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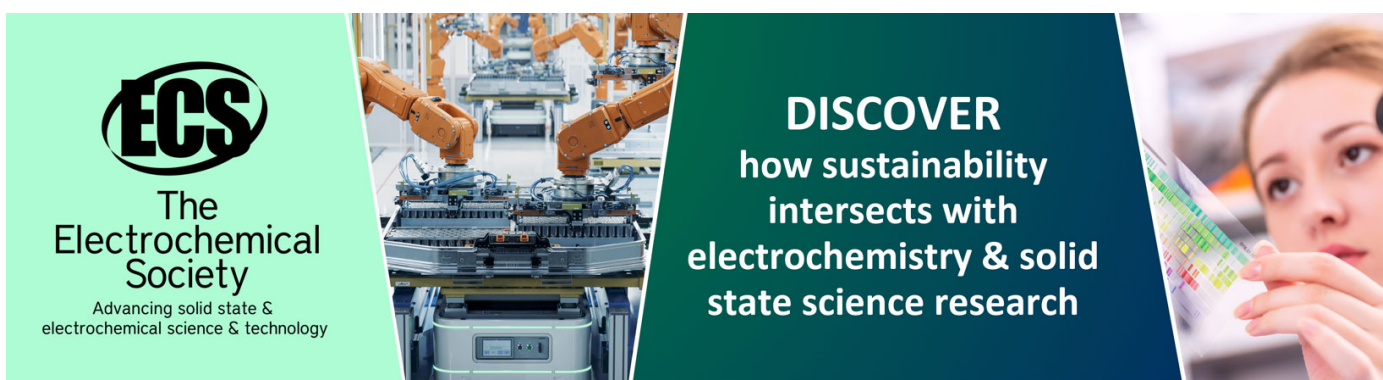
## Molecular Dynamics Simulations and Ion Beam Treatment of Polyethylene

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# Molecular Dynamics Simulations and Ion Beam Treatment of Polyethylene

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**Abstract.** A polymer like polyethylene (PE) has attracted intense research exploits in recent years due to their inherent versatile properties like high optical clarity, mechanical properties, light weight and high packing density. PE is the simplest of all commercial polymers used for making catheters, meshes, artificial joint, drug delivery packages (biomedical applications), light emitting diode, electrical bio-sensing, solid state battery, and plastic containers. Over the years, several techniques have been employed to enhance the properties of the polymer surface which include surface etching, laser deposition, plasma deposition, ion implantation technologies and doping. However, this study is concerned with ion-beam sputtering of PE to investigate its sputtering yield dependence. Moreover, molecular dynamics simulations of a PE system were performed to deduce the thermodynamics properties of the system at relatively high temperature (700 K). The results show that the sputtering yield of PE system is dependent on the incident angles and the ion energies. Additionally, the peak of the sputtering yield was found to be around 83° incident angle. Also, the temperature of the PE system varies with the time steps imposed on it. Finally, the structural and dynamical properties of the PE show minimal fluctuations as the density of the polymer linearly increases across the duration.

## 1. Introduction

In recent years, polymers have become important subject of matters to researchers because of their inbuilt properties which include mechanical, light weight, density, high optical clarity and resistant to collision [1]. These properties have placed much importance on the system to gain extensive applications in technological advancement. Moreover, polymeric materials are enhanced when bombarded with an energetic ion. This ion-beam technique describes a process by which particles are ejected from the polymer surface via ion-beam treatment with energetic particle (ion). This process is also known as sputtering. Furthermore, this technique causes a significant transformation in the structure and properties of the polymer surface which enhance the system for suitable applications in biomedical (artificial joint, catheters, meshes, etc.), electronic devices, domestic (rubber products) and pharmaceutical industry (drug delivery systems). A particular advantage of ion implantation technologies over other ways of improving polymer surface is that it is cheaper and effective for use in industrial processes [2–4].

