# SCRATCH MODELING OF POLYMERIC MATERIALS WITH MOLECULAR DYNAMICS

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It is impossible to determine the amount of money that is spent every replacing products damaged from wear, but it is safe to assume that it is in the millions of dollars. With metallic materials, liquid lubricants are often used to prevent wear from materials rubbing against one another. However, with polymeric materials, liquid lubricants cause swelling, creating an increase in friction and therefore increasing the wear. Therefore, a different method or methods to mitigate wear in polymers should be developed. For better understanding of the phenomenon of wear, scratch resistance testing can be used. For this project, classic molecular dynamics is used to study the mechanics of nanometer scale scratching on amorphous polymeric materials. As a first approach, a model was created for polyethylene, considering intramolecular and intermolecular interactions as well as mass and volume of the $CH_2$ monomers in a polymer chain. The obtained results include analysis of penetration depth and recovery percentage related to indenter force and size.

# ACKNOWLEDGMENTS

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# CHAPTER 1

# INTRODUCTION

## 1.1 General Introduction

Wear occurs when two materials rub against one another. The phenomenon of wear is a very costly one, and one that engineers must analyze with great scrutiny to be able to mitigate the resulting effects. Polymeric materials are cheap, have low density, and are easy to manufacture. For these reasons, they continue to grow in use, often replacing parts that were previously designed and built with metals. With traditional metallic materials, external liquid lubrication is often used to help reduce the effects of wear. However, lubrication does not work with polymeric materials. The polymer will absorb the lubrication, creating swelling and an increase in wear. Other methods must be applied to prepare and accommodate for wear with polymeric materials: one piece of the puzzle is scratch resistance.

Polymer materials are widely used as surface coatings. Surface coatings are especially susceptible to surface wear and scratching. The importance of tribological properties, and in particular scratch resistance, has been outlined in previous work from our laboratory [1]. Surface mechanical properties are vital to polymer engineering; polymers are easily scratched, and this scratching can lead to material degradation through the propagation of cracks.

Polymers are viscoelastic materials; they have both elastic and inelastic properties. When they are deformed due to an external stress, they will recover a portion of their initial deformation. The degree and rate of recovery are useful information for the engineers and designers using the material; they will be able to optimize their design and plan for when the material will fail in the future. This issue will be discussed in more detail later on.

The purpose of this work is to use molecular dynamics (MD) to simulate scratching applied to polyethylene. Computational research is a growing field that offers many advantages over traditional, physical experimental research. Computational research creates results in a way that is cheaper, quicker, and more detailed. The greatest advantage of computer simulations is the ability to obtain information that is not readily available experimentally; it allows us the capability to experiment in a variety of environmental conditions, such as those of very small scales and extreme temperatures and pressures that are otherwise difficult to repeat. Furthermore, a large amount of money is routinely spent on expensive laboratory equipment for physical experiments. Computational research allows the potential to save substantial money and time. We shall find out whether improved comprehension and provided details not accessible experimentally will be achieved in this work.

By simulating scratch at the nanometer scale, scientists can gain more information on the surface wear properties of polymeric materials. Scratch properties are determined through testing in laboratories with special equipment for this purpose. It is difficult to simulate a scratch on such a small scale with physical testing. With MD computer simulations, scratching can potentially be conducted without special equipment, and at a nanometer (or atomistic) scale that is difficult, if not impossible, to reproduce in a laboratory environment. Potentially, millions of dollars and thousands of hours can be saved with the use of computer simulating scratch properties. With computer simulations, important properties can be studied more efficiently than through any other method.

Polyethylene (PE), more specifically high density polyethylene (HDPE), is used as a prototype for this study. HDPE is used for the reason of simplicity, with the intention of extrapolating the model toward any other polymeric material. HDPE consists of $C_2H_4$ monomer units. The unique part about HDPE as opposed to regular PE or LDPE is that HDPE does not have any branching. HDPE consists of chains that are continuous, without any forking of the chains. This simplifies the simulation.

A lattice based, coarse-grain model is used with statistical segments and a mesoscopic scale, pioneered by Flory [2]. The mesoscopic scale is at the nanometer to micrometer scale rather than the atomic scale. Atomistic potentials have been analyzed and used to derive the potentials which are relevant at the mesoscopic scale (sections 1.5 and 2.3). The mesoscopic scale is obtained with the use of statistical segments; atoms are grouped into physical bodies that can be analyzed.

The objectives are as follows:

1. Create a polymer material with HDPE as a model
2. Create a realistic scratching simulation of the material
3. Visualize the scratching process under consideration
4. Analyze penetration depth and recovery percentage for various values of indenter size and applied force
5. Compare MD simulations with physical experiments as much as possible

6. Finally, to determine factors that influence scratching behavior such as chain orientation, possibly indicating optimum structure for specific applications

## 1.2 Molecular Dynamics

Molecular dynamics (MD) is a method of using computer simulation to study the motion of molecules or particles. MD was developed by Alder and collaborators at the Lawrence Livermore Laboratory in the 1950s [3]. Reasons for using MD instead of other methods are discussed in section 1.3 as well as another paper from this laboratory [4][5]. The principle of MD is simple: one solves Newton's second law of motion (force equals mass times acceleration) for the interacting many-body system numerically on a computer. In general, the particles may represent any physical object that is represented by a known series of potentials. If *U(r)* is the total potential associated with particle *i* (of mass $m_i$) and position $r_i(t)$ at time *t*, the related equation is:

$$m_i \left(\frac{d^2}{dt^2}\right) \vec{r_i}(t) = -\nabla_i U(\vec{r_i}), \quad i = 1, 2, ..N \qquad \text{Eq. 1}$$

MD has been used to study mechanical tensile properties [6], dialectical properties [7], electrical properties [8], and other properties on crystalline and polymeric materials as well as many others. Molecular systems consist of billions of molecules (or more). It would be extremely difficult to predict these systems analytically due to the volume of variables that must be calculated. MD uses numerical methods to estimate molecular systems.

MD is commonly used on crystalline materials, such as metals and ceramics. With crystalline materials, the properties are dependent on the crystal structure and defects in the crystal structure, such as dislocations. This is not the case with polymeric materials, which do not have a crystal structure. Simulating polymeric materials with MD is much more difficult in comparison with metals and ceramics because there are many problems associated with simulating a polymeric material. Kurt Binder lists these issues in great detail in his book on simulating polymer materials [9].

## 1.3 Other Simulations Models, Programs and Techniques

MD is a vast field that has many areas of applications. With each application, the focus and methods used change significantly. Each simulation program has its own specifics that make it correct for the particular simulation it is used for. Therefore, aspects that may work for one program or method may not apply to another one.

There are a few other simulations programs, some of which use MD techniques similar to the ones used here. One of these is LAMMPS, an open source set of programs and codes produced by Sandia National Laboratories. Using LAMMPS, a continuum model (models and scales explained in section 1.5) is applied on amorphous HDPE to model scratching in reference to the coefficient of friction [10].

Besides the variations of MD, there are other simulation models, most notably the Monte Carlo (MC) method. While MD uses basic physics over small amounts of time for simulating, MC relies on repeated random sampling and aggregation of results. During MD, every segment that makes up the material is simulated together, in parallel, while with MC one body is simulated at a time. A third common method of simulation is Brownian dynamics, which also has been done in our laboratory to study polymer chains and their entanglements [11].

## 1.4 Polymer Physics

As already noted, polymeric materials are inherently amorphous. This means that they are not organized in a specific pattern, as is the case with metals and ceramics, which organize in crystals. Instead, they are long chains strung together by a backbone of covalently bonded chains (often carbon). These covalent bonds, along with the secondary bonds between the chains, determine the properties of polymers. Using MD, we can model these two types of bond energies to create simulations of how a polymer material will behave.

PE is a very basic polymer, consisting of $C_2H_4$ monomers strung together. This is why PE, more specifically high density PE (HDPE), is used as a prototype. A single PE chain can be modeled as $CH_3 – (CH_2)_n – CH_3$, where n is between $10^3$ and $10^6$. Figure 1 is a schematic of a monomeric unit of polyethylene. With a good MD simulation of HDPE, other polymer materials can be modeled. There are some computer simulation studies using HDPE as a model [12][13][14].

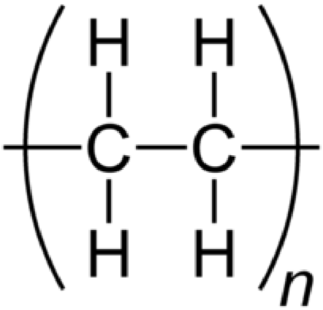


Figure 1: Monomer unit of polyethylene.

The covalent bonds between the carbon atoms have a potential energy curve that is dependent on how far apart they are from one another. This interaction is referred to as the intramolecular potential, *U(r),* as seen in Eq. 1 and 3. Similarly, monomers interact with other monomeric units that are not covalently bonded. These are secondary interactions, which is referred to as intermolecular interactions. The intermolecular interactions are much weaker than the intramolecular interactions, between four and five orders of magnitude weaker. The two types of potentials are essential for the entire MD simulation. Figure 2 and Figure 3 are models of the intramolecular and intermolecular interactions respectively. Both intramolecular and intermolecular interactions are modeled with a Lennard-Jones potential, which is explained more in later sections.

Figure 2: Intramolecular interactions between the monomers inside of a chain.

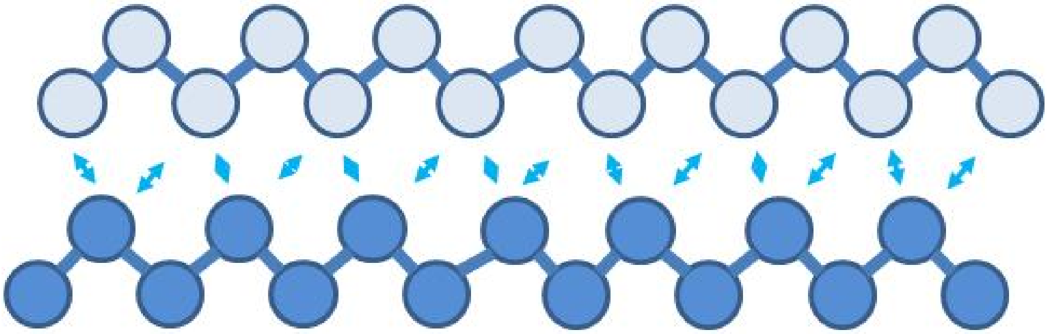


Figure 3: Intermolecular interactions between the chains.

It should be noted that although there are some simulations of purely amorphous (non crystalline) HDPE, it is extremely difficult to prepare such a material in the laboratory. Polymers are in actuality often semi crystalline, HDPE is such an example, with lamella sheets on top of one another (Figure 4).

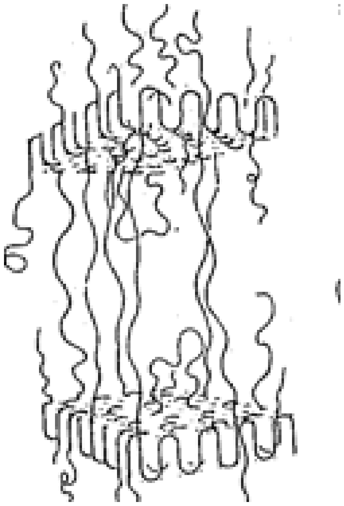


Figure 4: Lamella of PE [15].

## 1.5 Coarse Grain Model and Mesoscopic Scale

For MD simulations, there is a limitation on the time span and material size. This limitation has to do with the amount of calculation that is required to simulate every molecule (Eq. 7). It would take tremendous computer power to simulate every molecular interaction within a polymeric material.

To simulate larger scales (more than a few atoms), a coarse grain model is used. With a coarse grain model, groups of atoms are considered as one body (segment) or a pseudo atom. The coarse grain model is sometimes referred to as the bed spring model; each body has a spring -like reaction with the other bodies. This model is not to imply that the interaction is completely elastic. The spring-like intermolecular interaction is modeled with Lennard-Jones potentials.

With the coarse grain model, the first assumption used in this project is that the $C_2H_4$ monomeric unit is one body instead of four, ignoring all of the internal reactions inside of the molecule. This can be done because this project focuses on the movement of the entire material when acted upon with external forces; consequently, internal reactions between the atoms have a minimum effect. A further simplification is made by assuming a number of monomeric units into one physical body, further reducing any effects that the internal atomic interactions would have. In this case, 200 are assumed to be in one body or segment (Figure 5) as already noted before and described by Flory [2]. Each bead in Figures 2 and 3 should be considered a pseudo atom such as Figure 5.

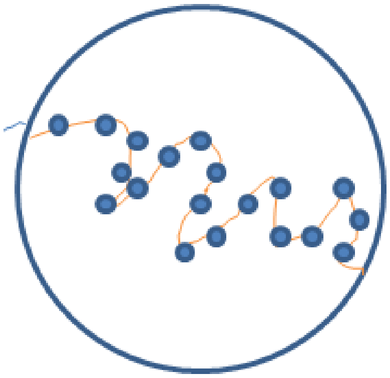


Figure 5: A pseudo atom or statistical segment in a coarse grain model. The small blue circles represent monomeric units of PE and the orange line shows the covalent bonds. The entire figure is considered as one body during the MD simulation.

With a coarse-grain model, one can simulate a larger scale over a larger time period with reasonable accuracy. The coarse grain allows the achievement of the goal: simulating scratch on a nano-meter scale. Usefulness of simulations on this scale has proven to be useful in other papers [16][17][18]. The scale is referred to as mesoscopic: it is smaller than micromechanics simulations but larger than atomistic simulations. Details of the statistical segments and model can be found in section 2.3.

Mesoscopic scale allows for the simulation of $10^{-7}$ to $10^{-6}$ meters with a time scale of roughly $10^{-7}$ seconds. Figure 6 shows this, along with other simulation and experimental methods scales. With simulations there is a linear relation with size and time; the shorter the time scale the smaller the length scale as well. For this project, one micrometer of distance is tested over the course of about ten nanoseconds.

