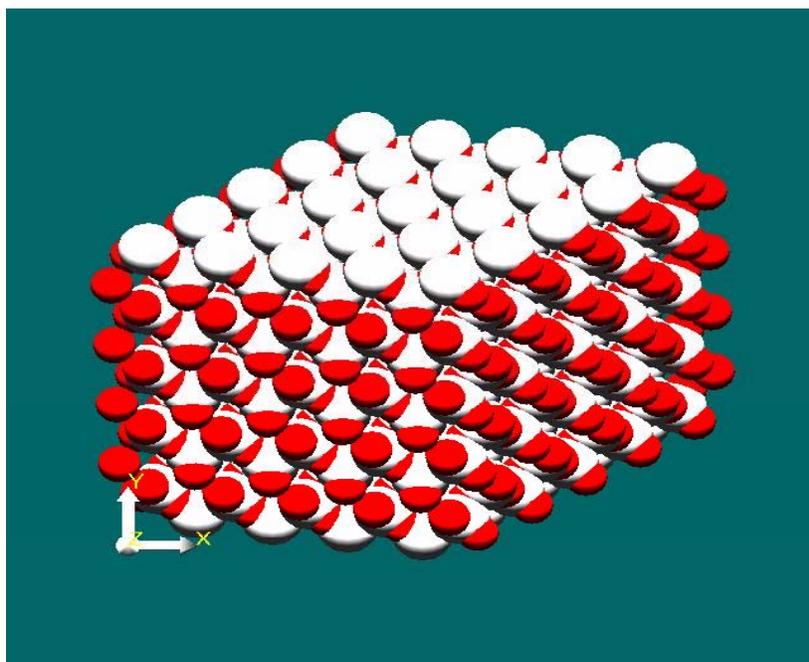
Figure 6.5 TINKER screenshot showing a 955-atom quartz molecule

6.2.2 Potential Function

The potential function used for the analysis was the same as in Ichikawa et. al. (2001), discussed in Chapter 3. It is shown as follows:

$$U_{ij}(r_{ij}) = \frac{z_i z_j e^2}{r_{ij}} + f_o(b_i + b_j)\exp(\frac{a_i + a_j - r_{ij}}{b_i + b_j}) - \frac{c_i c_j}{r^6_{ij}} + D_{ij}[\exp\{-2\beta_{ij}(r_{ij} - r^*_{ij})\} - 2\exp\{-\beta_{ij}((r_{ij} - r^*_{ij})\}]$$

$$(5.2)$$

The force field parameter values used in the above potential function for quartz were the same in the journal paper as shown in Table 3-4.

6.2.3 Simulation

MD simulation was performed then, to observe the strains of the quartz molecule under different pressures. The structure was first allowed to relax under no pressure and 300K temperature. This was done for 20,000 timesteps. After that a range of uniaxial pressures were applied on the molecule along the z-axis. This was done for 400,000 timesteps, with each timestep measuring 0.1 ps. All calculations were done under 300K temperature using Beeman integration algorithm, as described in chapter 2. Using this data, a .key file for TINKER was created. Values of the last 20,000 time steps were used for calculating average strains for the simulation. Once the strains corresponding to the stresses were calculated, stress strain curve was generated. The behavior of the molecule under applied pressures could be seen using the visualization scheme of TINKER. The average time for performing one MD simulation of 400,000 timesteps was 120 minutes. This was done using a machine with Pentium IV processor, 1.4 GHz processor speed and 228 MB RAM.
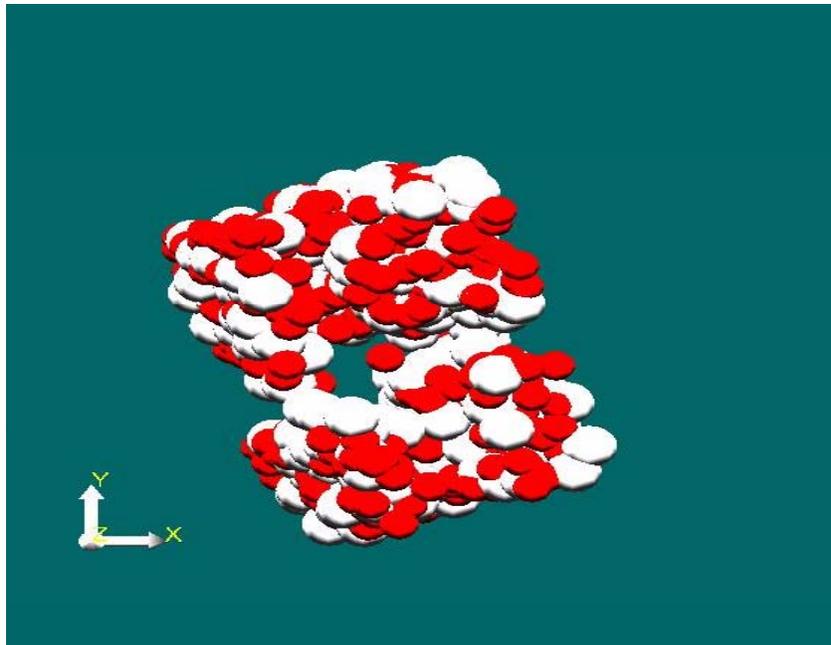
Figure 6.6 A compressed quartz molecule after 600 time step under 5 GPa pressure
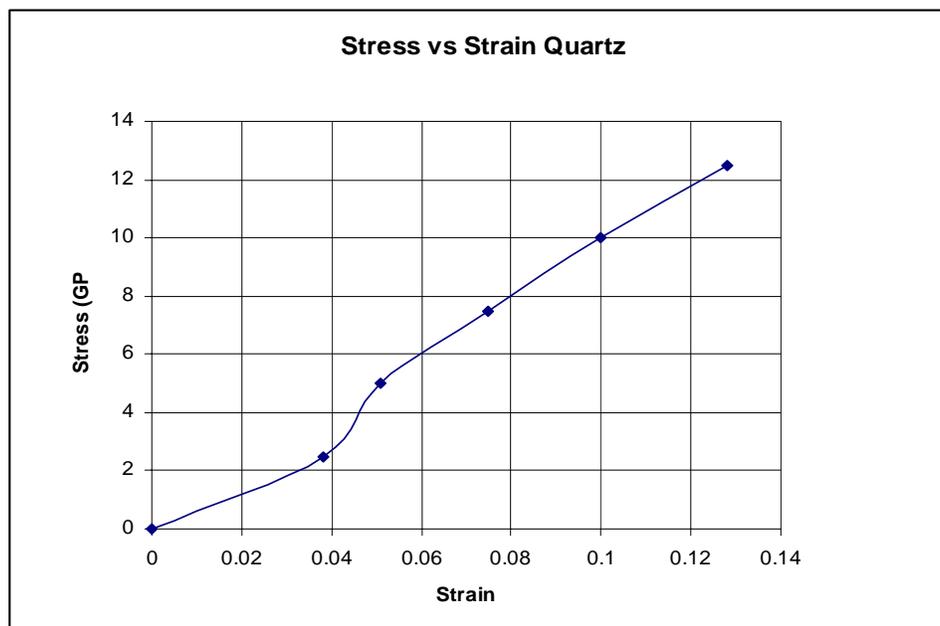
6.2.4 Results

Figure 6.7 Axial stress strain curve of quartz from MD simulation

**Table 6-2 Stress-strain data for MD simulation of quartz**

Stress (GPa)	Axial Strain
2.5	0.038
5	0.051
7.5	0.0748
10	0.100
12.5	0.128

6.3 Simulation of Albite

Albite is also one of the major compositions of granitic rocks, and on of the minerals of the feldspar series. The chemical formula of albite is $NaAlSi_3O_8$, called sodium aluminum silicate. The journal paper Ichikawa et al presents the results of molecular dynamics simulations performed on albite. In this chapter, we present the results of similar MD simulations performed in TINKER.