Molecular Dynamics (MD) is a deterministic method in which the system follows a well-defined trajectory in phase space. The obvious advantage of MD is that it gives a route to dynamical properties of the system: transport coefficient, time-dependent responses to perturbations, rheological properties



and spectra [5]. Computer simulation in molecular dynamics can be described as a type of simulation which allows the user to observe movement of atoms or molecules in nanoscale systems. It involves numerical solution of the classical equations of motion for particles which gives the trajectory of the system in phase space. The equation of motion for such system can be described by three different formalisms: the Lagrangian, the Hamiltonian and the Newtonian formalisms.

Over the years, polymers have been exposed to different kinds of ion beams techniques which include plasma treatment, chemical and physical etching but a treatment with a noble gas ion (like argon) which is inert in nature and has low reactivity with the target atom, and its effect on the polymeric materials still needs to be investigated. This effect of ion bombardment is probed to enhance the properties of polymeric materials. For instance, it was reported that ion beam treatment modifies polymer surface in terms of width and structure [2]. Furthermore, molecular dynamics simulations were used to study the mechanical properties of a polyethylene (PE) system [6]. However, further studies on effect of relatively high temperature, say 700 K still need to be investigated to explore the thermodynamics properties of polyethylene (PE) at such instances.

The acronym "LAMMPS" stands for Large-scale Atomic/Molecular Massively Parallel Simulator. LAMMPS is a molecular dynamic simulation code with potentials for metals, semiconductors, biomolecules, polymers and mesoscopic systems. It was developed by Sandia National Laboratory, US and designed to work efficiently on parallel (or single-core processor) computers. It employs force fields and boundary conditions in modelling a collection of particles. It is also capable of simulating systems with only a few number of particles and even more [7]. This software package was used for the molecular dynamics of the PE system. In addition, the simulations for the sputtering of the PE system were carried out by using TRansport of Ions in Matter (TRIM) software package [8].

In this paper, we investigated the thermodynamics properties of the PE system at different temperature instances using molecular dynamics simulations with LAMMPS software. Also, the PE system was sputtered with noble gas (Ar<sup>+</sup> ion) to investigate the factors affecting the sputter yield of the system. In addition, we investigated the influence of argon ion on the sputter erosion of the components of the PE system. The paper is divided into four sections as follows. The first section introduces the work with the intent of the research. The material and methods used to obtain our results are presented in section 2. Furthermore, results obtained are presented and discussed in section 3. Then, conclusions based on our deductions in are presented in section 4.

## 2. Methodology

This section gives the detailed procedures taking during simulations.

### 2.1. Sputtering of Polyethylene by Ion Bombardment

Ion beam treatment of polyethylene was performed using TRIM software package. In the set-up, the width of 100  $\mu\text{m}$  was used for the PE system. The polymer system was built from their composites in the stoichiometric ratio 1:3 for carbon C and hydrogen H, respectively. The experimental density of 0.92  $\text{g}/\text{cm}^3$  was used for the simulation. The bombardment of the polyethylene system by Ar<sup>+</sup> ion was performed for varied incident angles from 0° to 89°. Here, ion energies of 1 keV and 5 keV were considered, respectively. A detailed calculation with full damage cascade was employed with 1000 ions for each simulation to allow the simulations to run for a reasonably long time [9]. The choice of noble gas (argon) as ion is due to its inert nature. That is to say, it has low reactivity with the target atom.

### 2.2. Molecular Dynamics Simulations of Polyethylene

The polyethylene model adopted for this project is described in [6]. It contains of 10,000 atoms (i.e., 10 chains with 1000 monomers). Dreiding potential was used for the force field as it best describes the interactions between the monomers of the polyethylene system. In this project, LAMMPS software package was used to perform the molecular dynamics simulations of the polyethylene model. Initially, the equilibration sequence was performed to relax any high energy configurations that are artificially

created due to face cubic center lattice used to generate the polymer structure. The equilibration process involves four different steps as described below:

1. First, the relaxation was performed for 10000 time steps ( $\Delta t = 1$  fs) using NVT dynamics (Canonical Ensemble) at 700 K and the temperature of the system was regulated by Nose-Hoover thermostat.
2. Second, another relaxation was performed using NPT dynamics (Isothermal-Isobaric Ensemble) at 700 K for 40000 time steps ( $\Delta t = 0.5$  fs).
3. Third, the polyethylene structure was cooled down to a desired temperature for 40000 time steps ( $\Delta t = 0.5$  fs).
4. Finally, further relaxation sequence was performed for 40000 time steps using NPT dynamics at 100 K.