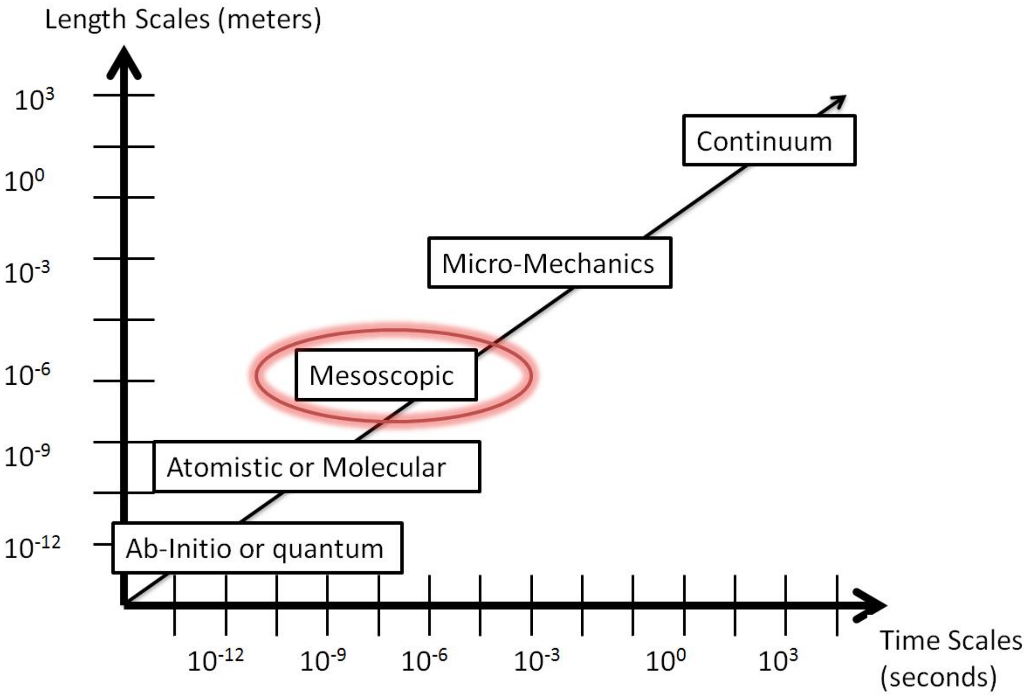


Figure 6: Length scales versus time scales for simulation and experimental scales.

## 1.6 Scratch Mechanics

In this project computer simulations are used with a MD approach to simulate scratch resistance testing of a polymer material. In physical scratch testing experiments one obtains two values: the penetration depth ($R_P$) and the residual depth ($R_h$). $R_p$ is the instantaneous depth at the moment when the indenter has hit a given location. Since we are dealing with viscoelastic materials, a recovery or healing takes place. Therefore, the residual depth $R_h$, also known as healing or recovery depth, is shallower than the $R_P$. For these simulations, analysis of $R_h$ is taken at a constant time or number of iterations (30 in this project) after the force of the scratch. The percentage of recovery is analyzed using the two variables $R_P$ and $R_h$, as in Eq. 2, where R is the percent recovery.

$$R = (R_p - R_h) * 100\% / R_p \qquad \text{Eq. 2}$$

$R_P$ and $R_h$ are analyzed in relation to the applied force and the size of the indenter. We shall see what effects of the force on the scratching depth will be and we shall also see whether the simulation results will allow us visualization of the healing process. Polymeric materials, being softer than metals and ceramics, are especially subject to scratching, often to the point of ruining the material. Therefore, it is important to analyze the mechanism of scratching.

## 1.7 Simulations Compared with Physical Experiments

There is a large volume of physical experimental tests involving polymers; some of the more recent can be found in Michler and Balta-Caleja's new book [19]. The amount of experimental information on polymeric materials, or any type of material, is several orders of magnitude larger than the amount from computer simulations. Simulations dealing with scratch and wear resistance are quite limited, and more commonly deal with crystalline materials than non-crystalline. One such report simulates scratch resistance on single crystal aluminum [20]. As expected, under an application of a load, the scratch groove can become a crack and propagate. The propagation goes along crystallographic planes, as would be expected. Polymeric materials, however, will not have crack propagation along crystallographic planes.

There are two basic ways scratch testing has been done in laboratories on a small scale: micro/nano-scratch testing machines and, more recently, tests have been done with the use of atomic force microscopy (AFM) and analyzed via scanning electron imaging (SEM) [21]. Micro-scratch testing techniques scratch polymers with an indenter 200 µm in diameter and a scratching length of a couple of millimeters [21][22]. For comparison, our simulation scratch length for this project is 1 µm and the diameter of the scratch indenter ranges from 50 nm to 250 nm. There are a few so-called nano scratch testers; however the scale used is not a lot smaller than that of the micro scratch testers [23]. Nano scratch testers have diameter tips on the range of 10 µm. However, we have not found any nano-scratch testing on HDPE.

With AFM, the scales are much closer in range. AFM techniques allow for scratching a sample a few square micrometers [24]. However, it is difficult to measure the $R_P$ and $R_h$ on such a small scale with the AFM. The depth of Rp and Rh are very small, on the nm scale, making measurements difficult. Also, the force needed for this small scale is difficult to reproduce with experiments. Many AFM techniques view the scratching with SEM instead of measuring how deep the scratch is, and how much it has recovered.

# CHAPTER 2

# SIMULATION METHOD

## 2.1 Overview

The simulation is broken down into three stages: material generation, scratching simulation with molecular dynamics (MD), and analysis of the results. First, a material must be created on a computer, which is done with a program titled Genmat (for generation of materials). Genmat has been created in our laboratory. Genmat creates the polymeric chains of the material which involves a polymerization process starting from unconnected particles (monomers, future polymer chain segments). The scratching simulation program, or simply Scratch, reads the output from Genmat and then simulates scratching using MD. However, Scratch will only output raw data on the xyz Cartesian coordinates of the particles. Two additional programs are needed to analyze this raw data: “Vis” and “Measure Scratch”. Vis is a 3D modeling program that animates the segments and Measure Scratch is used to analyze the raw data. Measure Scratch will direct us to the data points that we are interested in; the depth (y position) of the segments being scratched over time. Below is a flow chart of the multiple programs used.

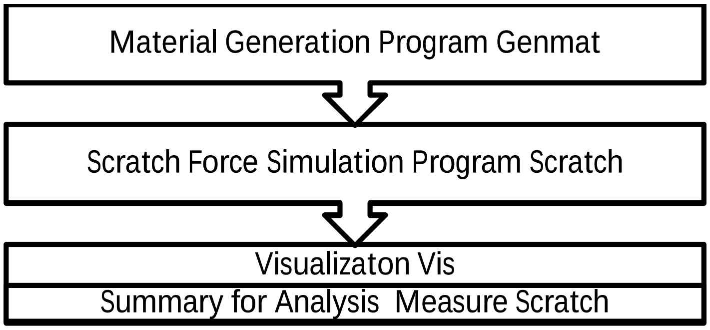


Figure 7: Flow diagram of programs used.

## 2.2 Material Generation Genmat

Genmat is a hexagonal lattice based coarse grain model polymeric material generation program. It has been developed in our laboratory over many years and has previous publications using it, although with many modifications [4][5][25]. It has three stages: lattice creation, optimization of chains, and second optimization of chains, after which the data is printed out onto data files.

The first phase, lattice creation, assigns one particle at each of the lattice points on the 3D matrix. The size of the matrix must be input from the user (a typical size is 12x12x30, but Genmat can create much larger size matrices). The second phase, also known as the first optimization phase, begins linking these particles into chains. The linking occurs in random directions, and it goes on until there are no more possible linkages between chains. The third phase, which is the second optimization phase, links together chains that have their ends next to one another. During this second optimization phase, vacancies can be created by two chains connecting and leaving one empty segment as seen in the below figure. Through these three phases, an amorphous polymer material is created. Figure 8 is a simplified diagram of the second optimization phase which shows the creation of vacancies through the process of creating longer chains.

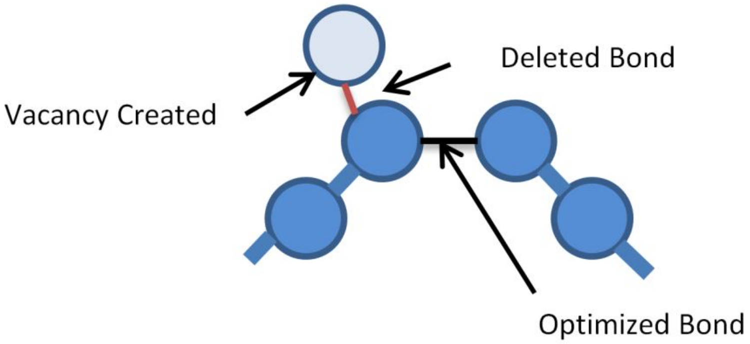


Figure 8: Simplified, 2D, diagram of the second optimization process that creates a vacancy and longer chains.

Genmat assumes a mesoscopic scale is used in association with statistical segments and a coarse-grain model. The material is created in a Cartesian space associated with x, y and z axes. The segments are close, but not quite touching each other. The bodies are considered 40 nm in diameter and the lattice is 44 nm apart for this project (other dimensions can be assumed and altered for future uses of the Genmat).

The distance between the centers of the segments is what is termed the inter-segmental distance. The inter-segmental distance is the distance at which the intermolecular forces are zero; where the segments want to be. The calculations for this distance are based on a statistical segment of PE and explained in the next two sections. Previous work from our laboratory goes into further detail of the material generation process [5][25] hence more detail on Genmat is not provided here. Below is a flow chart of the material generation program.

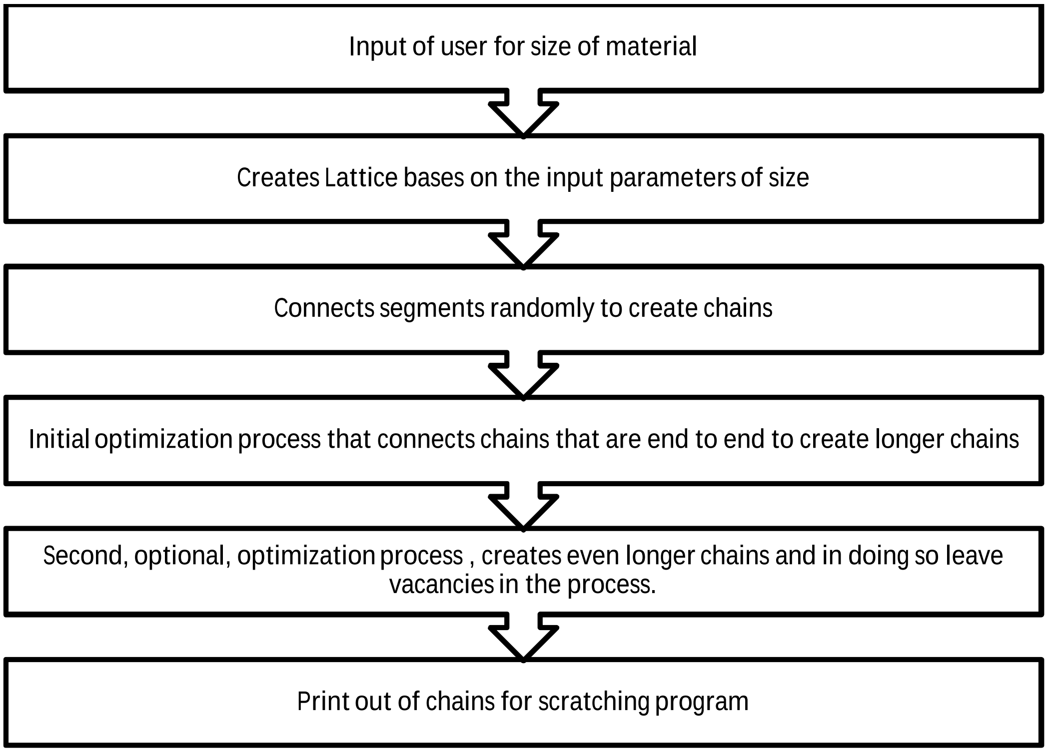


Figure 9: Simplified flow chart of Genmat.

## 2.3 Energy Potentials and Assumptions

Before going into the next step of the programming, Scratch, it is important to understand the atomic potentials used with MD, and particularly with polymeric simulation using MD. Any polymeric material is controlled by two interactions: the intramolecular, or covalently bonded interactions, and the intermolecular, or secondary bonds. As already noted in section 1.4, results are dependent on these two ineractions.

Previous work on simulating polymeric materials with MD has been done with reduced units in our laboratory [25][26]. Reduced units are not used for this project. This work is the first to attempt to use real units for distance, energy force, and time in respect to simulating scratch properties on a polymeric material with the use of MD and on a mesoscopic scale. In doing so, potentials for a polymeric material (HDPE as explained previously) must be assumed as well as molecular distances and weights.

Scratch uses the potentials to calculate the forces on each individual segment. For these simulations, both the intra and inter-molecular potentials are calculated with a Lennard-Jones potential:

$$\mathrm{U(r)_{intra/inter}} = 4 \in [(\sigma/\mathrm{r})^{12} - (\sigma/\mathrm{r})^{6}] \qquad \text{Eq. 3}$$

Here, *U(r)* is the energy of the bond in relation to the distance of the bond (r), ∈ is depth of the potential well and $\sigma$ is the value for which *U(r)* is zero, known as the collision diameter. The Lennard-Jones potential was first published by Gustav Mie in 1903 [27], and later popularized by Lennard-Jones in the 1920’s [28]. The Lennard-Jones potential is one version of the Mie potential; where the terms are 12 and 6, which is the case for this project. The Lennard-Jones is often used in computer simulations because of its relative ease of computation and simplicity. It has proven over many years to be a good approximation.

During MD the forces acting on the bodies are taken as:

$$\mathrm{F(r)} = -\mathrm{dU(r)/dr} \qquad \text{Eq. 4}$$

The total force on a segment is from the total of all the neighbor potentials and the external scratching force produced by the indenter as in Eq. 5.

$$\mathrm{F_i^{total}} = \sum_{\mathrm{i}}^{\mathrm{intra/inter}} -\frac{\mathrm{dU(r)}}{\mathrm{dr}} + \mathrm{F^{ext}} \qquad \text{Eq. 5}$$

Here, $\mathrm{F_i}$ is the force acting on segment *i*, $\sum_{\mathrm{i}}^{\mathrm{intra/inter}} -\frac{\mathrm{dU(r)}}{\mathrm{dr}}$ is the sum of all of the inter- and intra- forces from the neighboring segments, and $\mathrm{F^{ext}}$ is the external scratching force applied on any segments under the indenter. The intramolecular interaction is often studied and well defined in the scientific community; It consists of a single C-C covalent bond with the values of $\varepsilon$ = 334 kJ/mol and $\sigma$ = 154 pm. The intermolecular interaction is a much weaker force and as a consequence much more difficult to evaluate. It is often studied in the gaseous state for methane. Approximations generally range around the values of $\varepsilon$ = 627 J/mol and $\sigma$ = 400 pm [14][29][30].

As mentioned before, simulations repeated here have been performed on a mesoscopic scale, not an atomic scale. This means that the program applies to statistical segments, each of which represents a number of real segments. Figure 5 (section 1.5) shows a model of pseudo atom or statistical segment.

Two hundred monomers stretched out in a straight line would be just over 60 nm in length. However, the monomers are not assumed to be in a straight line. 40 nm is assumed to be the average diameter of a statistical segment ($\sigma$) thus taking into account reversal of direction of each chain. In this way, we consider the intra-segmental zero potential distance to be 40 nm i.e., $\sigma_{intra}$ = 40 nm. The intra-segmental force zero value is equal to 44 nm. The zero force value is equal to $2^{1/6}\sigma$ when using the Lennard-Jones potential.