6.3.1 Model

The first step for setting up the simulation was to get an .xyz structure file for albite molecule. As in the journal paper, the model was to be around a thousand atoms. The structure had 964 atoms. Once we had the coordinate and the connectivity data of the structure, the .XYZ file was created manually.
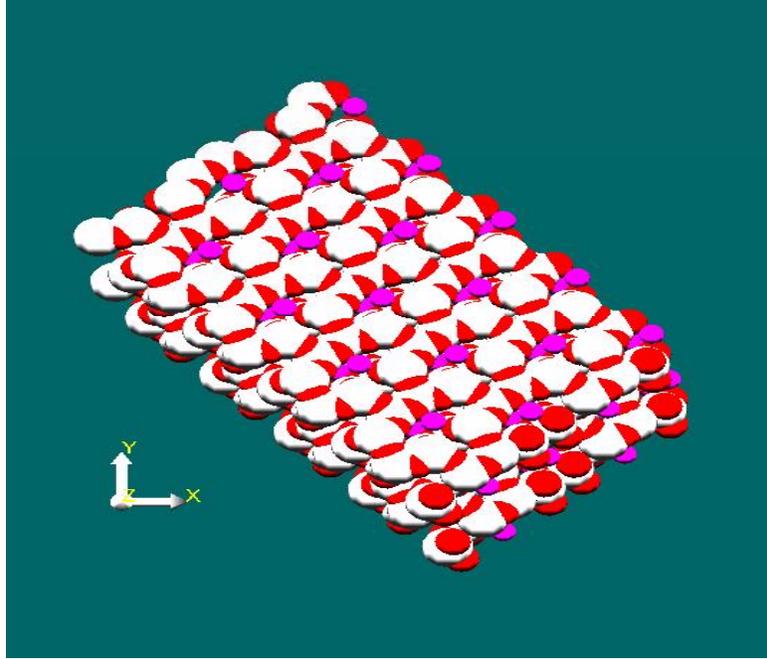
Figure 6.8 TINKER screenshot of albite structure

6.3.2 Potential Function

The potential function used in these simulations was the same as used in the journal paper:

$$U_{ij}(r_{ij}) = \frac{z_i z_j e^2}{r_{ij}} + f_o(b_i + b_j)\exp(\frac{a_i + a_j - r_{ij}}{b_i + b_j}) - \frac{c_i c_j}{r^6_{ij}} + D_{ij}[\exp\{-2\beta_{ij}(r_{ij} - r^*_{ij})\} - 2\exp\{-\beta_{ij}((r_{ij} - r^*_{ij})\}]$$

(5.3)

The force field parameter values used in the above potential function for albite were the same in the journal paper as shown in Table 3-4.

6.3.3 Simulation

MD simulation was performed then, to observe strain of the albite molecule under different pressures. The structure was first allowed to relax under no pressure and 300K

temperature. This was done for 20,000 timesteps. After that a range of uniaxial pressures were applied on the molecule along the z-axis.. This was done for 40,000 timesteps, with each timestep measuring 0.1 ps. All calculations were done under 300K temperature using Beeman integration algorithm, as described in chapter 2. Using this data, a .key file for TINKER was created. Values of the last 20,000 time steps were used for calculating average strains for the simulation. Once the strains corresponding to the stresses were calculated, stress strain curve was generated. The behavior of the molecule under applied pressures could be seen using the visualization scheme of TINKER. The average time for performing one MD simulation of 40,000 timesteps was 120 minutes.This was done using a machine with Pentium IV processor, 1.4 GHz processor speed and 228 MB RAM.

Figure 6.9 A compressed albite molecule after 600 timesteps under 5 GPa pressure

6.3.4 Results
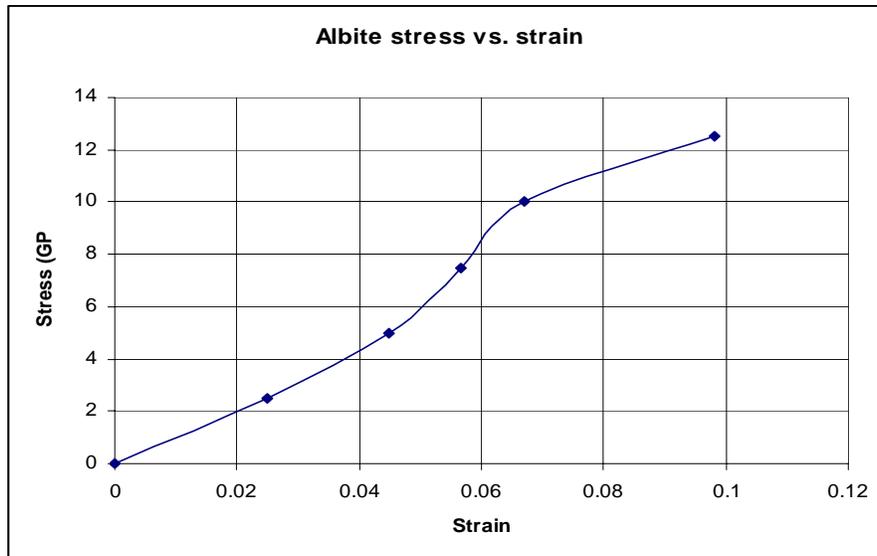
Figure 6.10 Stress-strain curve of albite from MD simulation

Table 6-3Stress-strain data in tabular form for MD simulation of albite

Stress(GPa)	Axial strain
2.5	0.025
5	0.045
7.5	0.0567
10	0.067
12.5	0.098

6.4 Simulation of Calcite

As we know, calcite is one of the most diverse and abundant of rock minerals on the face of the earth. It forms various kinds of rocks, igneous, sedimentary as well as metamorphic. MD simulation of calcite has been performed by many researchers for

various kinds of geological and material science studies. Here, we describe the results of MD simulation performed on a calcite molecule to study its mechanical properties.

6.4.1 Model

The first step for setting up the simulation was to get an .xyz structure file for calcite molecule. A Protein Data Bank (PDB) structure file of calcite was found at the webpage http://www.soils.wisc.edu/virtual_museum/calcite/index.html. The structure had 540 atoms. The file gave the coordinates as well as the connectivities of all atoms. Once we had the coordinate and the connectivity data of the structure, the .XYZ file was created manually.
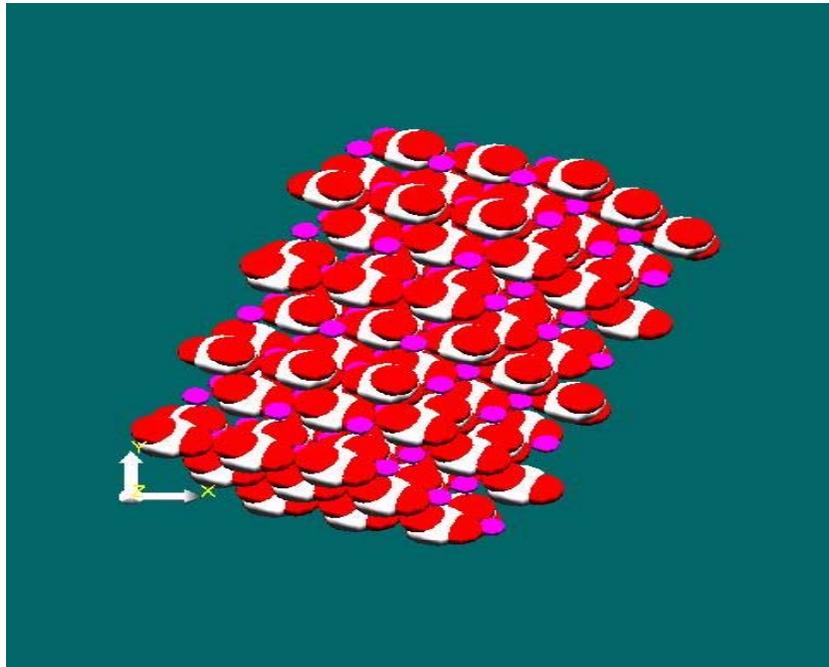

Figure 6.11 TINKER screenshot of calcite molecule

6.4.2 Potential Function

The potential function used for MD simulation of calcite was the same used for simulating $CaCO_3$ melts in Genge et. al. (1995). This is shown below:

$$\phi_{ij} = \frac{q_i q_j}{4\pi\varepsilon_o r_{ij}} + A_{ij} \exp\left(\frac{-r_{ij}}{B_{ij}}\right) \tag{5.4}$$

Values of force field parameters are:

Table 6-4 Potential parameters for calcite potential function

	$A_{ij}(eV)$	$B_{ij}(nm)$
O-O	2879.1262	0.0252525
O-C	1.7411309e11	0.0038700
O-Ca	3943.6977	0.0251570
Ca - charge	1.64203e	
O - charge	-0.89429e	
C - charge	1.04085e	