### 3. Results and discussions

In this section, the results of our simulations are presented and discussed.

#### 3.1. Ion Beam Treatment of the PE System

Figures 1 and 2 show the sputtering yield (atoms/ion) of the PE system for the erosion of carbon (C) and hydrogen (H) atoms against the incident angles (deg.) varied from  $0^\circ$  to  $89^\circ$  using ion energies 1 keV and 5 keV, in that order. It was observed that the hydrogen atoms eroded per incident  $\text{Ar}^+$  ion was higher than that of the carbon atoms at different incident angles ( $0^\circ$  to  $89^\circ$ ) for both ion energies (1 keV and 5 keV). This shows that the sputtering yield of PE system favours erosion of H atom with lower atomic number compared to C atoms when bombarded with  $\text{Ar}^+$  ion.

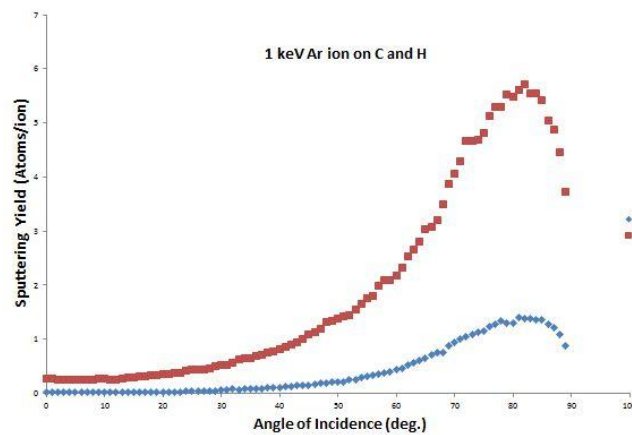


Figure 1: Sputtering yield for the erosion of C and H atoms from  $\text{Ar}^+$  ion-beam treatment of the PE system using ion energy of 1 keV.

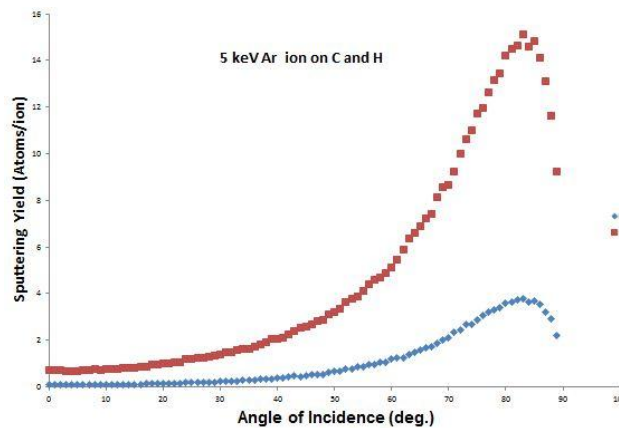


Figure 2: Sputtering yield for the erosion of C and H atoms from  $\text{Ar}^+$  ion-beam treatment of the PE system using ion energy of 5 keV.

The sputtering yield against the angle of incidence for both ion energies (1 keV and 5 keV) results presented for the PE system in the Figure 3 is higher for larger  $\text{Ar}^+$  ion energy as expected. Also, it shows the angular energy dependence of the polymer. Initially, the sputtering yield of the PE has a slight increase from the incident angle of  $0^\circ$  to  $60^\circ$ , and then increases significantly with the angle of incidence (between  $60^\circ$  -  $85^\circ$ ), until it finally decreases rapidly at higher incident angles. Furthermore, at normal incidence, the sputtering yield obtained for 5 keV is slightly higher than that of 1 keV ion energy and then increases with the incident angles, relative to the yield on PE system for 1 keV, and a maximum sputtering yield occurs around  $83^\circ$  for both  $\text{Ar}^+$  ion energies.