For the inter-segmental zero force value, we calculated the amount of free space in PE as 11 percent [31]. Therefore, a value of 44 nm is used as the inter-segmental distance. This represents the distance between the segments when they start out on the lattice. Due to the intra-segmental distance being shorter, those bonds will collapse, a process that will take place during the initial equilibration stage. This implies that the material will shrink a little during the equilibrium phase. Below is a table of the values used for the simulations, with consideration for the statistical segments.

|  | Type | ε (kJ/mol) | $\sigma$ (nm) | $r_{cutoff}$ (nm) |
|---|---|---|---|---|
| Intramolecular bond | Covalent | 334 | 40 | 70 |
| Intermolecular bond | Secondary | 0.63 | 44 | 77 |

Table i: Values used for the Lennard-Jones interactions of the simulation.

These two potentials, inter- and intra- molecular, must be calculated at every time step for every segment. The intra-segmental bond is simple: each bond has a force on the two segments involved in the interaction. For the inter-segmental interactions, every segment theoretically has a bond with every other segment minus the one or two it is directly bonded to. Calculating this bond between every segment would be very computer intensive and also not necessary; the forces drop too close to zero rather quickly. Therefore, a cutoff distance is used (as seen in Table i). If two segments are further away than the cutoff distance, an intermolecular interaction is not calculated. For these simulations, a cut off distance of 1.75 times the inter-segmental distance, $\sigma$, is used. Eq. 5 shows the energy potential (U(r)) with relationship to the distance apart of the segments (r).

$$\left\{\begin{matrix} \text{if } r < r_{\mathrm{cutoff}}\text{: } U(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{-12} - \left(\frac{\sigma}{r}\right)^{-6}\right] \\ \text{if } r \geq r_{\mathrm{cutoff}}\text{: } \quad U(r) = 0 \end{matrix}\right\} \qquad \text{Eq. 6}$$

A cutoff distance is also used for the intramolecular bonded segments. When the intramolecular bond has the energy equal to zero, the bond is essentially broken. If a covalent bond is moved pass the cutoff distance, we then consider the bond broken. This process creates two chains from what was one chain.  If the external scratching force is sufficient, the bond does break. Figure 10 shows the potentials in relation to distance. Given Eq. 4, Figure 11 shows the forces corresponding to the potentials used.

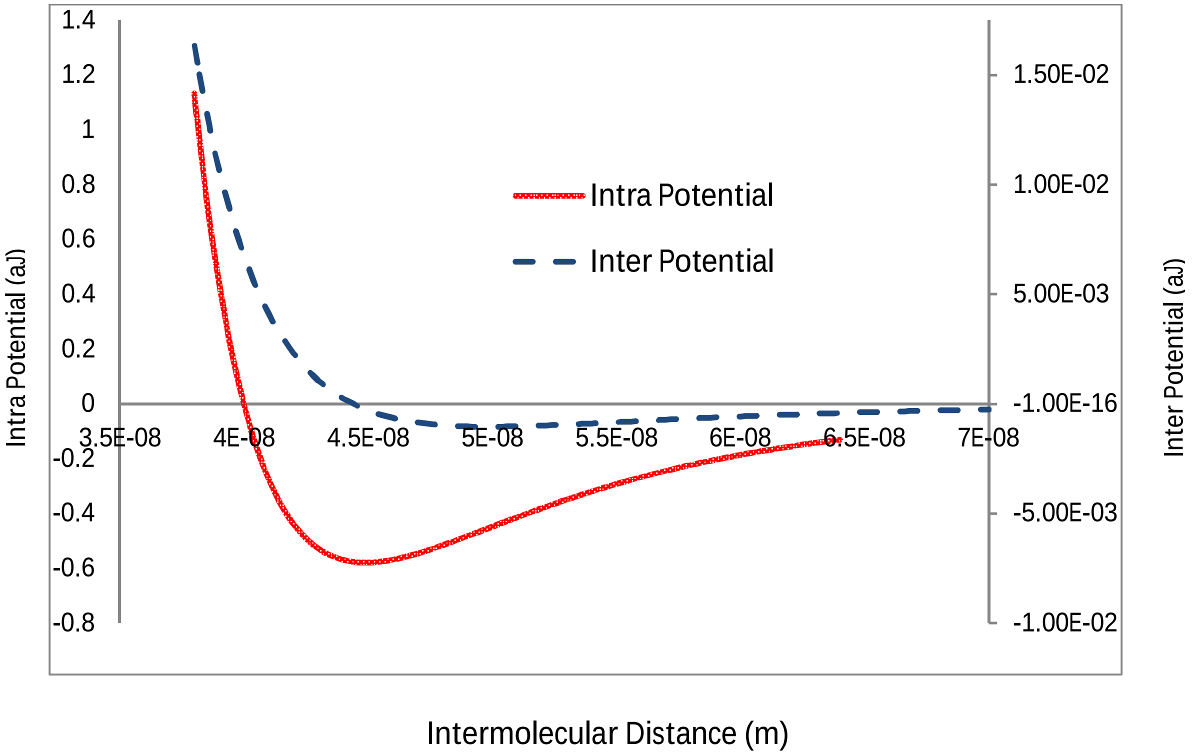


Figure 10: Potential energies of the intra-molecular bond and inter-molecular bond.

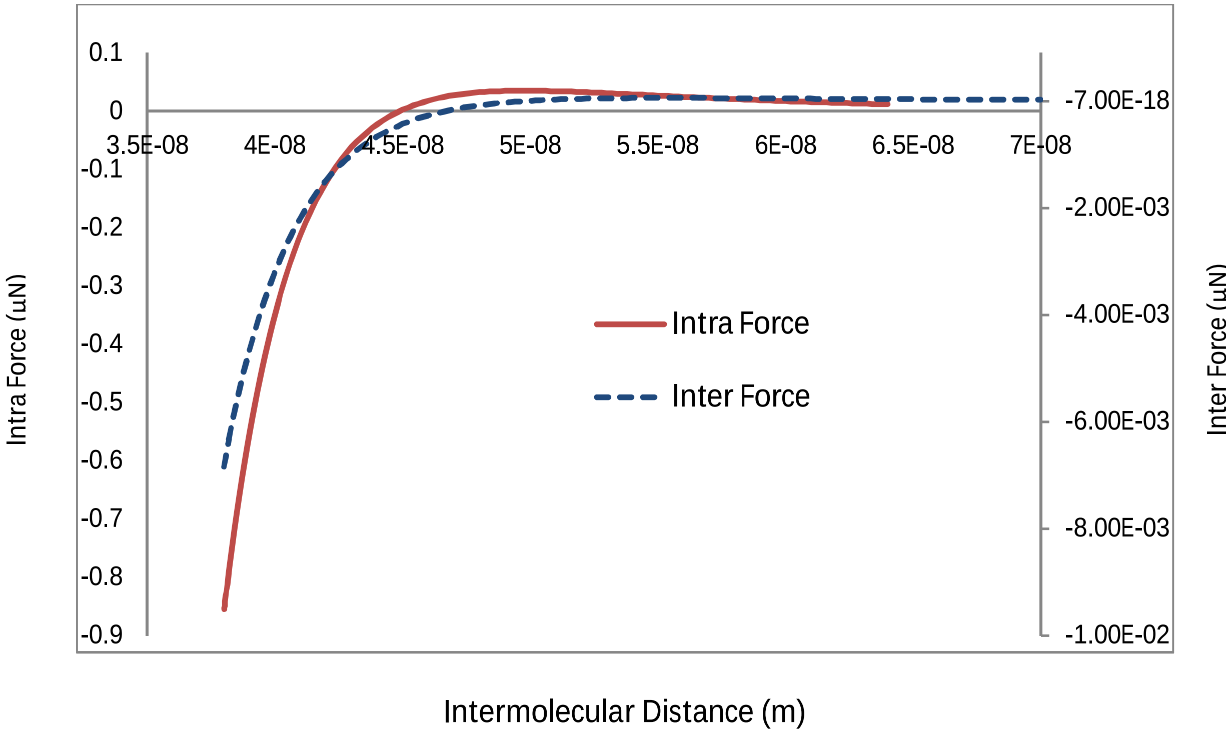


Figure 11: Intra and intermolecular forces in relation to distance.

The combined mass of all monomers constituting a statistical segment (such as 200 real segments) is considered as the mass of a segment. This mass is used in Newton's second law of motion for each segment:

$$F_i = m_i a_i \qquad \text{Eq. 7}$$

When representing a material in simulations, we have to capture essential features of the material, making plausible the assumption of one statistical segment having 40 nm in diameter and containing 200 $C_2H_4$ monomeric units is one such assumption. Each new simulation requires custom simulation procedures that work best for a given particular material property or representation of a particular type of experiments. In principle, a model can be designed that accounts for every electron, atomic, and nuclear potential presenting a given material. This model is termed ab-initio after the Latin term for “from the beginning”. However this model takes tremendous power to be able to simulate more than a few atoms. On the other hand, in the opposing limit, a model could be designed that will be able to give estimates on a much larger scale, e.g. the wing of an airplane. This model is referred to as the continuum model. However, this model has to make many assumptions, and will not be accurate on the micro-scale. For the programs in this project, the scale is limited to a few micrometers. Accuracy cannot be assumed within the limit of a nanometer, and simulating more than a couple of micrometers is not feasible.

The chains generated in these programs are linear: no branching or crosslinking. Thermoset polymers include crosslinks, which increase the hardness of the polymer. The present material generation program is limited to thermoplastic materials with no branching as of now.

## 2.4 MD Scratching Simulation “Scratch”

Using the material created with Genmat discussed in section 2.2 and the potentials discussed in section 2.3, Scratch uses MD to simulate an external scratching force on the material. Scratch requires at least two inputs: the force applied and the size of the indenter. Scratch is capable of changing other variables for future research such as: the speed of the scratch, the simulation time after the scratching force is through (zero force iterations), the geometry of the indenter, the potentials used for the material along with other properties of the material. From this information, the displacement in x, y, and z are calculated from the negative derivative of Eq. 8:

$$dx_i = F_i dt^2 / m_i \qquad \text{Eq. 8}$$

The segments move according to Eq. 7 and the addition of the external, scratching, force as in Eq. 8.

Genmat produces a material with particles (pseudo-atoms) that are initially sitting on the lattice positions. Scratch moves these pseudo atoms away from their initial positions first within the equilibrium/perturbation stage and then further more during the simulation of the external scratching forces. Figure 12 shows an example of a two dimensional material starting out on the lattice and moving away during initial equilibration. Figure 13 shows a three dimensional material before it has been scratched.

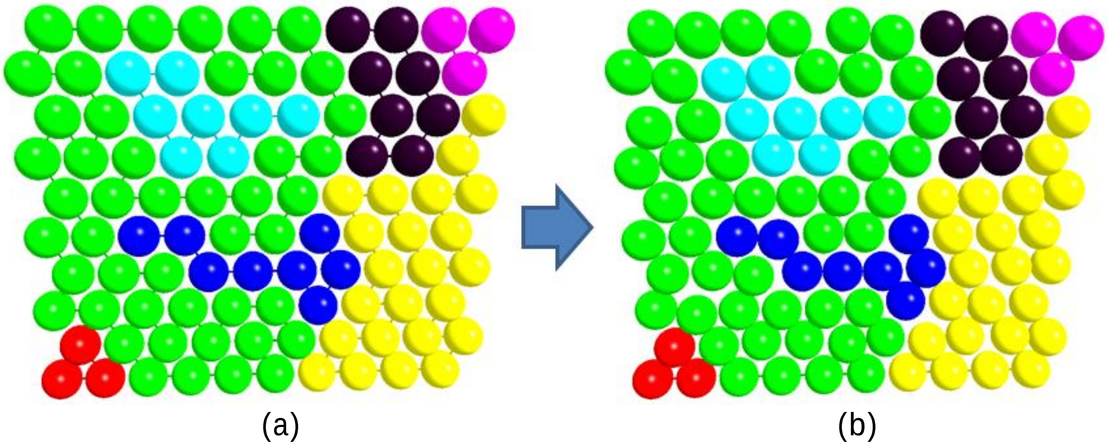

(a) (b)

Figure 12: A two dimensional lattice material on a lattice (a) and after equilibrium stage (b). Each color is a unique chain.

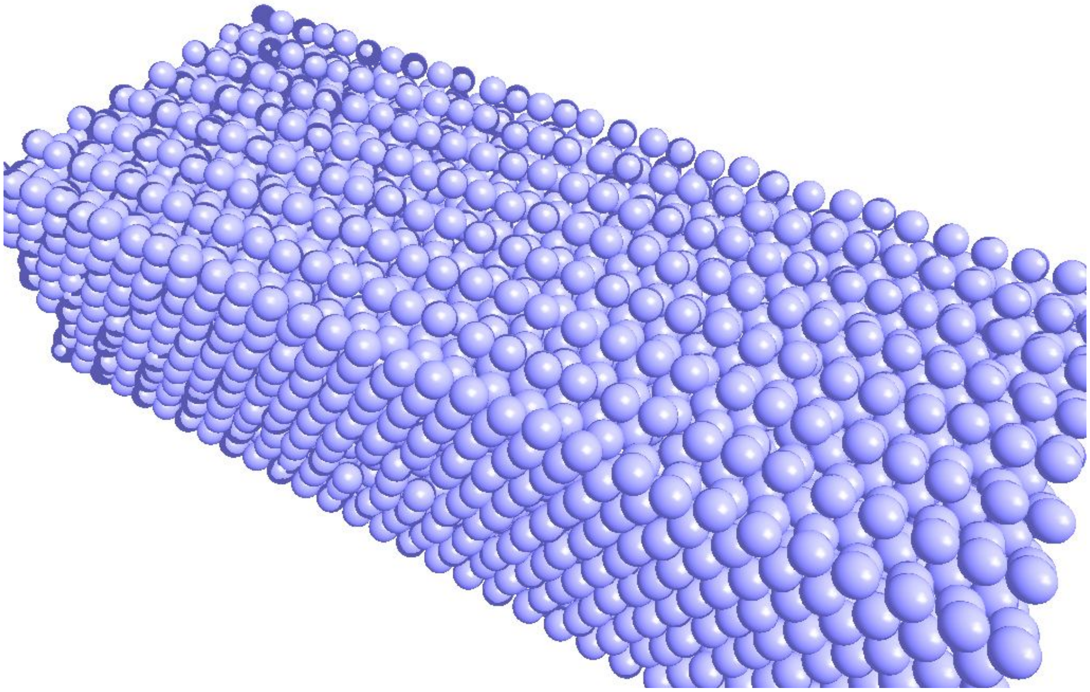


Figure 13: A three dimensional material after equilibrium stage but before scratching force applied.