6.4.3 Simulation

MD simulation was performed then, to observe strain of the calcite molecule under different pressures. The structure was first allowed to relax under no pressure and 300K temperature. This was done for 20,000 timesteps. After that a range of uniaxial pressures were applied on the molecule along the z-axis.. This was done for 40,000 timesteps, with each timestep measuring 0.1 ps. All calculations were done under 300K temperature using Beeman integration algorithm, as described in chapter2. Using this data, a .key file for TINKER was created. Values of the last 20,000 time steps were used for calculating average strains for the simulation. Once the strains corresponding to the stresses were calculated, stress strain curve was generated. The behavior of the molecule under applied pressures could be seen using the visualization scheme of TINKER. The average time for

one MD simulation of 40,000. timesteps was 120 minutes. This was done using a machine with Pentium IV processor, 1.4 GHz processor speed and 228 MB RAM.
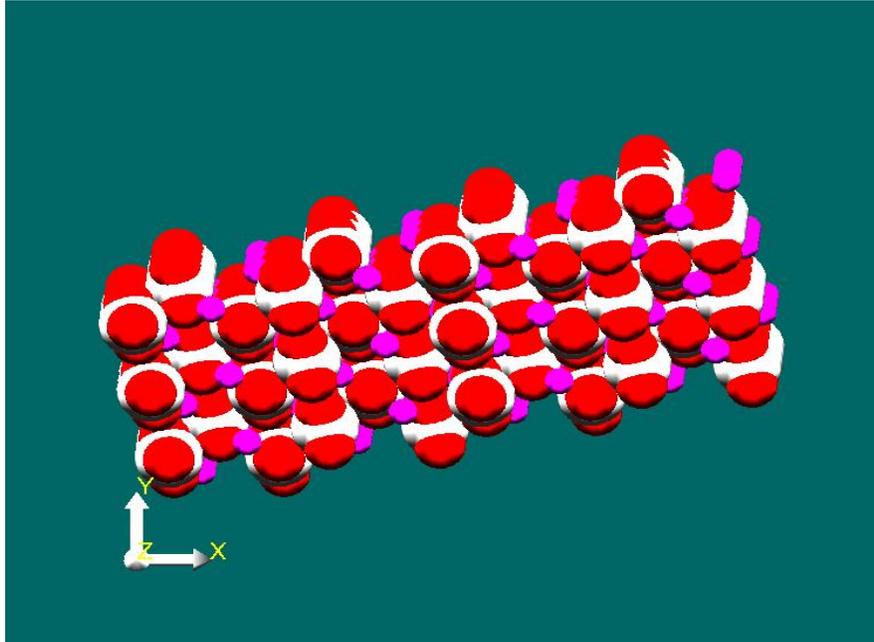

Figure 6.12 A compressed calcite molecule at 200th timestep under 10 GPa pressure
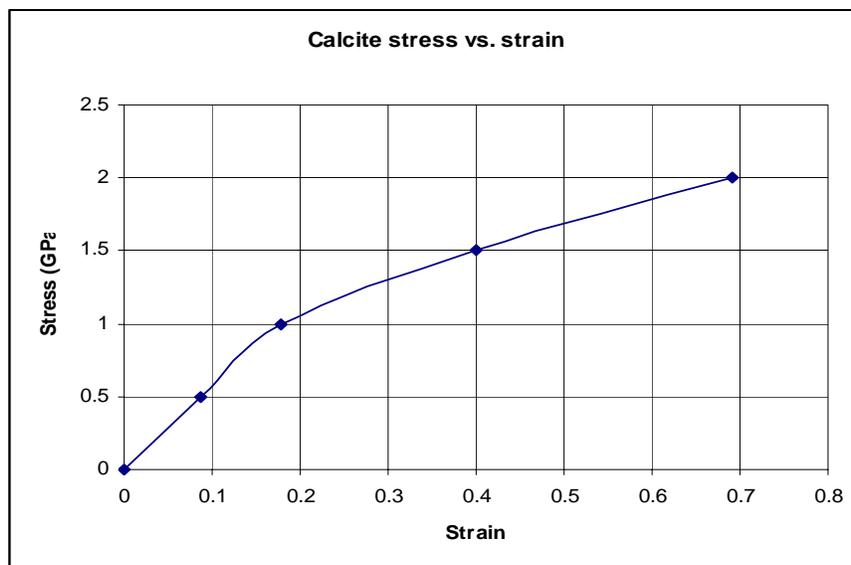
6.4.4 Results

Figure 6.13 Stress-strain curve of calcite from MD simulation

Table 6-5 Stress-strain data in tabular form for MD simulation of calcite

| Stress (GPa)	Axial Strain
0	0
0.5	0.087
1	0.178
1.5	0.401
2	0.691

6.5 Simulation of Kaolinite lamella

MD simulation of clays can help understand the nanoscale behavior of clays. Behavior of a single clay lamella is one of the less researched areas. MD simulation has been used to analyze the mechanical properties of a montmorillonite (MMT) clay lamella. A similar analysis was performed for a kaolinite clay lamella, for its mechanical properties. In this chapter, we present the results of the analysis.

Kaolinite or Aluminium Silicate Hydroxide ($Al_2Si_2O_5(OH)_4$), is one of the most common clays. Almost all clay deposits have some part of Kaolinite. Its structure is composed of silicate sheets (Si_2O_5) bonded to aluminum oxide/hydroxide layers ($Al_2(OH)_4$). Study of single lamella of kaolinite presents interesting prospects.

6.5.1 Model

The first step for setting up the simulation was to get an .xyz structure file for kaolinite molecule. A Protein Data Bank (PDB) structure file of kaolinite was found at the webpage http://www.soils.wisc.edu/virtual_museum/kaolinite/index.html. The structure had 230 atoms. The file gave the coordinates as well as the connectivities of all atoms. Once we had the coordinate and the connectivity data of the structure, the .xyz file was created manually.
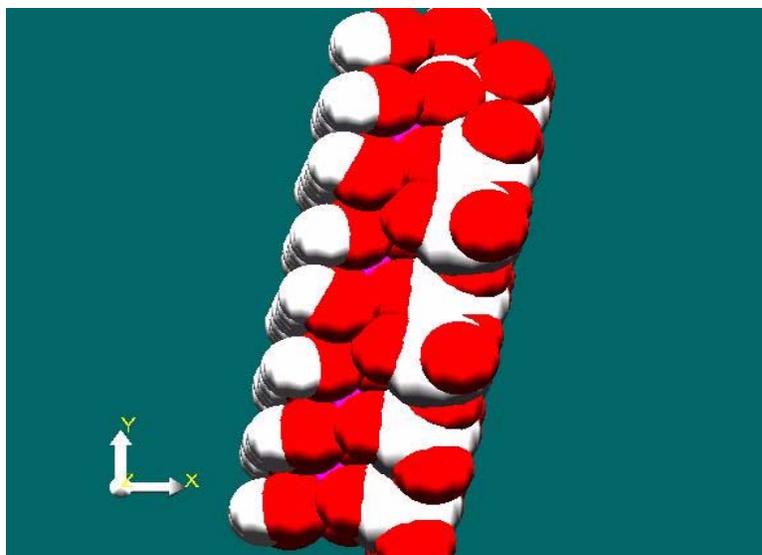
Figure 6.14 TINKER screenshot of kaolinite molecule

6.5.2 Potential Function

The potential function used for the simulation is the same as used in the paper for monmorillonite simulation. It is given in Table 3-5.

6.5.3 Simulations

MD simulation was performed then, to observe strain of the kaolinite clay lamella under different pressures. The structure was first allowed to relax under no pressure and 300K temperature. This was done for 20,000 timesteps. After that a range of uniaxial pressures were applied on the molecule along the z-axis.. This was done for 20,000 timesteps, with each timestep measuring 0.1 ps. All calculations were done under 300K temperature using Beeman integration algorithm, as described in Chapter 2. Using this data, a .key file for TINKER was created. Values of the last 20,000 time steps were used for calculating average strains for the simulation. Once the strains corresponding to the stresses were calculated, stress strain curve was generated. The behavior of the molecule under applied pressures could be seen using the visualization scheme of TINKER. The average time for

performing one MD simulation of 20,000 timesteps was 60 minutes. This was done using a machine with Pentium IV processor, 1.4 GHz processor speed and 228 MB RAM.

