



# Sputtering of octatetraene by 15 keV C<sub>60</sub> projectiles: Comparison of reactive interatomic potentials



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## ABSTRACT

Molecular dynamics computer simulations have been used to probe the effect of the AIREBO, ReaxFF and COMB3 interatomic potentials on sputtering of an organic sample composed of octatetraene molecules. The system is bombarded by a 15 keV C<sub>60</sub> projectile at normal incidence. The effect of the applied force fields on the total time of simulation, the calculated sputtering yield and the angular distribution of sputtered particles is investigated and discussed. It has been found that caution should be taken when simulating particles ejection from nonhomogeneous systems that undergo significant fragmentation described by the ReaxFF. In this case, the charge state of many particles is improper due to an inadequacy of a procedure used for calculating partial charges on atoms in molecules for conditions present during sputtering. A two-step simulation procedure is proposed to minimize the effect of this deficiency. There is also a possible problem with the COMB3 potential, at least at conditions present during cluster impact, as its results are very different from AIREBO or ReaxFF.

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## 1. Introduction

Modelling organic systems is an important subject of contemporary computer science due to high utilization of these materials in industry and laboratories. Investigations of projectile-induced phenomena are an example of such studies. These simulations are difficult to perform due to complexity of the chemistry involved within organic materials and the large size of systems that has to be used to contain the high kinetic energy deposited in the sample by the impinging projectile. There is also an issue of intrinsic limitations of interatomic potentials that are used to describe internal forces. All interatomic potentials are originally constructed for simulations of solid phases close to equilibrium conditions. They are usually tested against experimental properties like bulk moduli or phonon frequencies. However, there are no measurements of these quantities at conditions that usually occur during a projectile impact. In this case comparison with quantities such as sputtering yields, kinetic and angular distributions of the ejected particles is the only way of verification of applicability of a given force field for modelling sputtering phenomena.

The Reactive Bond Order (REBO) [1,2] was one of the first reactive interatomic potentials used successfully to model processes induced by energetic projectiles in organic systems [3]. Since then

several more sophisticated force fields have been developed. The Adaptive Interatomic Reactive Bond Order (AIREBO) [4], the Reactive Force Field (ReaxFF) [5], and a third generation of Charge-Optimized Many Body (COMB3) [6,7] potentials are the most prominent examples. Almost all computer studies of keV projectile-induced chemistry performed to date on organic materials use REBO or AIREBO potentials [8]. Unfortunately, both these potentials are restricted to materials composed of only hydrogen and carbon atoms. Although other potentials capable of modelling more complex organic systems were available, they were too computationally expensive to be practically applied to model phenomena stimulated by projectile impacts in systems composed of a few hundred thousand atoms. Such samples are needed to properly absorb the kinetic energy delivered to the system by cluster projectiles with kinetic energy typically used in experiments. The situation has changed since optimized versions of ReaxFF [9] and COMB3 [3] have recently become available as a part of the LAMMPS modelling software [10]. Several simulations of cluster projectile impacts at systems composed of more than just C and H atoms already have been published [11–14]. Similar simulations with the COMB3 potential have not been done so far.

Coulomb interactions are an important part of binding energies of atoms in molecules in the ReaxFF potential [5]. As a result, this potential uses a procedure which calculates partial charges on atoms in the system. In the version of ReaxFF released within the LAMMPS package, partial atomic charges in molecules are

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calculated by procedure based on the Electronegativity Equalization Method (EEM) [15]. The EEM method works on a chemical concept of electronegativity and electrohardness. A difference of electronegativities drives the electron transfer from the electropositive to the electronegative atom assuming that they form a chemical bond, while large electrohardness attenuates this transfer. The method was developed for equilibrium configurations where molecules are stable. It has been reported, however, that the EEM has problems, as it allows long-range (even through space) charge transfer even between nonconnected particles [16]. For instance, it can assign a nonzero overall charge to parts of dissociated molecules. During keV projectile impact, in the initial stage of bombardment molecules are getting close together, some of these molecules undergo dissociation and some of formed fragments are ejected later. The EEM approach, may lead, therefore, to ejection of many charged particles. Such behavior will be in a conflict with the experimental observations which show that ion emission composes only a minor fraction of all ejected particles [17]. Recently a novel, so called atom-condensed Kohn-Sham density functional theory approximated to second order (ACKS2) approach has been proposed [18]. This approach is believed to circumvent residual charge deficiency of the EEM method as the ACKS2 essentially ensures that charges can only transfer between connected atoms. Unfortunately, this procedure has not been implemented yet into available charge equilibration codes.

The goal of this paper is to probe the effect of the interatomic AIREBO, ReaxFF and COMB3 potentials on sputtering of the organic sample composed of octatetraene molecules by 15 keV  $C_{60}$  projectiles. In particular, potential problems with partial charge calculations in ReaxFF will be investigated.