To simulate a bulk material, further assumptions are made in the Scratch. The bottom row is locked, the segments on the bottom row will not move in any direction. This prevents segments from falling under the material and can be thought of as the substrate on which the material is situated. Precaution must be taken to ensure that this bottom row is a large enough distance away from the segments being scratched with the indenter so that it does not affect the results. Also, virtual boundaries along the sides are introduced; a sort of bounding box. This prevents the material from flattening out during the scratching process. The segments along the edge can move in any direction, unlike the locked bottom row, but cannot move passed the boundaries. This can be thought of as simulating a small section of material in the bulk. It is used in place of the period boundary condition that is commonly used in atomistic MD. Similar to the locked segments on the bottom row, the indenter is kept several segments away from the edges. Figure 14 displays the locked bottom row and the virtual boundaries along the x and z axes. Figure 15 is a top view of the material, showing how the scratching force is applied and also showing the virtual boundaries.

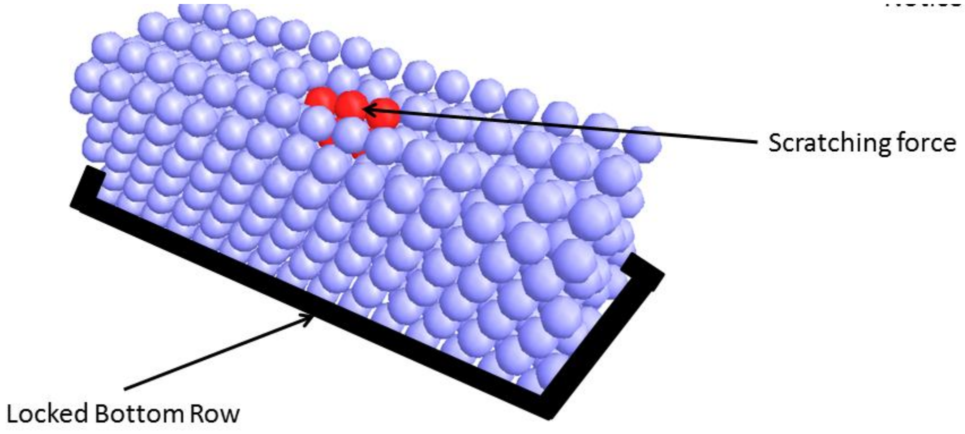


Figure 14: Example of material showing the locked bottom row and the scratching force in red.

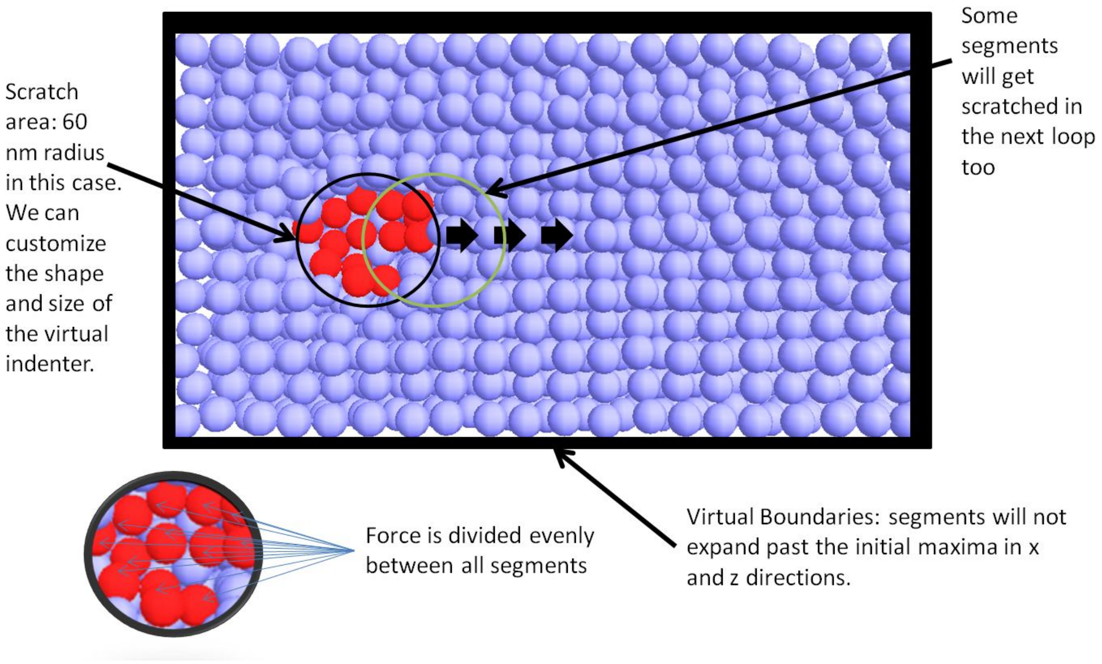


Figure 15: Top view of material being scratched.

Scratch runs through what are called time steps and iterations or loops. Time steps are considered as *dt* in Eq. 1 and 8. After each time step the coordinate positions of every segment are calculated. Each time step corresponds to five pico seconds (i.e., $dt = 5$ ps). An iteration is thus equivalent to 2000 time steps, thus one iteration is equal to 10 ns. After each iteration, output files are produced for visualization and analysis. Before the material is scratched with any external force, it goes through many iterations so as to achieve an equilibrium stage.

External forces are applied to simulate the scratching. The segments on the top, middle, row are met with an external force. The number of segments depends on the size of the indenter. The force is divided evenly between all segments that are being scratched. Initially, only the segments on the top row are acted upon with the external scratching force. If the force is enough to penetrate to deeper rows, other segments are added to the total number of segments being scratched. The scratching starts a few columns away from the far left side and proceeds to the right. The force moves every iteration. Many segments will be scratched in multiple iterations, depending on the size of the indenter. After the scratching has been completed through the material, 30 iterations are simulated afterwards. This is done to see the recovery of the material. Figure 16 diagrams Scratch.

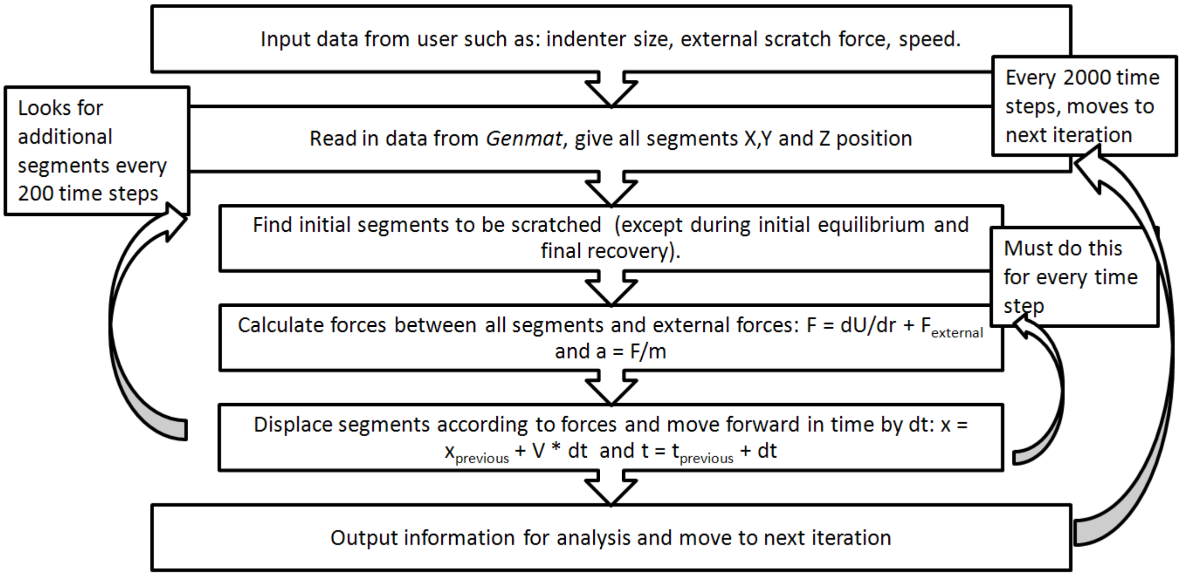


Figure 16: Flow diagram of Scratch.

## 2.5 Visualization and Analysis Programs: “Vis” and “Measure Scratch”

Scratch outputs many files that provide large amounts of information on the chains and where they are located. Vis and Measure Scratch are needed to read and evaluate this data. Vis lets us see what is going on during the simulation visualizing the material as it goes through the simulation. This explains what is going on during Scratch. Vis is where the images of the material are shown before they were created and it has the ability to show us the entire material, or just individual chains. All previous images of the material are taken via this program. Figure 17 is an example of Vis and the control box for the program.

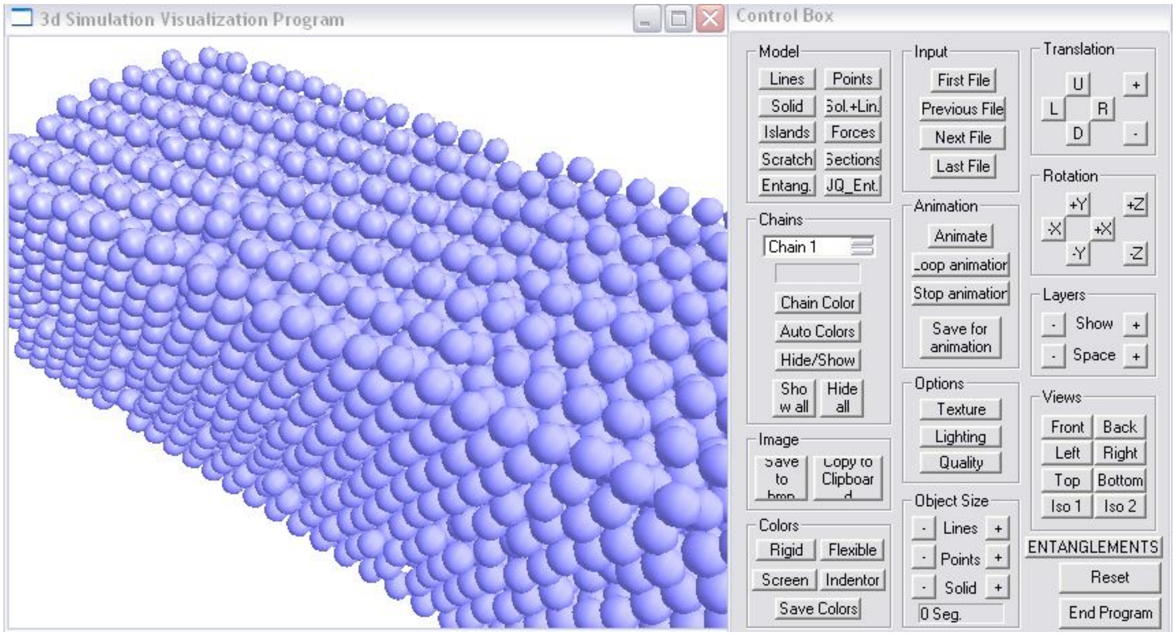


Figure 17: Screen shot of Vis and control box.

Although Vis provides large amounts of information about a material, it does not produce any data to evaluate. For summary data of $R_P$ and $R_h$, Measure Scratch is used. Measure Scratch filters all of the output files in order to be able to create spreadsheets for analysis. Measure Scratch reads all of the individual simulations step files, calculates static and dynamic properties, and exports to a simple character-delimited text file.  All of the following results were analyzed with Measure Scratch.

The main task of Measure Scratch is to show how the depth of the segments changes in relation to the rest of the material i.e., how far the segments were pushed by the external force. This is measured by the average of the all the segments pushed during each scratching iteration. First the absolute y values are taken, and averaged for each group of segments. Since the interest is not the absolute position, but relative position from the starting point, the original (max) y position is subtracted from all of the positions. The maximum position for any group of segments will be zero; the top of the material. The values for one group of segments do not, necessarily, correspond with the values for the neighboring segments, though they will be very close because all of the segments start at the top of the material and the material has relatively uniform surface.

The residual (or healing) depth, $R_h$, and recovery percentage (R from Eq. 2), must be taken at a fixed number of time steps after the scratching force and not at the last time step. Otherwise, if $R_h$ is taken at the last time step, then the first segments will have more time to recover than the last segments. After 30 iterations, R is less than one percent per iteration. Figures 19-22 in section 3 are examples of the output given from Measure Scratch, graphed out onto a spreadsheet.

# CHAPTER 3

# RESULTS

## 3.1 Overview

The depth resulting from the indenter application over time is analyzed. The depth will peak while being forced down through the scratch and then recover over time. Analysis of this process is performed. Three values followed are those defined in Eq. 2: penetration depth ($R_P$), residual depth ($R_h$) and percent recovery (R). $R_P$ is the distance between the initial y position and minimum y position during the simulation. $R_h$ is the difference between the initial y position and the position 30 iterations after the indenter has reached its maximum depth ($R_P$). R pertains to that position after 30 iterations.

Two variables have large effect: applied force and indenter size. The larger the indenter area, the more the force is distributed among the segments. Comparisons are through variations of force and indenter size. The indenter size has a minimum diameter of 80 nanometers, which is double the diamter of one segment. This minimum size is to ensure that at least one segment is under the indenter at all times.