Figure 6.15 A compressed kaolinite molecule after 50 timesteps under 10 GPa pressure
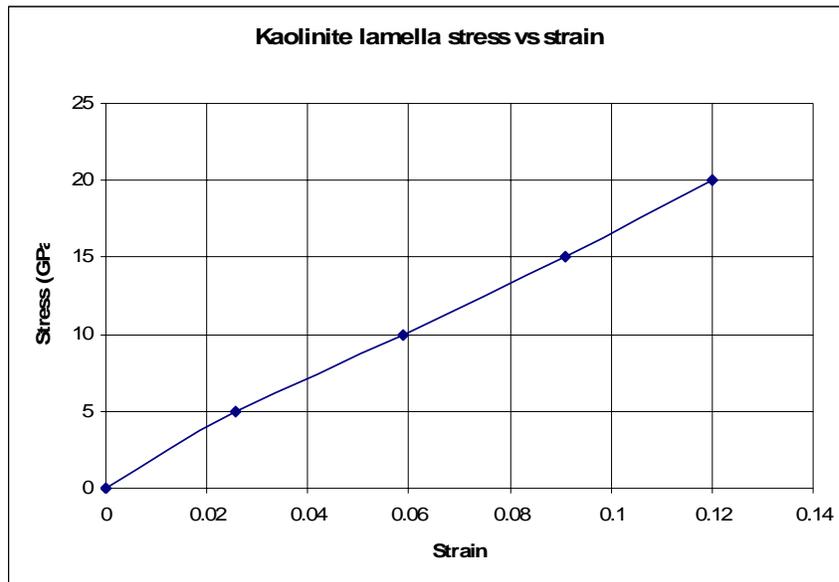
6.5.4 Results

Figure 6.16Stress-strain for MD simulation of Kaolinite lamella

Table 6-6Stress-strain data for kaolinite in tabular form

Stress(GPa)	Axial strain
0	0
5	0.0257
10	0.059
15	0.091
20	0.12

6.6 Simulation of Palygorskite

6.6.1 Mineral Description

Palygorskite, also known as attapulgite, is a peculiar mineral. Its forms felted masses closely resembling a woven cloth. It is generally classified as clay mineral as it behaves like and is present in many types of clay. But it also has the ability to form large crystal masses. This mineral exhibits nanotube-like structures at micro-level. The tertrahedra pointing in the same direction form 2:1 ribbons that extend in the direction of the z-axis (into the paper as shown in Fig. 1). The width of these ribbons is the average width of two tetrahedras. These form rectangular channels like nanotubes which have Ca/Mg cations.

The chemical formula for palygorskite is $(Mg,Al)_2Si_4O_{10}(OH)-4H_2O$, hydrated magnesium aluminum silicate hydroxide. The channel like structures in palygorskite structure along with the charge makes this clay a very good absorbent. Another physical impact of these channel-like microstructures is the property of elongate. This property is useful for many industrial applications. Some of the applications of palygorskite are in drilling fluids, paints, industrial floor absorbents, paper, pharmaceuticals and environmental absorbents. Hence, we see that the microstructure of palygorskite has a major impact in its macro properties. The study of palygorskite using MD simulation then presents a very interesting problem, which will help us to analyze the physical properties

of palygorskite at nanolevel. It will also provide us with capabilities to explore other properties of palygorskite later on.

6.6.2 Model

A Protein Data Bank (PDB) structure file for palygorskite was found at the webpage http://www.soils.wisc.edu/virtual_museum/palygorskite/index.html. This file had all the coordinate and connectivity data for the palygorskite molecule. Once we had the coordinate and the connectivity data of the structure, the .xyz file was created manually.
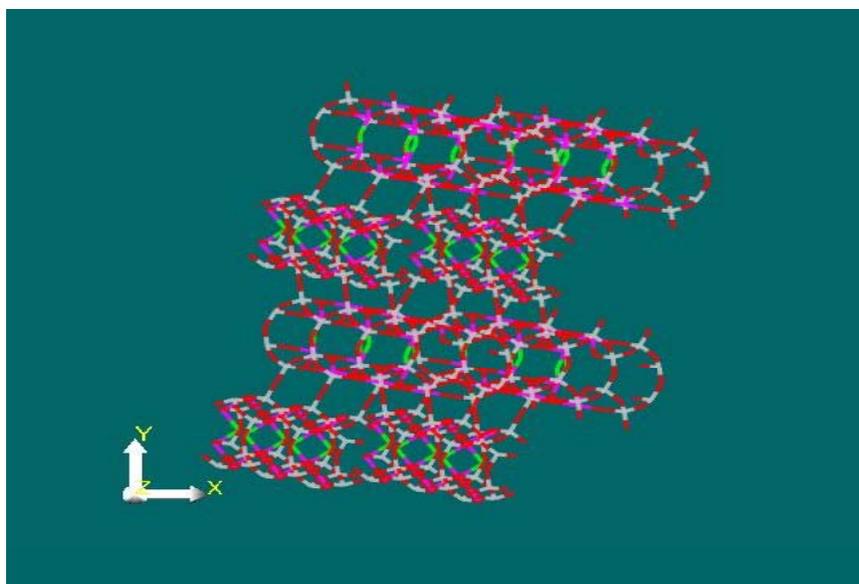

Figure 6.17 TINKER screenshot of the palaygorskite molecule

6.6.3 Potential Function

The potential function used for the simulation is the same as used in Manevitch et al. It is given in Table 3-5.

6.6.4 Simulation

 MD simulation was performed then, to observe strain of the palygorskite under different pressures. The structure was first allowed to relax under no pressure and 300K temperature. This was done for 40,000 timesteps. After that a range of uniaxial pressures were applied on the molecule along the z-axis. This was done for 20,000 timesteps, with each timestep measuring 0.1 ps. All calculations were done under 300K temperature using Beeman integration algorithm, as described in chapter 2. Using this data, a .key file for TINKER was created. Values of the last 40,000 time steps were used for calculating average strains for the simulation. Once the strains corresponding to the stresses were calculated, stress strain curve was generated. The behavior of the molecule under applied pressures could be seen using the visualization scheme of TINKER. The average time for performing one MD simulation of 20,000 timesteps was 120 minutes. This was done using a machine with Pentium IV processor, 1.4 GHz processor speed and 228 MB RAM.
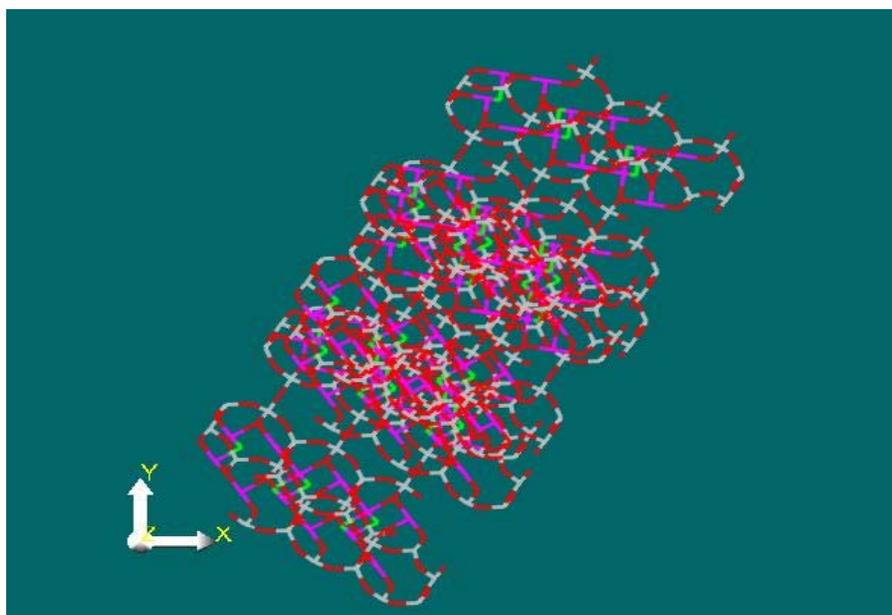
Figure 6.18 A compressed palygorskite molecule after 450 timesteps under 5 GPa pressure