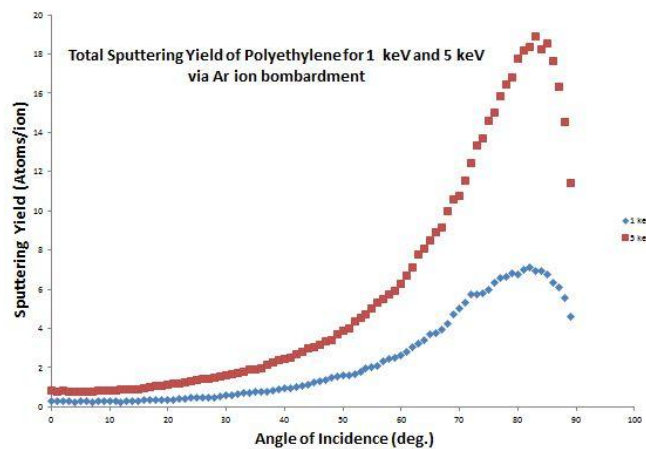


Figure 3: Sputtering yield of the PE system treated with  $\text{Ar}^+$  ion-beam for both ion energies (1 keV and 5 keV).

### 3.2. Molecular Dynamics of the PE System

The Figure 6 represents the evolution of temperature (K) with time steps (fs) as the PE system relaxes from 700 K - 700 K. The time series of the polymer describes how the temperature varies across the time steps for the system as shown in the Figure below.

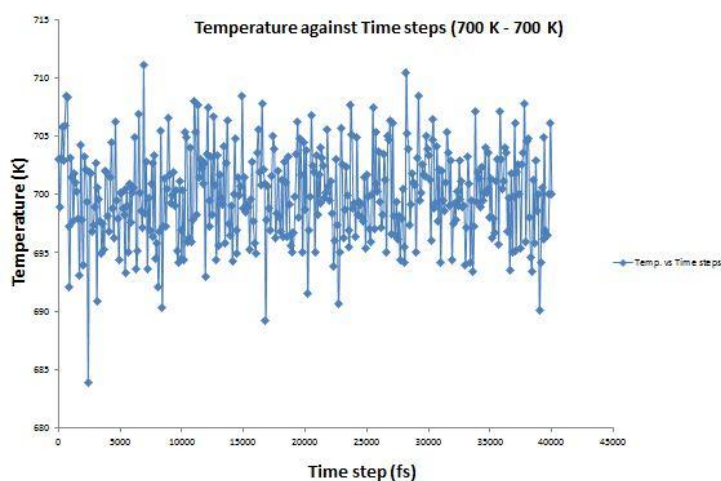


Figure 4: Temperature (K) against Time steps in femtoseconds (fs) as the PE system relaxes from 700 K - 700 K.

The evolution of density ( $\text{g/cm}^3$ ) versus duration (fs) presented in the Figure 4 exhibits a linear projection for the PE system as it relaxes at temperatures (700 K - 700 K) except at the initialisation of the simulation as shown in the Figure 4. The structural and dynamical properties of the system presented in the Figure show minimal fluctuations as the density of the polymer linearly increases across the duration. This behavioural property of the system is thought to be caused by absence of ion beam treatment.