## 3.2 Selected Example of Visualized Scratch

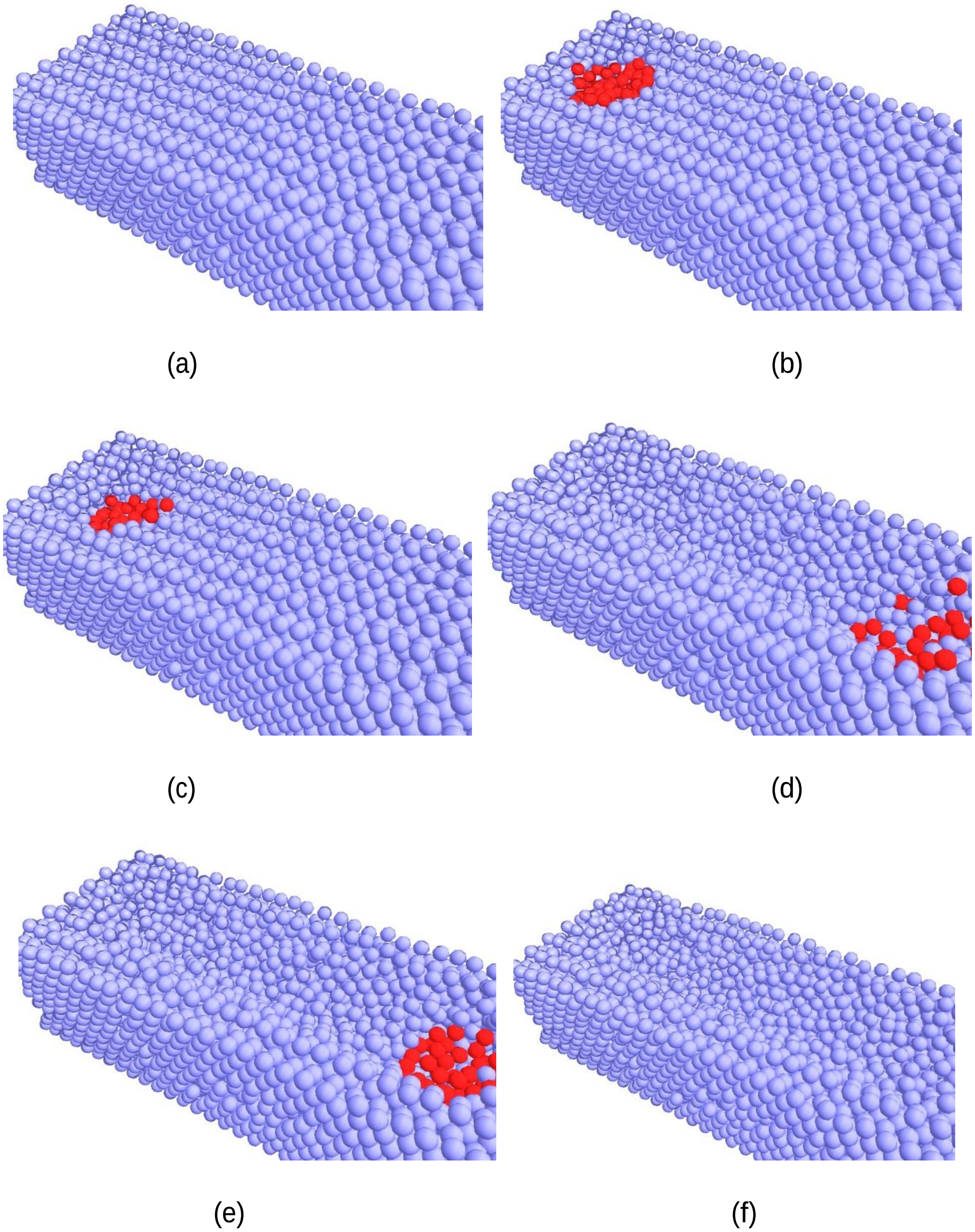

(a)
(b)
(c)
(d)
(e)
(f)

Figure 18: (a) before equilibrium, (b) first force iteration, (c) second force iteration, (d) second to last force iteration,(e) last force iteration,(f) after ten zero force iterations.

Figure 18 shows examples of the scratching process. The example shown is a relatively small material, with ten rows, 15 layers and 30 columns. The indenter size is 245 nm and the force is .75 nN.

### 3.3 Scratching Depth over Time

The scratching depth over time graph is the most important. We thus provide information that is otherwise impossible to see in lab experiments; in a lab experiment one only gets two data points, $R_P$ and $R_h$, instead of the whole process. Here, we see the segments to be scratched over time, a great advantage for simulations. Initially, we see the top of the material, which is not perfectly even. Then, the segments will dip down while they are being forced to do so by the indenter. The segments will tend to slightly drop when the indenter is just before (and after), being dragged down with the neighboring segments. After the indenter stops forcing the segments down, the material will start to recover, moving towards its original position. If the material is completely elastic and it is given an infinite amount of time, the material would fully recover. On the other hand, if the material is completely inelastic, the material will not recover at all, having an $R_h$ equal to $R_P$. Since HDPE is viscoelastic $R_h$ will be somewhere between the initial depth and $R_p$. With MD, it is not feasible to give the material infinite time to recover, thus $R_h$ is analyzed at 30 iterations after the indenter has stopped. Figures 19 through 22 provide several examples of the data obtained using Measure Scratch.

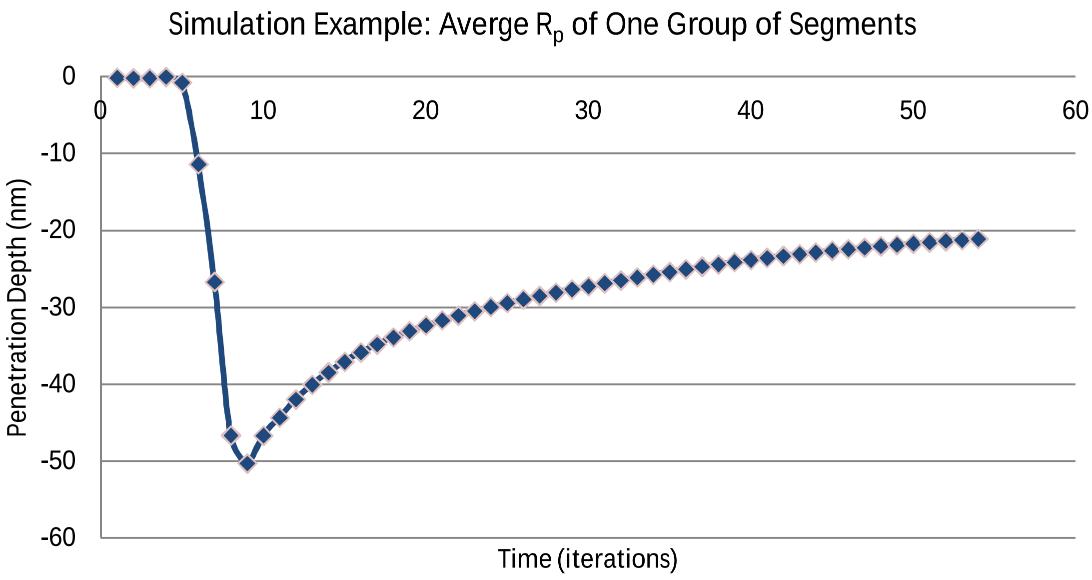


Figure 19: Average $R_P$ of one group of segments over time. This group of segments starts at the top of the material, then is forced down with the indenter and then recovers over time. $R_p$ is easy to identify in this figure, being the bottom of the peak (about -50 nm), as is $R_h$ (about -25 nm).

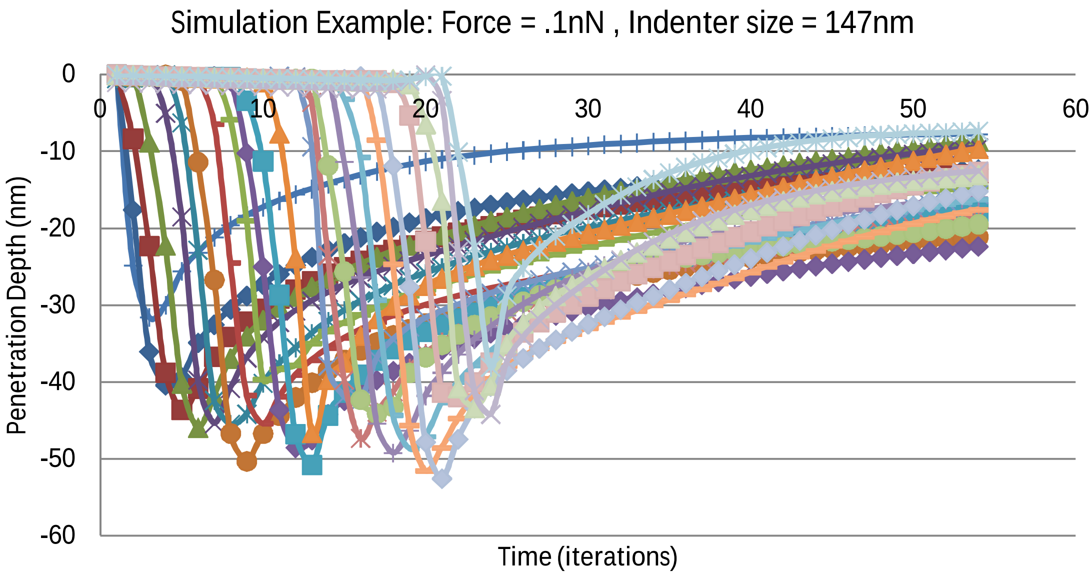


Figure 20: An example of analysis program output. The lines represent the position of an average of segments that are under the indenter at a given time. The segments penetrate downwards with the indenter, and then recover over time.

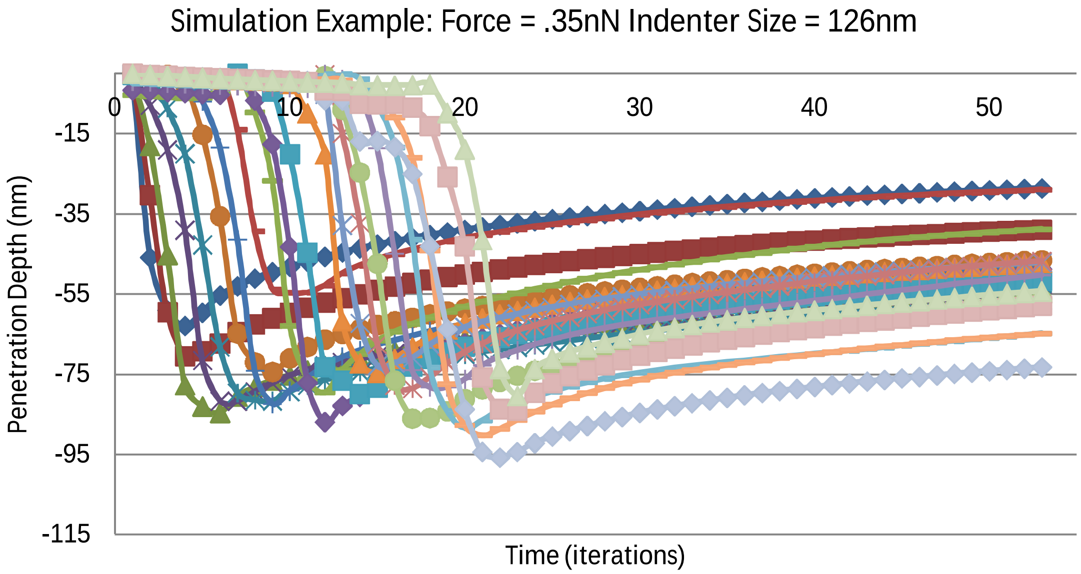


Figure 21: A second example of data given by the analysis program with different parameters and on a different material.

## 3.4 Penetration Depth of all segments at given time

Using the same data, another viewpoint of the scratch can be produced. In the first model, the lines represent the dependent, y, as a function of time, while in this one the functions represent a section of the material (i.e., y as a function of x). In these graphs, the lines represent time instead of segments. This is akin to looking at the top of the material at a given time. With these graphs, we are able to see how the material evolves over time; seeing the wave of material dips and recoveries. Looking at all of the times on a single graph can be confusing, so selected times are shown including: the initial time before any scratching force has been applied, a point in the middle of the scratch, a point right after the scratching has been completed and a final point after the material has had time to recover, as shown in Figure 22.

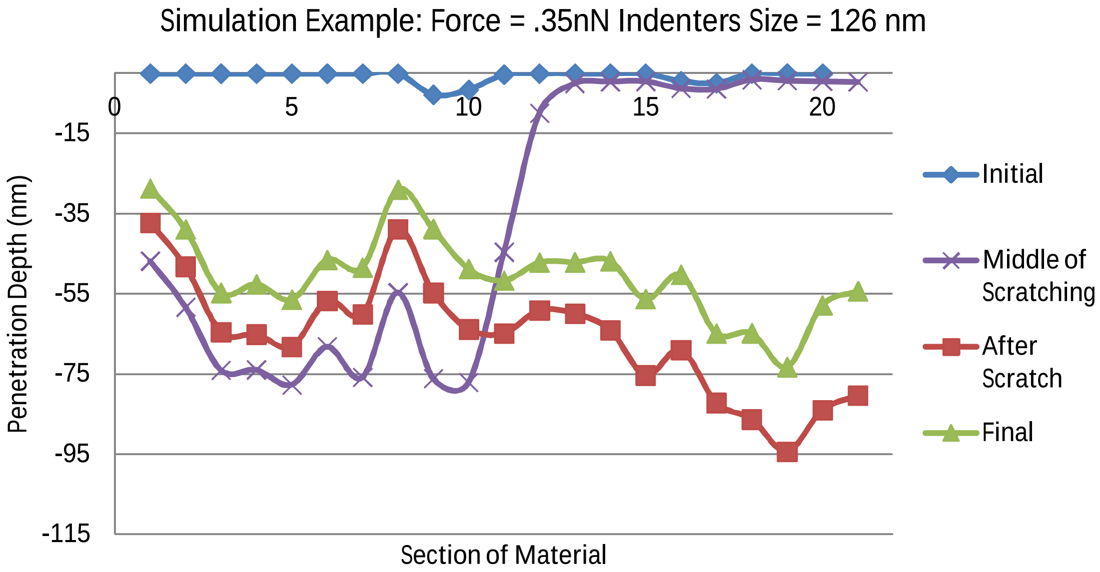


Figure 22: A look at the scratching of the material at different times.

## 3.5 Summary of Data

Below are figures taking into account all of the data for a given material and summarizing the $R_P$, $R_h$ and R. This is done in two ways: one by keeping the force constant and looking at it as a function of indenter size; the other by keeping the indenter size constant and looking at the function of force applied.

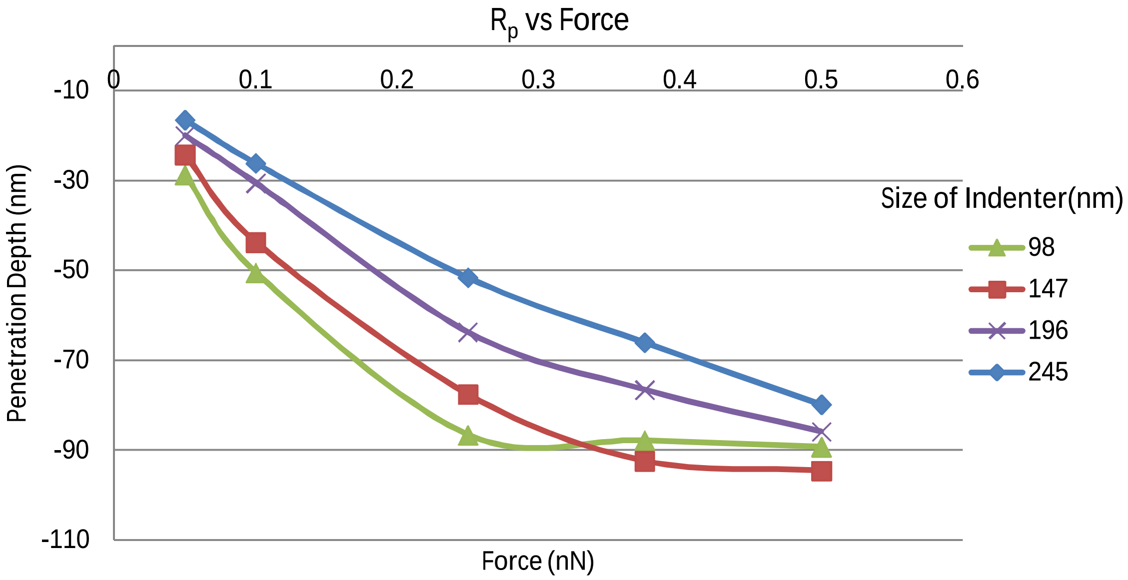


Figure 23: Penetration depth as a function of external scratching force applied for material one with four different indenter sizes. With increasing force the $R_P$ also increases in a mostly linear fashion.