6.6.5 Results

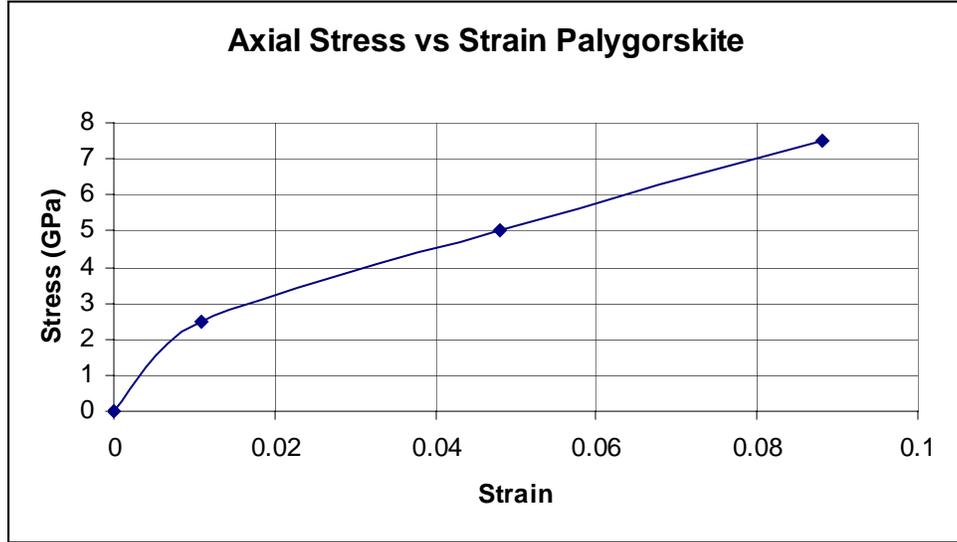**Figure 6.19 Stress strain curve for MD simulation of Palygorskite**

Table 6-7Stress strain data of palygorskite in tabular form

Stress(GPa)	Strain
0	0
2.5	0.011
5	0.048
7.5	0.088
10	0.33

Chapter 7 Conclusions

The conclusions of this study have been discussed below with respect to the objectives presented in Chapter 1. These can be listed as shown below:

1. A computational model was developed for estimating mechanical properties of rock and clay minerals at nanolevel

An already existing program for Molecular Dynamics simulation of biologic applications, TINKER, was modified for the simulation of rock and clay minerals. This was necessary because there were no provisions for uniaxial pressure applications in the existing code. The code was modified to include this feature in the software. These changes are listed below:

a) Isotropic stress calculation was done by taking average of the diagonal of the stress tensor. For uniaxial stress case, diagonal was set to zero except for the (3,3) element. This applies pressure only in the z-direction of the structure.

b) After each timestep the periodic box of the structure is modified according to a scale. The scale was modified for uniaxial stress case. It had to be changed as there was compression only in the z-direction in this case.

c) Only the z-direction of periodic box was scaled for every timestep. Other two directions had no pressure application and hence no changes in periodic box dimensions.

The source files were then compiled to obtain executables, which were then linked to the Graphic User Interface to get the modified software. This source code modification is discussed in detail in Chapter 4, section 4.7. Later on, the same code can be further modified to include various other pressure application schemes. Thus, virtually all geotechnical and rock mechanics analyses will be possible using this tool.

Once, we had a tool to analyze a structure under uniaxial pressures, it was then possible to analyze rock and clay structures using their material parameters.

2. Modified code can be applied for nanolevel simulation of rock and clay minerals

In this study we were able to apply this code for simulating rock and clay minerals. In order to do so, material parameters were obtained for these minerals. Nanoscale simulations for these minerals had been reported earlier in journals, which were studied and the material parameters were obtained from these studies. For the simulation of rock and clay minerals, following information was obtained:

1. Model: This describes the interaction of individual particles at the atomic level. A specific potential function describing the model was determined, which could appropriately determine the material behavior.

2. Material parameters: These parameters are the variables for the potential function describing the model. They are empirically determined using the macrolevel properties of the minerals.

The above information was chosen as per the previous studies of similar kinds on similar or same material. For instance, granitic rocks have been previously simulated (Ichikawa et. al. (2004)), and hence, same model and material parameters were used for our study. A guide for simulating rock and clay minerals in TINKER has been provided as Appendix A, at the end of this report.

3. The elasticity modulus values for the rock and clay minerals calculated using the modified code agree fairly well with the already known or published values

Using the modified code and the material parameters, stress strain response of certain rock and clay minerals under uniaxial pressures was generated. Elastic properties and modulus values of these materials were then derived from these responses. The values

were shown to be very close to the published or already known mechanical properties of those minerals.

(1) Simulation of Carbon Nanotube for verification

As described in Chapter 6, a (14, 1) carbon nanotube was simulated under uniaxial pressure. This was done to validate our results against already published data.

Table 7-1 Carbon Nanotube results

Material	MD simulation	Published	Source
(14,1) Carbon Nanotube	E = 980 GPa	E = 1000 GPa	Krishnan et. al. (1998)

(2) Simulation of rock and clay minerals

A summary of results along with published data is presented for comparison in the next page:

Table 7-2 Summary of results

Material	Molecular Dynamics	Published	Source
Quartz	E = 113.2 GPa υ = 0.06	E = 120 GPa υ = 0.08	Ichikawa et. al.(2004)
Albite	E = 159 GPa υ = 0.5	E = 175 GPa υ = 0.35	Ichikawa et. al. (2004)
Calcite	E = 25 GPa υ = 0.1	E = 29.8 GPa[#]	http://www.bsu.edu/web/cwjohnson2/calcite.html[#]
Kaolinite lamella	E = 167 GPa υ = 0.4	E = 192 GPa*	Manevitch et. al. (2004)*
Palygorskite	E = 94.3 GPa	na	Na

[#] The article at the given weblink presents the value of modulus of elasticity of calcite based on Indiana limestone.

* Manevitch et. al. reports the value of a Montmorillonite clay lamella to be around 192 GPa. This is of the same order for the values obtained Kaolinite clay lamella (167 GPa).

4. Lessons learnt

The main conclusion of this study is that we can use nanoscale simulations based on Molecular Dynamics to get the mechanical properties of geotechnical materials like rock and clay minerals at molecular level. In this study we have developed a model to analyze such materials at nanolevel and compared the results with already published data. Later,

we can improvise these techniques and use it to analyze these materials under different and extreme conditions.

From this study, it can be observed that molecular mechanics methods are fairly effective for estimating physical properties of minerals. Stress-strain properties of the minerals simulated agree quite well with the known properties. Also, the results match those achieved by previous researches. Molecular Dynamics simulation can thus be used and developed for further studies in this field. This study has various advantages as described in Chapter 1. Development of this tool will surely open a window of great possibilities.

The little discrepancies in the real values and the MD simulation results can be due to the following factors:

1. Outright human errors like calculation errors or wrong data input. Although utmost care was taken to avoid these errors, these might still not be completely eliminated.

2. Modeling errors: The models that were used to depict the micromolecular behavior of minerals have some inherent assumptions. These models are obviously not exact representations of the natural phenomena, but very close. Each model has its own advantages and disadvantages. Hence, this causes a little discrepancy.

3. Potential Parameters: The potential parameters chosen for a particular potential function are developed by empirical studies. They might have some inherent errors yet to be taken care of.

All these factors make MD simulation results a little different than actual experimental ones. But, the results are very reliable to a great extent. Also, they help us study the mineralogical behavior under extreme conditions, which otherwise is not possible in reality.

Appendix A

## Guide for MD simulation of rock and clay minerals in TINKER

In this guide, step by step procedures will be describes, to be followed if one is attempting similar simulations as in this thesis. Molecular Dynamics simulation is one of the many functions performed using TINKER. Here, this particular function will be the only one examined. This guide is proposed to be a reference of any future work in MD simulations of geotechnical materials using TINKER. This guide only provides operations using FFE in MS Windows operating system.

Firstly, a brief outline of the software TINKER will be given. Operating and moving around the software will be described. After that, information on how to input variables will be provided which will be followed by output analysis.

TINKER is software which was basically created to perform biological simulations. It was then modified to simulate many more types of atoms. TINKER software package has two parts; TINKER, containing the entire source files, executables and example files. The other part is Force Field Explorer (FFE), which is the Graphic User's Interface (GUI) for the software. We will deal mostly with the latter for performing a simulation.

TINKER can be easily installed in any computer working on any operating system. The self extracting package can be downloaded for free from the webpage http://dasher.wustl.edu/tinker/. These kits are from 25 MB to 55MB in size, according to the operating system.   FFE can be run by simply double clicking the shortcut icon on the desktop.