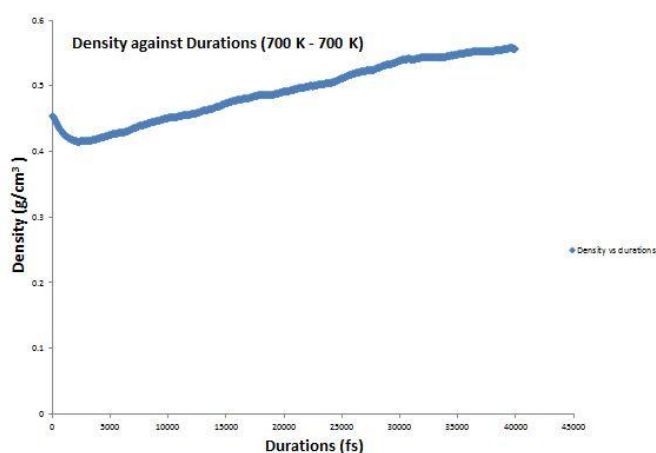


Figure 5: Evolution of density ( $\text{g/cm}^3$ ) with duration in femtoseconds (fs) as the PE system relaxes from 700 K - 700 K.

The Figure 6 represents the evolution of total energy (Kcal/mole) versus time steps (fs) for the PE system. It describes the ensemble averages for the system. In the Figure 6, the initial temperature 700 K and final temperature 700 K are imposed on the system for the NPT simulation. It can be seen that as the energy drops, the PE system could not reach an equilibrium point over the simulation run of 40,000 time steps.

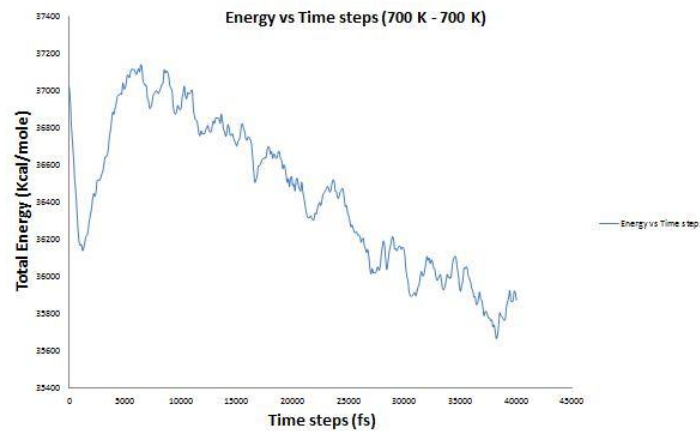


Figure 6: Total Energy (Kcal/mole) versus Time steps (fs) as the PE system relaxes from 700 K - 700 K.

#### 4. Conclusion

In this project, molecular dynamics simulations of polyethylene (PE) system of 10 chains with 1000 monomers was performed with LAMMPS software package to investigate the thermodynamics properties of the PE system at relatively high temperature (700 K). It is noteworthy that different simulations have been performed on the system by Hossain et al. at temperatures 100 K and 500 K to study the deformation mechanisms of the PE model. However, in this work, the thermodynamics properties of the PE system are explored to see how the system behaves at 700 K temperatures. This is because the PE system is suitable for biomedical applications (e.g. catheter, meshes, drug delivery systems, etc.) in its pure form.

Moreover, the PE system is treated with argon ion beam using TRIM software package to investigate the factors that affect the sputtering yield of the system for the ion energies 1 keV and 5 keV at different angles of incidence ( $0^\circ$  -  $89^\circ$ ). This is because the modified polymer is reviewed to have excellent applications in fabricating electronic devices, drug delivery packages, and biomedical applications.

In conclusion, the factors affecting the sputtering yield of the polyethylene system are observed to be angles of incidence and the ion energies. It was observed that the sputtering yield of the PE system increases with increasing the ion energies incident on the system (see the Figure 3). Also, it was observed that the sputtering yield changes for the varied angle of incidence ( $0^\circ$  -  $89^\circ$ ) of the argon ion on the PE system, and a maximum sputter yield is obtained around  $83^\circ$  for argon ion energies 1 keV and 5 keV.

Furthermore, the study of the thermodynamics properties of the system over 700 K by molecular dynamics simulation method gives a fundamental approach towards understanding the structure and internal motions of the PE system. So, from the results presented above, the following conclusions can be drawn:

- The temperature of the PE system is dependent on the time steps imposed on it.
- The density of the system depends on the duration of the simulation run.
- The total energy of the PE system depends on the time steps imposed on the system.

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