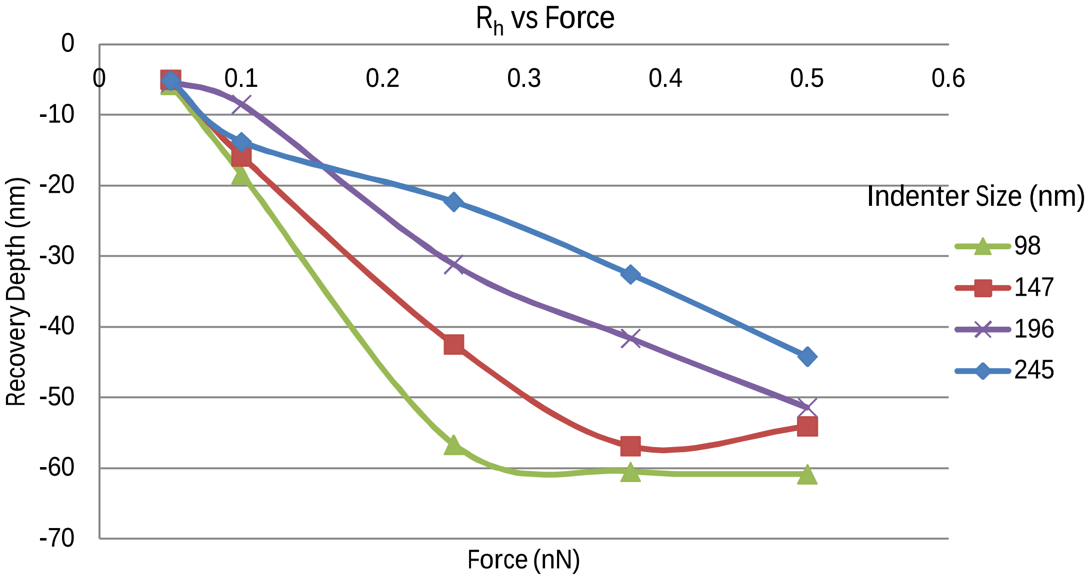


Figure 24: Residual depth of material one as a function of the external scratching force applied with four different sizes of indenter. As with $R_P$, with increasing force the $R_h$ also increases in a mostly linear fashion.

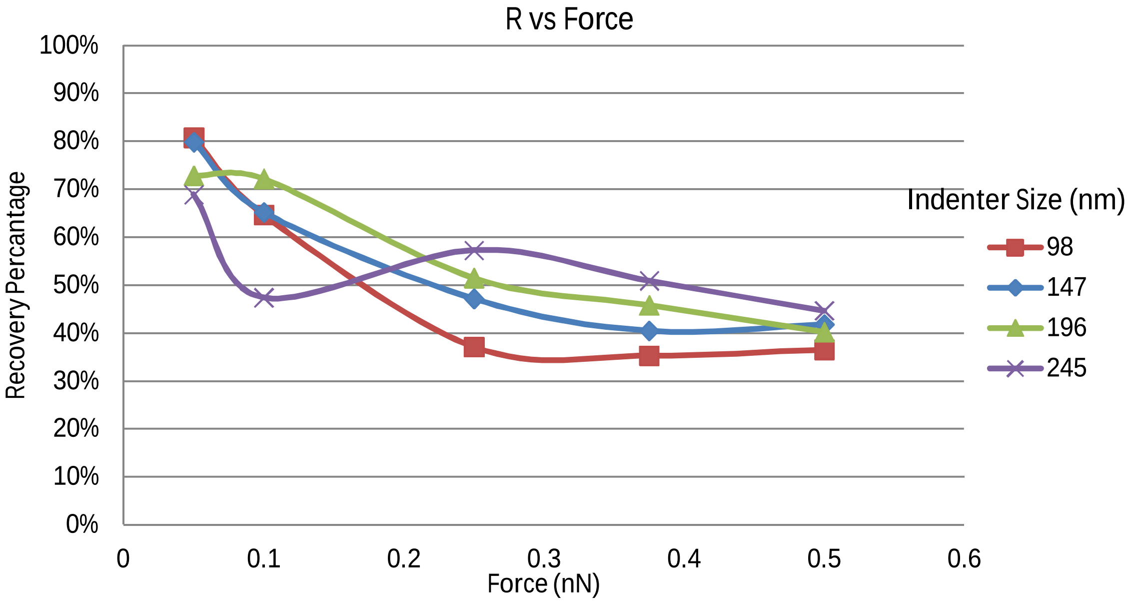


Figure 25: Recovery percentage of material one as a function of external scratching force applied with four different indenter sizes.

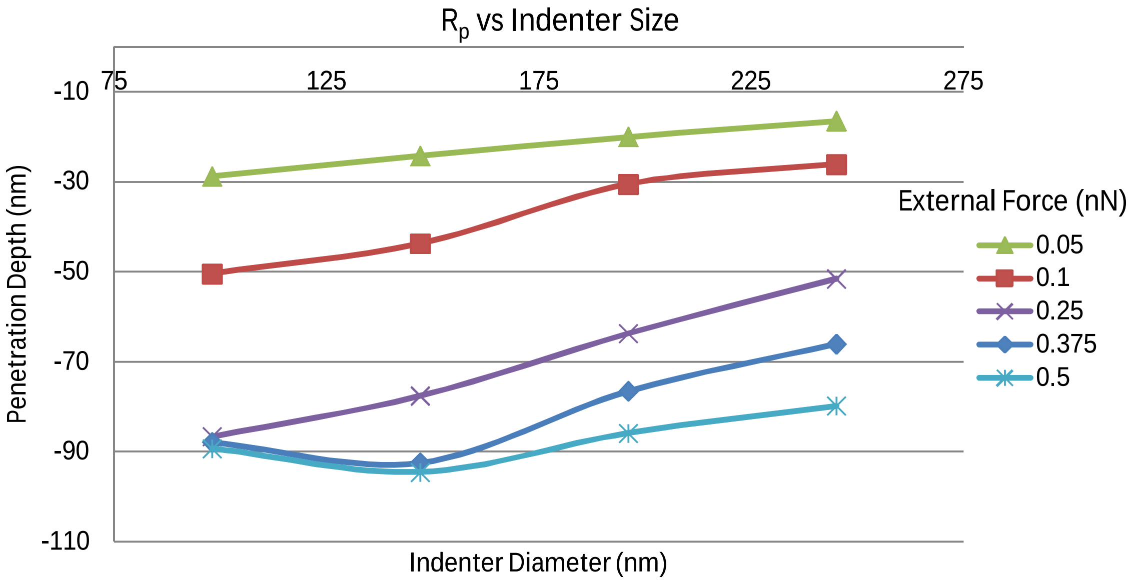


Figure 26: Penetration depth of material one in relation to the size of the indenter used. Five forces are used. With increasing indenter size, the $R_P$ decreases due to the force spreading over a wider area (or higher number of segments).

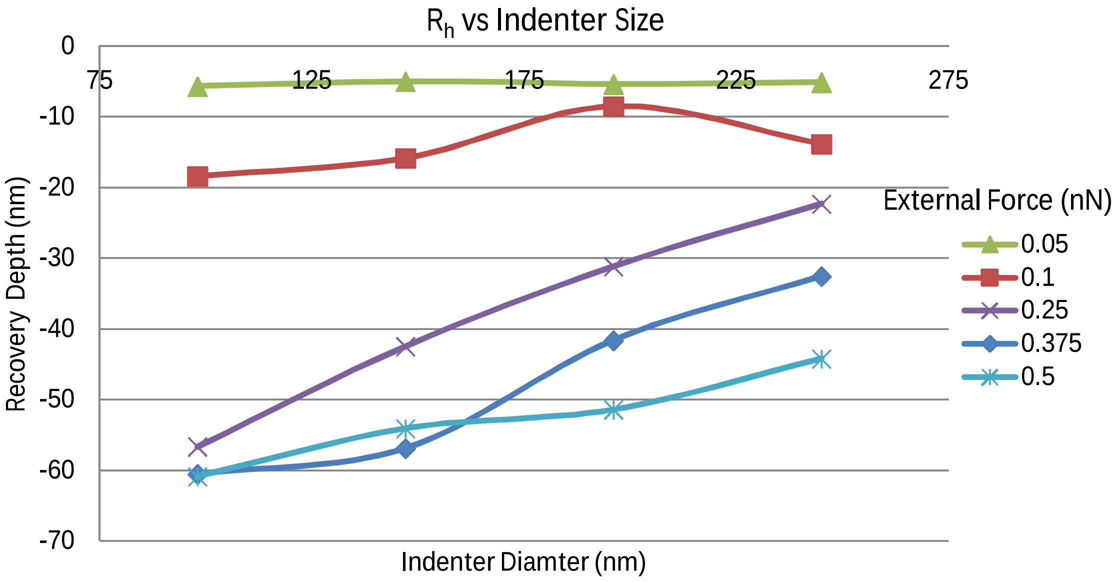


Figure 27: Residual depth of material one with relation to the size of the indenter used. Five forces are used. As with $R_P$, with increasing indenter size the $R_h$ decreases.

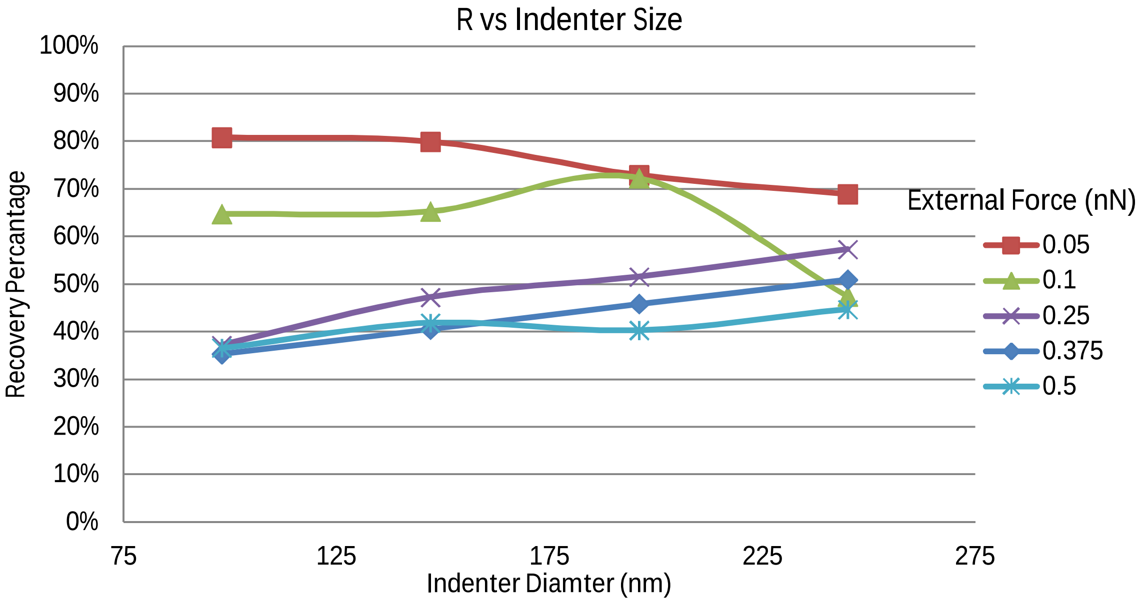


Figure 28: Recovery percentage with relation to size of indenter for material one. Five forces are used.

# CHAPTER 4

# DISCUSSION

## 4.1 Overview

The results show trends such that some of them are expected; $R_P$ and $R_h$ increase with force and decrease with indenter size while R decreases with force. Indenter size has little effect, something one cannot infer from even detailed knowledge of expected results. Two factors of the material have a large influence on the deformation from the scratch: chain orientation and vacancies.

## 4.2 Vacancies and Chain Orientation

Vacancies, also called point defects, have perhaps the largest effect, especially in cases of vacancies close to the surface. For the purposes of the code, vacancies are hardly ever produced on the top row in order to have a consistent surface. However, when there is a vacancy on the second or third row, it has a large effect on the $R_P$, $R_h$ and thus R. If the force is sufficient, the segments will drop into these holes that are produced with vacancies, and will not recover. The volume of vacancies can be controlled with Genmat, which provides a way to control the density of the polymer Needless to say, more vacancies give us a less dense material. In general, the denser a material is, the harder it is, and therefore the more resistant to penetration it is. This is true for both simulated materials and physical experiments.

The intramolecular interaction associated with bonded segments is much stronger than the intermolecular, pulling the segments chained together. The way the chains are oriented will affect how much the segments recover after deformation. If a segment that is being acting on by the external force is bonded to a neighboring segment on the top row that is not being acted on by the external force, the segment will penetrate less and recover more. This is one more effect that has been made clear by the simulations.

## 4.3 Neighboring Segments Effects and the Crooked Smile

When scratching the material, caution must be taken to avoid the edges of the material as explained earlier. The idea of creating model is to assume that we are scratching a small portion on a much larger bulk material, not that we are scratching a very small area on a very small material. It is not feasible to simulate a large material with MD, so compromises and estimations must be made.

A common trend seen during the scratching simulation is a crooked smile such as that in Figure 29: the crooked smile pattern. The pattern is somewhat visible on Figure 22 in section 3. The very first part of the scratch does not penetrate as deeply, and the several last segments have a gradual linear decrease of penetration. The reason for this pattern is the neighboring segment effect. When a segment penetrates down due to the external force, it brings its neighbors (especially the intramolecular bonded neighbors) down with it. The segments on the ends have fewer neighbors that are acted upon with the external scratching force.

The scratch occurs in a pattern with the second half of the curve being slightly deeper then the first half. This crooked smile pattern is an extension of the neighboring effect: the later segments have a small effect from all the previous segments being forced.

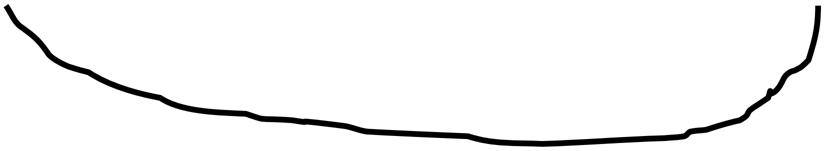


Figure 29: The crooked smile trend of a scratch indentation.

## 4.5 Extrapolation and Comparison with Laboratory Results

LAPOM has a micro-scratch testing machine and has published papers on scratching polymeric materials. During the scratch testing, $R_P$ and $R_h$ are measured. Two different types of tests are run, one with a constant force and one with an increasing force. During a test with HDPE, a force of five Newton penetrates about 50 µm. The same tests show that a force of 30 N gives a penetration depth of 450 µm. The tests have an $R_h$ of about 20 µm and 120 µm, respectively. These values correspond to an R of 60% and 73%. These tests were conducted with a micro tip with a diameter of 200 µm.