Now, let us begin with getting familiar to TINKER. A typical FFE screen looks as shown below:
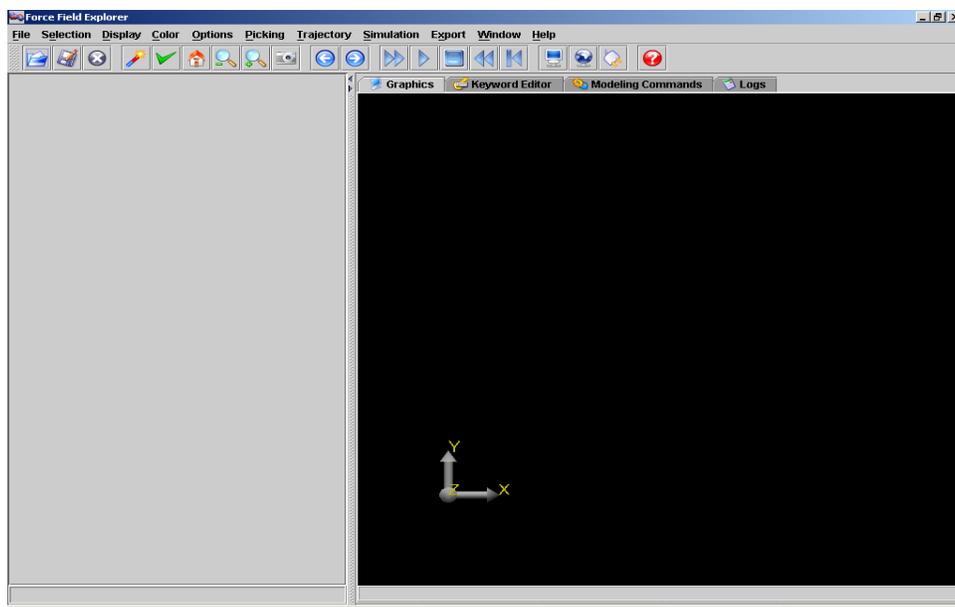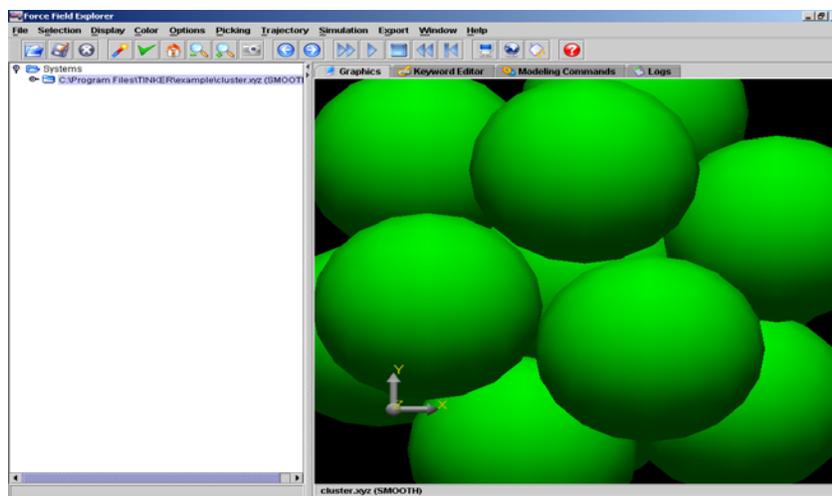
Figure A.1 FFE screen just after starting it

It shows many buttons and tabs. To open any molecule and visualize it, you have to follow the following steps:

1. Click on File>Open
2. Go to the C:/Program Files/Tinker/examples folder
3. Choose cluster.xyz file and click open

Following structure will appear on FFE screen:

Figure A.2 FFE showing a cluster of Argon atoms using Spacefill display

The above operation loads a .xyz file in TINKER, and you can visualize the structure using FFE. The structure can be roatated using left click and translated using the richt mouse click. Also, one can change the display of the atoms, by clicking on the Display tab and choosing tube, wireframe or ball and stick option. Below is an example of a ball-and-stick display for Anion.xyz in the same folder. This option shows the atoms as balls and the bonds between them as sticks.
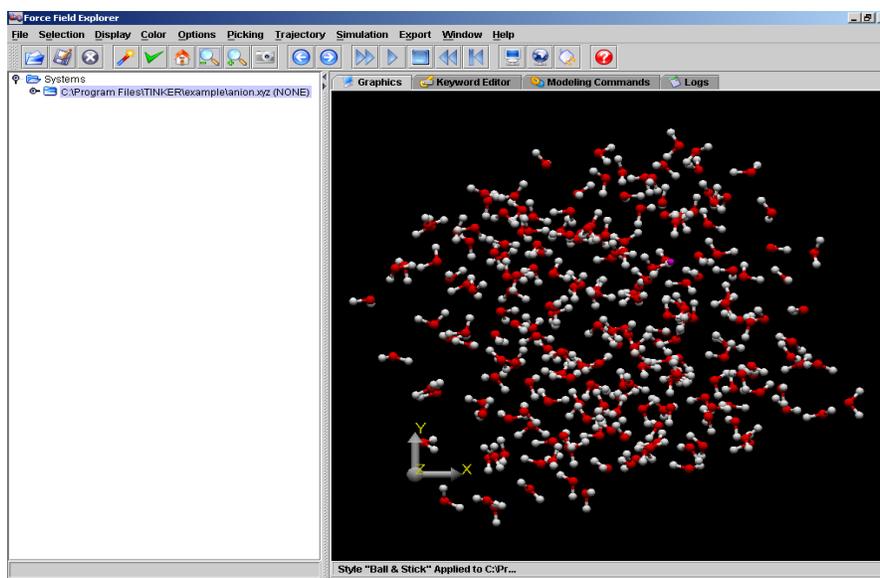
FigureA.3 Aninon.xyz using the ball-and-stick display option

These .xyz files describe the initial structure of any atom prior to the simulation. For loading these files, one also needs a .key file associated with it. This .key file describes the atom types in the .xyz file and also describes the simulation properties for the analysis to be performed. This .key file can be accesses using the Keyword Editor tab on the right side above the structure's graphics.
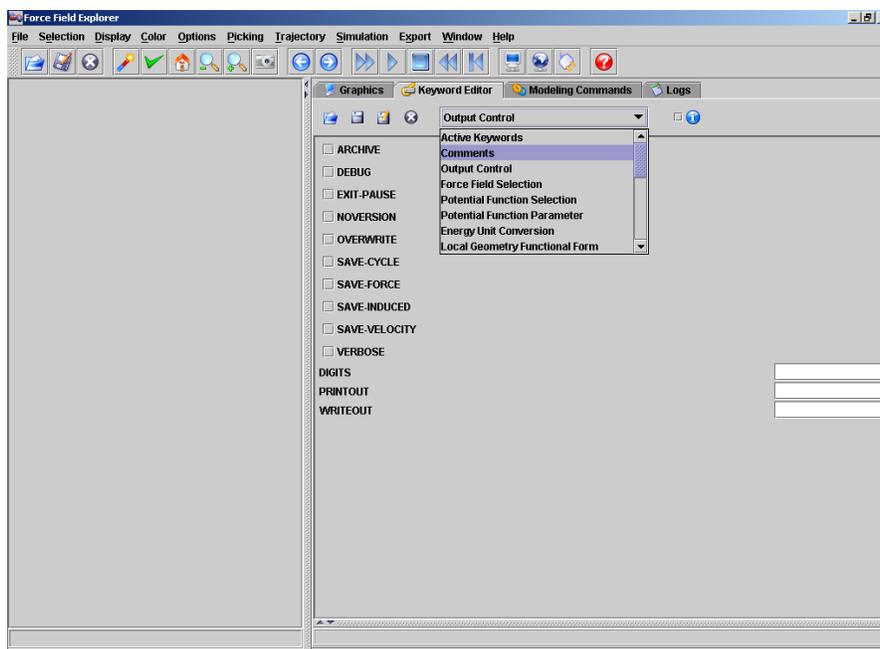
FigureA.4 Keyword Editor in FFE

This keyword editor has a list in its tab, showing various options to choose from for selecting the .key file format.

The next tab is the Modeling Command tab. This tab allows choosing the type of analysis to be performed from a list of functions. We will concentrate on the Dynamics function, denoting MD simulation function.

To run a simulation, the first thing we need is a structure to analyze. This is got by creating an .xyz file for the structure. This file when opened in a text editor looks as follows:

----

643 FEP Test Calculation (18.6216 Ang Cube, 1 Ion, 214 Waters)

```
  1 X-    7.816054    0.206446    1.620340    4
  2 O     8.975422    6.329660   -1.089552    1    3    4
  3 H     8.649951    5.996599   -0.253267    2    2
  4 H     9.802212    5.867212   -1.226637    2    2
  5 O    -5.451873    0.004527    4.941494    1    6    7
  6 H    -5.797181    0.235998    4.079279    2    5
  7 H    -5.070984   -0.865436    4.821825    2    5
  8 O     6.632490   -4.733971    4.660547    1    9   10
  9 H     5.792710   -4.284941    4.563732    2    8
 10 H     6.401614   -5.611853    4.964274    2    8
 11 O    -5.901418    3.345272   -3.248920    1   12   13
 12 H    -6.081743    3.568850   -2.335832    2   11
 13 H    -6.738690    3.029154   -3.588447    2   11
 14 O    -0.438149    4.033357    7.487553    1   15   16
 15 H    -1.223467    4.577646    7.430479    2   14
 16 H     0.271947    4.605314    7.196243    2   14
 17 O     7.484061   -8.917570    6.689538    1   18   19
 18 H     6.533105   -8.997770    6.615488    2   17
 19 H     7.770691   -8.646658    5.817367    2   17
 20 O     8.449722   -5.835494    8.965620    1   21   22
 21 H     8.586515   -6.293543    9.794903    2   20
 22 H     7.692337   -5.272200    9.124681    2   20
 23 O     0.513816   -7.770088    7.165836    1   24   25
 24 H     1.115986   -7.478267    7.850281    2   23
 25 H     1.041646   -8.343828    6.610452    2   23
 26 O    -0.244922   -7.321659   -1.095825    1   27   28
 27 H    -0.875948   -6.810932   -1.602971    2   26
 28 H    -0.704561   -7.532262   -0.283045    2   26
 29 O     8.470337   -8.161118    4.174096    1   30   31
```

30 H   8.779481   -8.841196   3.575635   2   29

This is a truncated anion.xyz file for Fig. 7.3. The first line mentions the number of atoms in the structure, and a few other details as needed. From the next line onwards, information about each atom is provided. First no. is the serial no. of the atom, followed by its atomic symbol and the x, y and z coordinates. Next, atom class number is mentioned which is defined for each atom type in the .key file. Next we have the serial number of all the atoms connected to that particular atom.

Now, once we have the structure file for the atom, we need to determine the .key file for it. For this we need to have to have the simulation properties decided. This file can be created using the FFE itself. The following steps may be followed to create a .key file.

1. Go to Keyword Editor -> Potential Function Selection.

Here we can chose all the terms we need to put according to our potential function. All these terms are briefly described in TINKER manual.

2. Potential Function Parameter

Each of the terms above has a few variables which need to be defined before proceeding to the simulation. Here you can define the force field parameters for each atom type using the spaces given. The usual convention is to mention the atom class type first, and then the parameters sequentially, as described.

Also, under this section, we describe the atom class type. Each atom type is assigned a specific number, called atom class type. This is the same number we referred to while describing .xyz file. So for each atom type, we define the atomic number, atomic weight and the valence of the atom.

3. Van der Waals functional form

In this tab, format of van der Waals function has to be chosen. It can wither be a Lennard-Jones format, Buckingham's form or Gaussian. Various parameters for these may be defined here.

4. Crystal Lattice and Periodic Boundaries

Under this tab, the periodic cell for the structure being simulated is defined. A, B and C axes denote the x, y and z cell lengths for the structure.

These are some of the most important sections under the keyword editor for creating a .key file. The name of the .xyz file should be the same as the .key file. Once, we have the .xyz and .key file ready, we are ready to perform the simulation.

5. Output file format

Using this file you can choose the format in which you want the output in. Choosing .arc output is recommended as we can view the animated version of the simulation using the .arc file.

Here's how a typical .key file looks like in text format:

Output Control
ARCHIVE

Force Field Selection
PARAMETERS   ../params/smooth

Potential Function Parameter
ATOM   175   AR   "ARGON ATOM"   18 39.948 0

CHARGE   175   0.000

VDW   175   3.361   0.2824

Random Number

RANDOMSEED   123456789

Constriant And Restraint

BASIN   2.600   0.0001

We now proceed to the Modeling Commands tab. Here we chose the Dynamics command from the list.
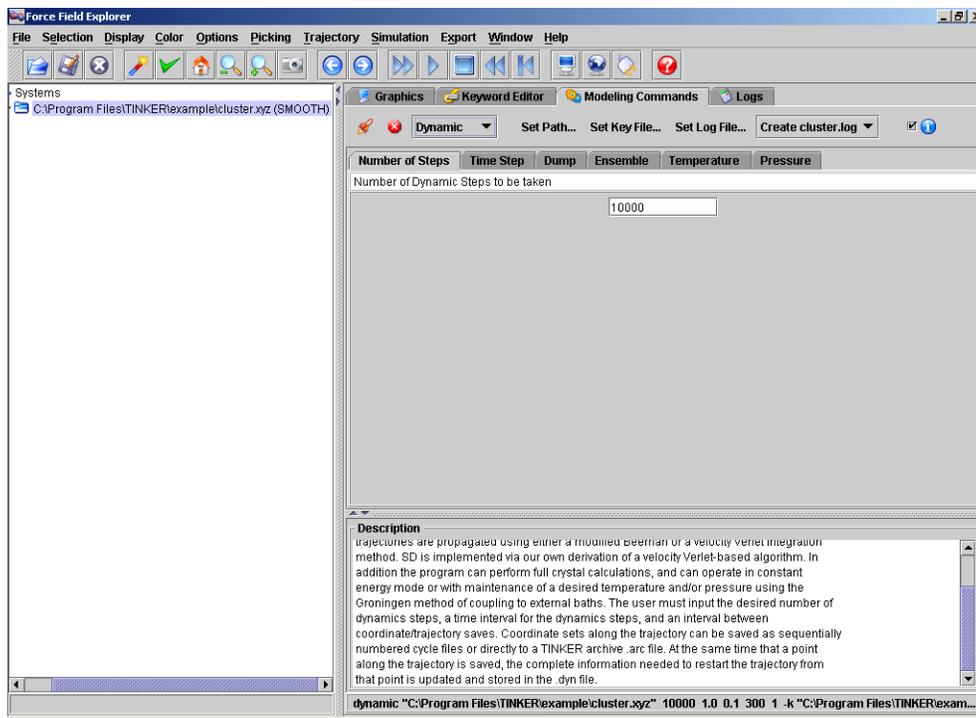

Figure A.5 Dynamic command under Modeling commands tab in FFE

Here we see a few more sub-tabs. The first one is the Number of steps, where we can mention the number of time steps we want the simulation to run. Time step value can also be entered. We can chose from four different types of ensembles. Usually we use either an NVT or an NPT ensemble. Temperature and pressure to be chosen depend on the simulation. Once, all the above values are entered, we just have to hit the left-most button, showing a rocket. This launches the command. The calculations have started and the screen looks as below:
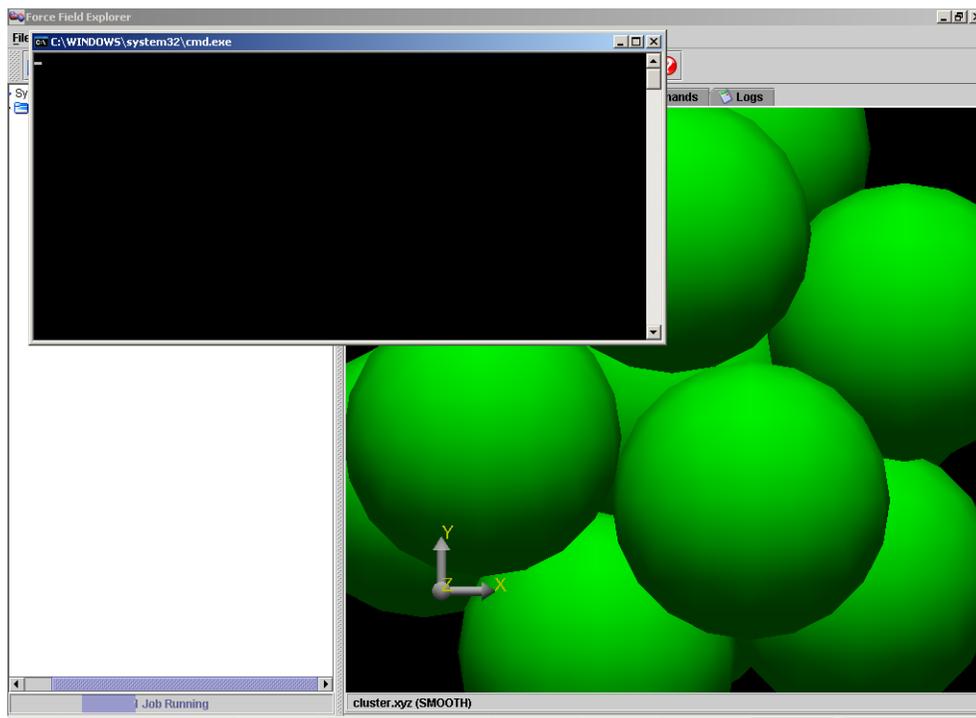
Figure A.6 A simulation running in TINKER-FFE