In these simulations, with an indenter diameter of 196 nm and a force of 0.1 nN, the results are: $R_P$ = 31 nm, $R_h$ = 9nm, R = 72%. The diameter of the micro indenter is six orders of magnitude more than the diameter used in the simulation and the force is ten orders of magnitude higher. It is difficult to compare the values of such different scales. The values themselves are several orders of magnitude different, but general trends can be viewed.

Five Newton is used as a starting force for the micro-scratching tests, while one tenth of a nano-Newton is used on the simulation test. That is ten orders of magnitude difference. The diameter of the simulation indenter is three orders of magnitude smaller than the micro scratch tester indenter, and the penetration depth is another three orders of magnitude smaller. To be able to extrapolate, one of these two variables would have to be much closer in magnitude. No scratching with a smaller micro or nano- indenter with HDPE could be found by us.

AFM techniques do come much closer to the nano- and micrometers scale. However, they do not offer such data as $R_P$ and $R_h$. With AFM scratching, the type of deformation is analyzed with the use of SEM [24]. AFM scratching can use a scratching force from a micro-Newton up to one Newton. It is not possible to analyze the depth of the indenter over time with AFM like it is with a micro-scratch tester or with our simulations.

# CHAPTER 5

# SUMMARY AND CONCLUSION

MD can be used to simulate polymeric materials with reasonable accuracy, as has been shown in multiple reports mentioned earlier. Here, MD is able to mimic the viscoelastic and amorphous characteristics of polymeric materials. This capability has been used here to simulate scratch resistance testing. The simulation results show clearly that force gives an increasing scratch depth and slightly less recovery, in agreement with experiments. Also, the larger the indenter size, the lower the depth due to the force being spread out over a larger area. At the same time, larger indenter area does result in slightly less percentage recovery. A larger amount of material leads to the material recovery at a slower rate. After the scratching, the material does recover significantly and quickly like a viscoelastic material should under elastic strain. Thus, the simulations have succeeded in capturing the essential feature of the scratch resistance testing, providing much more information than the experiments can provide.

The only previous work on scratch testing polymeric materials used reduced units and did not specify the specific polymer. In this project HDPE is successfully model, this project allows for the future work that showing that testing a specific model is indeed possible. Proving that HDPE is possible to model, this project allows for future work that can be conducted to model all of the various polymeric materials.

It is feasible that in the future MD simulations on scratch resistance can be run for any conceivable polymeric material. Such a tool would be valuable in the hands of scientist and engineers designing products that will have to withstand wear in their environment.

# CHAPTER 6

# FUTURE WORK

HDPE is used in this work only as a prototype. The idea is to be able to simulate any polymer based material. These sets of programs can be used for simulations other than amorphous HDPE. By simply changing the potentials, mass, and size of the segments, any polymer based material can be reasonably simulated. Other uses for the code include the ability to simulate indentation instead of scratching and allowing for variation of the size of the coarse grain model to simulate larger (or smaller) scales.

Many materials are designed with more than one phase; they are heterogeneous instead of homogenous. Engineers use heterogeneous materials because they allow for custom tailored properties for specific applications. Genmat allows for two or more phase materials. To simulate a material with more than one phase, several potentials would have to be used; not only the inter- and intra- interactions for each phase but also the interactions between the two phases. Thus immiscible polymer blends and nano-composites are possible to be simulated. This fits with the industrials practices; polymers are often blended and altered to match the desired properties of the designer.

A very popular trend with polymeric materials is injecting nano fiber materials such as carbon nanotubes. The use of nano-filler materials has shown a strong potential for increasing the mechanical properties, yet more testing needs to be done before these materials can make it to the commercial level. These nano-composite materials may also be able to be tested with MD simulations. Simulating nano-composite materials could potentially save large amounts of money. Nano-composite material are increasingly being studied and used in aerospace and other fields that require high strength with low weight. Nano-composites are a relatively new field that requires a lot of work to be done in classifying.

Furthermore, nanometer and micrometer scale indentation simulations are also possible, even not difficult to do. Nano-indentation is basically the same thing as scratching without moving the indenter in a horizontal direction. Work is currently being done with this code to modify it for nano-indentation.

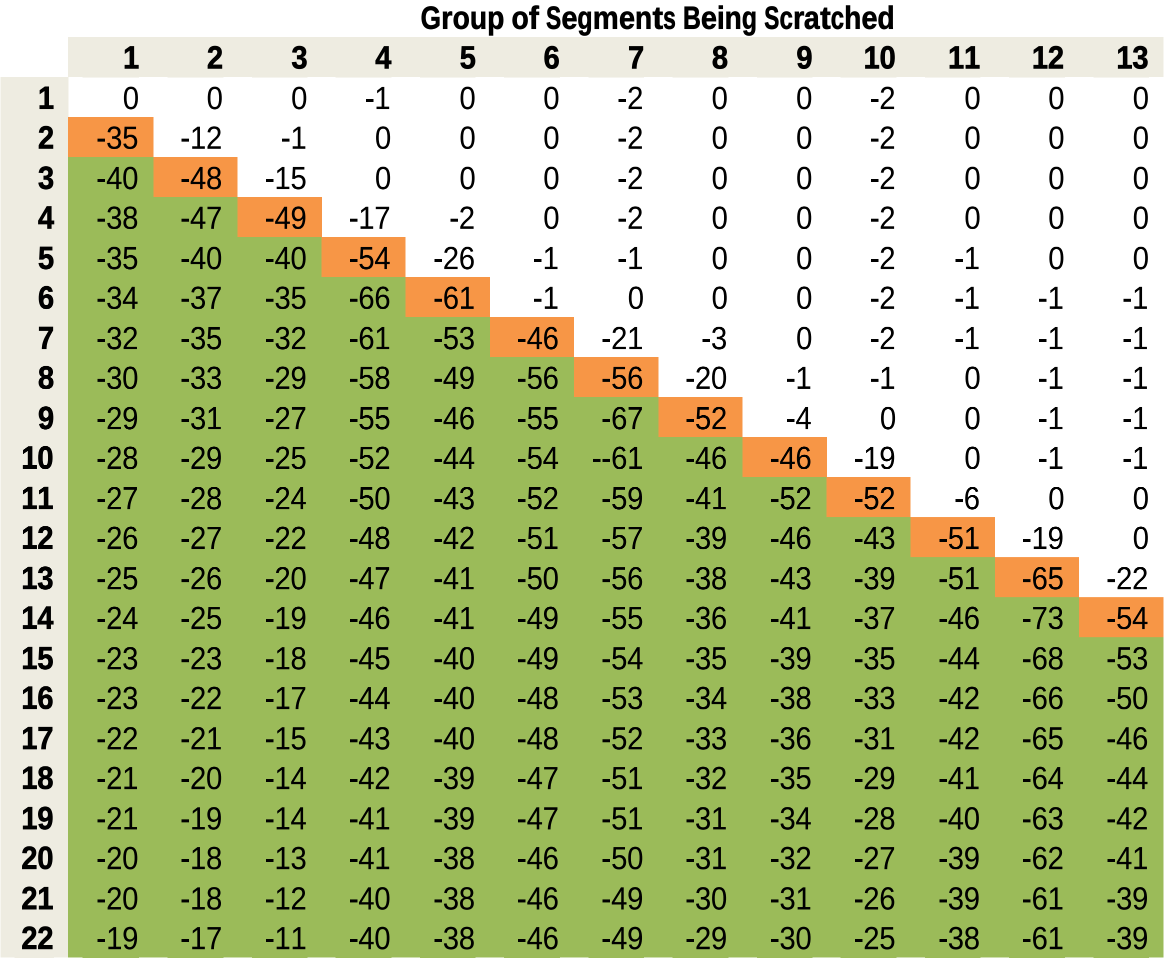
Also, the scale could be altered to simulate anything from atomistic simulations to micro-scale size simulations. Using a coarse-grain model gives more flexibility in regards to scale. It is possible to alter the program slightly and allow the ability to simulate a much larger scale. Simulating a larger scale can be used for validation with micro-scratch testing.

# APPENDIX

## EXAMPLE TABLE

The table below is an example of the data taken from the scratching program. This is used to give us the depth as well as the recovery trend of the material. The example given is taken from a simulation test that used an external force of 0.1 nN and an indenter size of 98 nm. The vertical column is time and the horizontal rows are groups of segments under the indenter at the beginning of the scratch to the end of the scratch. The orange highlight represents when that group of segments is exactly under the indenter, being forced into the material. The green highlight represents the recovery period for that group of segments. The units are in nanometers.

Example Table: Depth of segments being scratched



**Group of Segments Being Scratched**

| time loops | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **1** | 0 | 0 | 0 | -1 | 0 | 0 | -2 | 0 | 0 | -2 | 0 | 0 | 0 |
| **2** | -35 | -12 | -1 | 0 | 0 | 0 | -2 | 0 | 0 | -2 | 0 | 0 | 0 |
| **3** | -40 | -48 | -15 | 0 | 0 | 0 | -2 | 0 | 0 | -2 | 0 | 0 | 0 |
| **4** | -38 | -47 | -49 | -17 | -2 | 0 | -2 | 0 | 0 | -2 | 0 | 0 | 0 |
| **5** | -35 | -40 | -40 | -54 | -26 | -1 | -1 | 0 | 0 | -2 | -1 | 0 | 0 |
| **6** | -34 | -37 | -35 | -66 | -61 | -1 | 0 | 0 | 0 | -2 | -1 | -1 | -1 |
| **7** | -32 | -35 | -32 | -61 | -53 | -46 | -21 | -3 | 0 | -2 | -1 | -1 | -1 |
| **8** | -30 | -33 | -29 | -58 | -49 | -56 | -56 | -20 | -1 | -1 | 0 | -1 | -1 |
| **9** | -29 | -31 | -27 | -55 | -46 | -55 | -67 | -52 | -4 | 0 | 0 | -1 | -1 |
| **10** | -28 | -29 | -25 | -52 | -44 | -54 | --61 | -46 | -46 | -19 | 0 | -1 | -1 |
| **11** | -27 | -28 | -24 | -50 | -43 | -52 | -59 | -41 | -52 | -52 | -6 | 0 | 0 |
| **12** | -26 | -27 | -22 | -48 | -42 | -51 | -57 | -39 | -46 | -43 | -51 | -19 | 0 |
| **13** | -25 | -26 | -20 | -47 | -41 | -50 | -56 | -38 | -43 | -39 | -51 | -65 | -22 |
| **14** | -24 | -25 | -19 | -46 | -41 | -49 | -55 | -36 | -41 | -37 | -46 | -73 | -54 |
| **15** | -23 | -23 | -18 | -45 | -40 | -49 | -54 | -35 | -39 | -35 | -44 | -68 | -53 |
| **16** | -23 | -22 | -17 | -44 | -40 | -48 | -53 | -34 | -38 | -33 | -42 | -66 | -50 |
| **17** | -22 | -21 | -15 | -43 | -40 | -48 | -52 | -33 | -36 | -31 | -42 | -65 | -46 |
| **18** | -21 | -20 | -14 | -42 | -39 | -47 | -51 | -32 | -35 | -29 | -41 | -64 | -44 |
| **19** | -21 | -19 | -14 | -41 | -39 | -47 | -51 | -31 | -34 | -28 | -40 | -63 | -42 |
| **20** | -20 | -18 | -13 | -41 | -38 | -46 | -50 | -31 | -32 | -27 | -39 | -62 | -41 |
| **21** | -20 | -18 | -12 | -40 | -38 | -46 | -49 | -30 | -31 | -26 | -39 | -61 | -39 |
| **22** | -19 | -17 | -11 | -40 | -38 | -46 | -49 | -29 | -30 | -25 | -38 | -61 | -39 |

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **23** | -18 | -16 | -11 | -39 | -37 | -45 | -48 | -29 | -30 | -24 | -37 | -60 | -38 |
| **24** | -18 | -15 | -10 | -39 | -37 | -45 | -48 | -28 | -29 | -23 | -37 | -60 | -37 |
| **25** | -17 | -15 | -10 | -38 | -37 | -45 | -47 | -28 | -28 | -22 | -36 | -59 | -36 |
| **26** | -17 | -14 | -9 | -38 | -36 | -45 | -47 | -27 | -27 | -21 | -36 | -59 | -36 |
| **27** | -16 | -13 | -9 | -37 | -36 | -44 | -46 | -27 | -27 | -21 | -35 | -58 | -35 |
| **28** | -16 | -13 | -8 | -37 | -36 | -44 | -46 | -26 | -26 | -20 | -35 | -58 | -35 |
| **29** | -16 | -12 | -8 | -36 | -36 | -44 | -45 | -26 | -26 | -19 | -35 | -57 | -34 |
| **30** | -15 | -12 | -7 | -36 | -35 | -43 | -45 | -25 | -25 | -19 | -34 | -57 | -34 |
| **31** | -15 | -11 | -7 | -35 | -35 | -43 | -44 | -25 | -25 | -18 | -34 | -57 | -33 |
| **32** | -15 | -11 | -7 | -35 | -35 | -43 | -44 | -25 | -24 | -18 | -34 | -56 | -33 |
| **33** | -14 | -11 | -7 | -34 | -35 | -43 | -44 | -24 | -24 | -17 | -33 | -56 | -33 |
| **34** | -14 | -10 | -6 | -34 | -34 | -42 | -43 | -24 | -24 | -17 | -33 | -56 | -32 |
| **35** | -14 | -10 | -6 | -34 | -34 | -42 | -43 | -24 | -23 | -16 | -33 | -55 | -32 |
| **36** | -14 | -10 | -6 | -34 | -34 | -42 | -43 | -24 | -23 | -16 | -33 | -55 | -32 |
| **37** | -14 | -10 | -6 | -33 | -34 | -42 | -43 | -23 | -23 | -16 | -33 | -55 | -31 |
| **38** | -13 | -10 | -6 | -33 | -34 | -42 | -42 | -23 | -23 | -16 | -33 | -55 | -31 |
| **39** | -13 | -9 | -6 | -32 | -33 | -41 | -42 | -23 | -23 | -15 | -32 | -55 | -31 |
| **40** | -13 | -9 | -5 | -32 | -33 | -41 | -42 | -23 | -22 | -15 | -32 | -54 | -30 |
| **41** | -13 | -9 | -5 | -32 | -33 | -41 | -41 | -22 | -22 | -15 | -32 | -54 | -30 |
| **42** | -13 | -9 | -5 | -31 | -32 | -41 | -41 | -22 | -22 | -15 | -32 | -54 | -30 |
| **43** | -13 | -9 | -5 | -31 | -32 | -41 | -41 | -22 | -22 | -14 | -32 | -54 | -29 |
| **44** | -12 | -9 | -5 | -31 | -32 | -40 | -41 | -22 | -22 | -14 | -32 | -53 | -29 |
| **45** | -12 | -8 | -5 | -30 | -31 | -40 | -40 | -22 | -21 | -14 | -32 | -53 | -29 |
| **46** | -12 | -8 | -4 | -30 | -31 | -40 | -40 | -21 | -21 | -14 | -32 | -53 | -28 |
| **47** | -12 | -8 | -4 | -30 | -31 | -40 | -40 | -21 | -21 | -14 | -31 | -53 | -28 |
| **48** | -12 | -8 | -4 | -29 | -31 | -40 | -40 | -21 | -21 | -14 | -31 | -53 | -28 |
| **49** | -12 | -8 | -4 | -29 | -30 | -39 | -39 | -21 | -21 | -13 | -31 | -52 | -27 |
| **50** | -12 | -8 | -4 | -28 | -30 | -39 | -39 | -21 | -21 | -13 | -31 | -52 | -27 |
| **51** | -12 | -7 | -4 | -28 | -30 | -39 | -39 | -20 | -21 | -13 | -31 | -52 | -27 |
| **52** | -12 | -7 | -3 | -28 | -29 | -39 | -39 | -20 | -20 | -13 | -31 | -52 | -27 |
| **53** | -12 | -7 | -3 | -27 | -29 | -39 | -39 | -20 | -20 | -13 | -31 | -52 | -26 |
| **54** | -11 | -7 | -3 | -27 | -29 | -39 | -38 | -20 | -20 | -13 | -31 | -51 | -26 |
| **55** | -11 | -7 | -3 | -27 | -29 | -38 | -38 | -20 | -20 | -13 | -31 | -51 | -26 |