After some time, depending upon the computation requirements of the simulation, the simulation will stop and the results will be shown in a .log file as shown below:
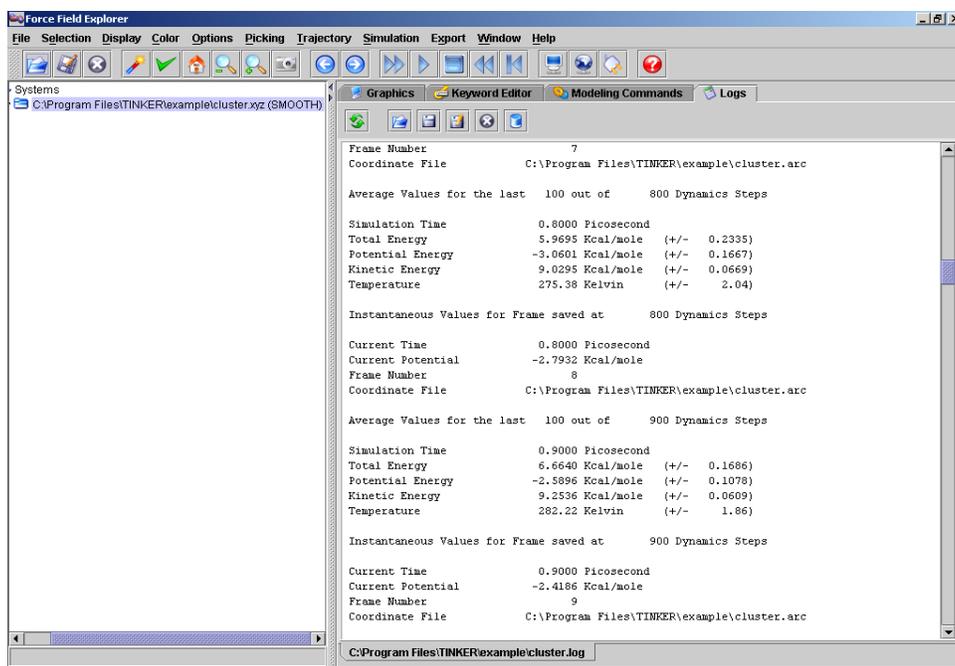
Figure A.7 A .log file showing results for the simulation performed

From the .log file we can get all the information needed to calculate the required parameters. The simulation is complete now.

Now, to view the animated version of the simulation, one just has to double click the .arc file which would have been created till now. Here we can visualize the trajectories of all the atoms as the time steps increase till the end of the simulation.

Troubleshooting

The most common problems I encountered in my simulations have been listed below:

1. The .xyz and .key file has been created but does not load. An hourglass is shown in FFE screen.

There is a problem with the .xyz input file. Pleas note that values in all TINKER input files have to space delimited. If there is a tab between the columns in a .xyz file, TINKER is unable to recognize the separation.

Another reason may be that atoms are coincident or connections are not right. But usually, this error produces a message.

2. <u>MD simulation command starts but does not stop, even after a long time.</u>

You have to manually stop the command by crossing out the DOS window.

The trouble may be due to the fact that you forgot to choose the ensemble to be used for the simulation. It may also happen if you forget to choose the algorithm to be used. If this doesn't fix the problem, refer to the next solution.

3. <u>The MD simulation command starts but does not stop. When manually stopped, the results show nothing and the last line shows:</u>

<u>Calculating molecular trajectory using Beeman/Verlet Algorithm.</u>

This problem may occur if you have something wrong with your potential functions. Choosing wrong potential parameters may cause the calculations to become unstable and thus unable to proceed.

4. <u>The log file shows some values but the value of potential energy is shown an NaN, or in stars.</u>

This may happen if you have chosen charge term in your potential function and few atoms are coincident or very close. This causes the potential energy to go to infinity thus making the solution undefined.

5. <u>The simulation runs, but even though I choose NPT ensemble, the pressure for the system never remains constant.</u>

The pressure will never attain the exact value that you have given. The average value though, of the system, will be very close to the entered value for the last few time steps.

If the value fluctuates drastically, then you may have to choose the periodic boundary conditions. This can be done by making the upper part of the structure connected to the lower, right to the left and so on. Also, you have to define the periodic cell boundaries by mentioning the, b and c axes lengths for the cell.

Chapter 8 Bibliography

Allinger, N. L., J. Amer. Chem. Soc., 99, 8127 (1977)

A. Krishnan, E. Dujardin, T.W. Ebbesen, P.N. Yianilos and M.M.J. Treacy "Young's Modulus of Single-Walled Nanotubes", Phys. Rev. B 58, 14013-19 (1998)

Cai W., (2004) "Introduction to Molecular Simulations" Course Notes, Stanford University

Fosdick, L. "Molecular Dynamics: An Introduction" Course Notes, High Performance Scientific Computing, University of Colorado at Boulder, Colorado, United States of America. (1995).

Genge M. J., Price G. D. and Jones A. P. "Molecular dynamics simulations of $CaCO_3$ melts to mantle pressures and temperatures: implications for carbonatite magmas" Earth and planetary science letters. 131 (1995) 225-238

Griebel M. and Hamaekers J. (2004) "Molecular dynamics simulation of the elastic modulii of polymer-carbon nanotube composites" Computer methods in applied mechanics and engineering. 193 1773-1788

Ichikawa, Y., Kawamura K., Uesugi K., Seok Y. and Fujii N. (2001). "Micro- and macro behavior of granitic rock: observations and viscoelastic homogenization analysis" Computer methods in applied mechanics and engineering. 191 (2001) 47-72

Liu B., Huang Y., Jiang H., Qu S. and Hwang K.C. "The atomic scale finite element method" Computer methods in applied mechanics and engineering. 193 (2004) 1849-1864

Liu W. K., Karpov E. G., Zhang S. and Park H. S. "(2004) An introduction to computational nanomechanics and materials" Computer methods in applied mechanics and engineering. 193 1529-1578

Manevitch O. L. and Rutledge G. C. "Elastic Properties of a Single Lamella of Montmorillonite by Molecular Dynamics Simulation" Journal of Physical Chemistry B 2004, 108, 1428-1435

Murray H. H. (2000) "Traditional and new applications for kaolin, smectite and palygorskite: a general overview" Applied Clay Science 17 207-221

Ponder W. J. "TINKER: Software tools for molecular design" (2004) User's guide for TINKER Version 4.2, Washington University School of Medicine, Saint Louis, Missouri, USA

Schnieders M., "Force Field Explorer: A Graphical User Interface to TINKER" (2004) User's guide to Force Field Explorer Version 4.2 Washington University School of Medicine, Saint Louis, Missouri, USA

Teppen B. J., Rasmussen K., Bertsch P. M., Miller D. M., and Schafer L. "Molecular Dynamics Modeling of Clay Minerals: Gibbsite, Kaolinite, Pyrophyllite, and Beidellite" Journal of Physical Chemistry. B (1997) 101 1579-1587

Zhang P., Huang Y., Geubelle P. H., Klein P. A. and Hwang K. C. "The elastic modulus of single-wall carbon nanotubes: a continuum analysis incorporating interatomic potentials" International Journals of Solids and Structures. 39 (2002) 3893-3906

http://www.crystalmaker.com

http://dasher.wustl.edu/tinker/

http://www.soils.wisc.edu/virtual_museum/palygorskite/index.html

http://www.soils.wisc.edu/virtual_museum/calcite/index.html

http://www.soils.wisc.edu/virtual_museum/kaolinite/index.html