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **$R_P$** | -40 | -48 | -49 | -66 | -61 | -56 | -67 | -52 | -52 | -52 | -51 | -73 | -54 |
| **$R_h$** | -15 | -11 | -6 | -34 | -34 | -42 | -42 | -23 | -22 | -15 | -32 | -54 | -29 |
| **R** | 64% | 78% | 87% | 49% | 44% | 25% | 37% | 56% | 57% | 71% | 37% | 26% | 47% |

| **14** | **15** | **16** | **17** | **18** | **19** | **20** | **21** | **22** |
|---|---|---|---|---|---|---|---|---|
| 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| -1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| -1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| -1 | -1 | -1 | -1 | -1 | 0 | 0 | 0 | 0 |
| -1 | -1 | -1 | -1 | -1 | 0 | -1 | 0 | -1 |
| -1 | -1 | -1 | -1 | -1 | -1 | -1 | -1 | -1 |
| -1 | -1 | -1 | -1 | -1 | -1 | -1 | -1 | -1 |
| -1 | -1 | -1 | -1 | -1 | -1 | -1 | -1 | -1 |
| -1 | -1 | -1 | -1 | -1 | -1 | -1 | -1 | -1 |
| -1 | -1 | -1 | -1 | -1 | -1 | -1 | -1 | -1 |
| 0 | 0 | -1 | -1 | -1 | -1 | -1 | -1 | -1 |
| -3 | -1 | -1 | -1 | -1 | -1 | -1 | -1 | -1 |
| -43 | -13 | -1 | -2 | -1 | -1 | -1 | -1 | -1 |
| -40 | -42 | -16 | -2 | -1 | -1 | -1 | -1 | -1 |
| -34 | -49 | -56 | -18 | -2 | -1 | -1 | -1 | -1 |
| -31 | -45 | -59 | -55 | -20 | -3 | -1 | -1 | -1 |
| -29 | -42 | -53 | -60 | -52 | -10 | 0 | 0 | -1 |
| -28 | -40 | -49 | -59 | -55 | -52 | -12 | -1 | -1 |
| -27 | -39 | -47 | -55 | -50 | -52 | -53 | -23 | -2 |
| -26 | -37 | -45 | -53 | -47 | -47 | -60 | -69 | -29 |
| -25 | -36 | -44 | -51 | -45 | -44 | -54 | -81 | -70 |
| -24 | -35 | -43 | -49 | -43 | -42 | -52 | -75 | -64 |
| -23 | -34 | -41 | -48 | -41 | -41 | -50 | -74 | -62 |
| -22 | -33 | -40 | -47 | -40 | -39 | -49 | -72 | -60 |
| -21 | -32 | -40 | -45 | -38 | -37 | -47 | -71 | -59 |
| -21 | -31 | -39 | -44 | -37 | -36 | -46 | -70 | -58 |
| -20 | -30 | -38 | -43 | -36 | -35 | -45 | -69 | -57 |
| -20 | -30 | -37 | -43 | -35 | -33 | -44 | -68 | -56 |
| -19 | -29 | -36 | -42 | -34 | -32 | -43 | -67 | -55 |
| -19 | -28 | -36 | -41 | -33 | -31 | -42 | -67 | -54 |
| -18 | -28 | -35 | -40 | -33 | -30 | -41 | -66 | -53 |
| -18 | -27 | -34 | -40 | -32 | -29 | -41 | -65 | -53 |
| -18 | -26 | -33 | -39 | -31 | -29 | -40 | -65 | -52 |
| -18 | -26 | -33 | -39 | -31 | -29 | -40 | -65 | -52 |
| -17 | -26 | -33 | -38 | -31 | -28 | -39 | -64 | -51 |
| -17 | -25 | -32 | -38 | -30 | -27 | -39 | -64 | -51 |
| -17 | -25 | -31 | -37 | -29 | -26 | -38 | -63 | -50 |
| -16 | -24 | -31 | -36 | -29 | -26 | -37 | -63 | -49 |
| -16 | -24 | -30 | -36 | -28 | -25 | -37 | -62 | -48 |
| -16 | -23 | -29 | -35 | -28 | -25 | -36 | -62 | -48 |
| -15 | -23 | -29 | -35 | -27 | -24 | -36 | -61 | -47 |
| -15 | -22 | -28 | -35 | -27 | -24 | -36 | -60 | -46 |
| -15 | -22 | -28 | -34 | -27 | -23 | -35 | -60 | -45 |
| -15 | -21 | -27 | -34 | -26 | -23 | -35 | -59 | -45 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| -15 | -21 | -27 | -33 | -26 | -23 | -34 | -59 | -44 |
| -14 | -21 | -27 | -33 | -25 | -22 | -34 | -58 | -43 |
| -14 | -20 | -26 | -33 | -25 | -22 | -33 | -57 | -43 |
| -14 | -20 | -26 | -32 | -24 | -21 | -33 | -57 | -42 |
| -14 | -20 | -26 | -32 | -24 | -21 | -32 | -56 | -41 |
| -13 | -20 | -25 | -31 | -23 | -21 | -32 | -56 | -40 |
| -13 | -20 | -25 | -31 | -23 | -21 | -32 | -55 | -40 |
| -13 | -19 | -25 | -30 | -23 | -20 | -31 | -54 | -39 |
| -13 | -19 | -25 | -30 | -22 | -20 | -31 | -54 | -38 |
| | | | | | | | | |
| -43 | -49 | -59 | -60 | -55 | -52 | -60 | -81 | -70 |
| -15 | -21 | -27 | -33 | -25 | -21 | -32 | -56 | -41 |
| 65 | 56% | 54% | 45% | 55% | 59% | 46% | 31% | 41% |

# REFERENCES

1. Brostow, W.; Hinze, A.; Simoes, R.; Tribological behavior of polymers simulated by molecular dynamic, Journal of Material Research, 19: 3 (2004)

2. Flory, P. J.; *Statistical Mechanics of Chain Molecules*, Hanser, 1988

3. Alder, B.J.; Wainwright, T.E.; Studies in Molecular Dynamics. I. General Method. Journal of Chemical Physics, 31: 2 (1959)

4. Brostow, W.; Simoes, R.; Tribological and Mechanical Behavior of Metals and Polymers Simulated by Molecular Dynamics. Journal of Materials Education, 27 (2005)

5. Brostow, W., Donahue III, M.; Karashin, C.; Simoes, R.; Graphic Modeling and Computer Animation of Tensile Deformation in Polymer Liquid Crystals (PLCs). Material Research Innovations, 4: 75 (2004)

6. Correia, A.S.; Valashani, S.M.; Pires, F.; Simoes, R.; Modeling the Mechanical Behavior of Polymer-Based Nanocomposites,Proceedings of the International Materials Symposium VI – Materials' 2011, Guimareas, April 20, (2011).

7. Simoes, R.; et. al.; Low Percolation Transitions in Carbon Nanotube Networks Dispersed in a Polymer Matrix: Dielectric Properties, Simulations and Experiments. Nanotechnology, 20: 3 (2009).

8. Simoes, R.; Cunha, A.M.; Brostow, W.; The Influence of Matrix Mediated Hopping Conductivity, Filler Concentration, Aspect Ratio and Orientation on The Electrical Response of Carbon Nanotube/Polymer Nanocomposites. Composites Science and Technology, 71: 5 (2011).

9. Binder, K. *Monte Carlo and Molecular Dynamics Simulations in Polymer Sciences*. Oxford, 1995.

10. Solar, M.; Meyer, H.; Gautheir, C.; Benzerara, O.; Schirrer, R.; Baschnagel, J.; Molecular Dynamics Simulations of the Scratch Tests on Linear Amorphous Polymer Surfaces: A Study of the Local Friction Coefficient, Wear, 271: 11-12 (2011).

11. Brostow, W.; Drewniak, M.; Medvedev, N.N.; Brownian Dynamics Simulation of Dilute Polymer Solutions: Chain Overlap and Entanglements. Macromolecular Theory and Simulations, 4: 4 (1995)

12. Curgul, S.; Vliet, K.J.; Rutledge, G.; Molecular Dynamics Simulation of Size-Dependent Structural Thermal Properties of Polymer Nanofibers. 40: 23 (2007)

13. Qungbin, Z.; Quingzhong, X.; Yan, K.; Hao, L.; Li, Q.; Gao, X.; Investigation of Molecular Interactions between SWNT and Polyethylene/ Polypropylene/ Polystyrene/ Polyaniline Molecules. Journal Physical Chemisty 111: 12 (2007).

14. Weber, T.A.; Eugene, H.; Molecular Dynamics simulations of Polymers. I Structures., Journal of Chemistry and Physics, 71: 11 (1979).

15. Brostow, W. and Corneliussen, R. D. *Failure of Plastics*. New York, New York : Macmillin Publishing, 1986.

16. Brostow, W.; Cunha, A.M.; Quintanilla, J.; Simoes, R.; Crack Formation and Propagation in Molecular Dynamics Simulations of Polymer Liquid Crystals (PLCs), Macromolecular Theory & Simulation 11: 308 (2002)

17. Simões, R.; Cunha, A. M.; Brostow, W.; Computer Simulations of True Stress Development and Viscoelastic Behavior in Amorphous Polymeric Materials. Computational Materials Science 36: 319 (2006).

18. Simões, R.; Cunha, A.M.; Brostow, W.; Molecular Dynamics Simulations of Polymer Viscoelasticity: Effect of the Loading Conditions and Creep Behavior, Modelling & Simulation in Materials Science & Engineering 14: 157 (2006)

19. Michler, Goerg H. and Balta-Calleja, Francisco J. *Nano- and Micromechanics of Polymers,* Hanser, 2012.

20. Chandrasekaren, N.; Raff L.M.; MD Simulation of Indentation and Scratching of Single Crystal Aluminium, Wear, 240: 1-2 (2000).

21. Dasari, A.; Misra, R.D.K.; Microscopic Aspects of Surface Deformation and fracture of High Density Polyethylene. Materials Science and Engineering, 367 (2004).

22. Briscoe, B.J.; Enrico, P.; Sinha, S.; Scratch Hardness and Deformation Maps for Polycarbonate and Polyethylene, Polymer Engineering and Science, 36: 24 (1996).

23. Coniglio R.; Randall, N.X.; Bellarton, B.; Stedbut, J.V.; The Nano-Scratch Testers (NST) as a New Tool for Assessing the Strength of Ultra Thin Hard Coatings and the Mar Resistance of Polymer Films, Thin Solid Films, 332: 1-2 (1998).

24. Dasari, A.; Duncan S.J.; Misra, R.D.K,; Micro- and Nano- scale Deformation Processes during Scratch Damage in High Density Polyethylene. Materials Science and Technology, 19: 2 (2003).

25. Brostow, W.; Cunha, A.M.; Simoes, R.; Generation of polymeric structures on a computer, Materials Research Innovations 7: 19 (2003)

26. Blonski, S.; Brostow, W.; Kubat J.; Molecular Dynamics Simulations of Stress Relaxation in Metals and Polymers, The American Physical Society, 49: 10 (1994).

27. Mie, G.; Zur kinetischen Theorie der einatomigen Körper. : Annalen der Physik, 11 (1903).

28. Lennard-Jones, J.E.; On the Determination of Molecular Fields - II. From the Equation of State of a Gas. Royal Society of London, 106 (1924).

29. Edalat, M.; Pang, S.S.; Mansoori, G.A.; Optimized Parameters and Exponents of Mie (n,m) Intermolecular Potential Energy Function Based on the Shape of Molecules. International Journal of Thermoplastics, 1: 2 (1980).

30. Kobyashi, M.; Tadokor, H.; Intermolecular Forces and Thermodynamic Functions of Orthorhombic Polyethylene Lattice. 3, Journal of Chemical Physics , 66: 3 (1977).

31. McCoy, J.D.; Mateas, S.; Zorlu, M.; Curro, J.G.; The Role of Excluded Volume in Polyethylene Intermolecular Potentials, of Chemical Physics, 102: 21 (1995).

32. Jost, H.P.; Lubrication (Tribology) Education and Research A Report on the Present Position and Industry's Needs *Her*. Majesty's Stationary Office, (1966).

33. Wilson, S.; Bernath, P.;  McWeeny, R.; *Handbook of Molecular Physics and Quantom Chemistry*. Wiley, 2003.

34. Wolf, B.A. and Enders, S.; *Polymer Thermodynamics: Liquid Polymer-Containing Mixtures* Springer, 2011.

35. Jorgensen, W.L.; Madura, J.D.; Swenson C.J.; Optimized Intermolecular Potential Function for Liquid Hydrocarbons. American Chemical Society, 106: 22 (1984).

36. Koteyanskii, M.; Theodorou, D.N.; *Simulation Methods for Polymers*. Dekker, 2004.

37. Xiang, C.; Sue3, H.J.; Chu J.; Coleman B.; Scratch Behavior and Material Property Relationship in Polymers. Journal of Polymer Science Part B: Polymer Physics, 39: 1 (2001).

38. Brostow, W.; Ill, D.M.; Karashin C.E.; Simoes, R.; Tribology with Emphasis on Polymers: Friction, Scratch Resistance and Wear, Journal of Materials Education, 24 (2003).

39. Whittington, S.G.; *Numerical Method for Polymeric Systems*, Springer, 1998