## 2. Computer model

A detailed description of the molecular dynamics computer simulations used to model cluster bombardment can be found elsewhere [8]. Briefly, the motion of particles is determined by integrating Hamilton's equations of motion. The forces among atoms in the system are described by an AIREBO potential [4], ReaxFF-Ig [9] and COMB3 force-fields. ReaxFF-Ig is an extension of the ReaxFF potential, which contains a dispersion correction, based on a low-gradient model, that includes long range attractive interactions. All potentials are splined at short distances with a ZBL potential to properly describe high energy collisions between atoms. An example for a specific case of C–C interaction is shown in Fig. 1. The shape and size of the sample are chosen based on a

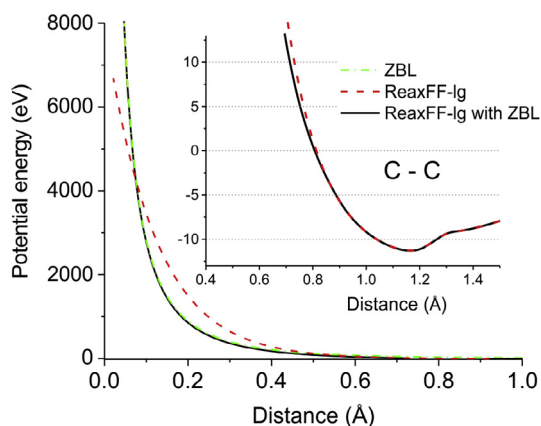
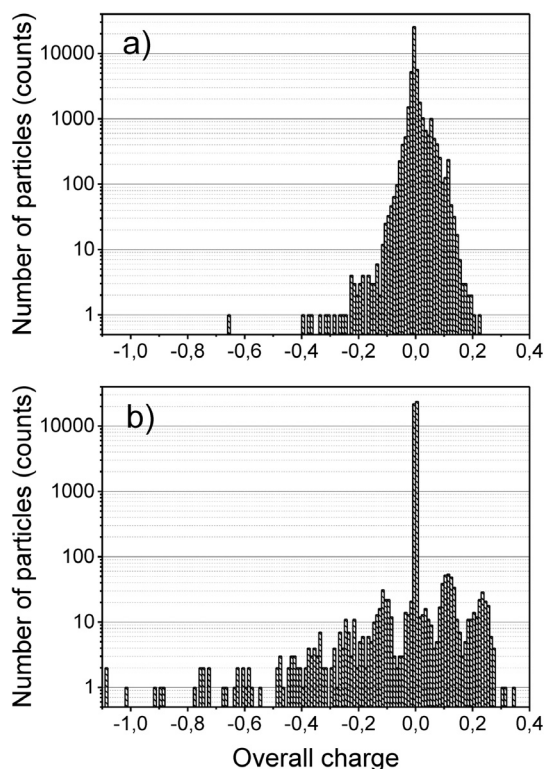


Fig. 1. Fitting of the ReaxFF-Ig potential for the C–C interaction to the ZBL potential. The inset shows that the covalent bonding is unaffected.

visual observation of energy transfer pathways stimulated by impact of  $C_{60}$  projectiles. Consequently, a hemispherical sample with a radius of 16 nm is used. Its surface is bombarded by 15 keV  $C_{60}$  projectiles at normal incidence. The model system contains 45,686 all-trans-1,3,5,7-octatetraene ( $C_8H_{10}$ ) molecules or 822,348 atoms. The unsaturated octatetraene molecules were selected as they are simple, yet having alternating double and single bonds, they exhibit more chemical pathways than saturated hydrocarbons. Octatetraene molecules are known to crystallize in a monoclinic structure [19]. In order to create a model system, a periodic octatetraene cell was equilibrated in an NPT ensemble to achieve minimum potential energy. Consecutively, the cell was replicated to the shape of a hemisphere and reequilibrated with free boundary conditions and the NVT ensemble to minimize energy of the sample. This procedure resulted in a density of the final octatetraene sample of  $0.956 \text{ g/cm}^3$  for AIREBO,  $1.050 \text{ g/cm}^3$  for ReaxFF-Ig and  $0.971 \text{ g/cm}^3$  for COMB3. The experimental value of the density is  $1.013 \text{ g/cm}^3$  [19]. All potentials give densities within 5% of this value. Rigid and stochastic regions with a thickness of 0.7 and 2.0 nm, respectively, were used around the hemisphere to preserve the shape of the sample and to simulate the thermal bath that keeps the sample at the required temperature and helps inhibit the pressure wave reflection from the system boundaries [8,20]. The simulations are run at 0 K target temperature in an NVE ensemble and extend up to 50 ps, which is long enough to achieve saturation in the ejection yield vs time dependence. As it has been shown that the efficiency of a sputtering process of organic materials weakly depends on the cluster projectile impact point [21], thus only a single impact is probed.

## 3. Results and discussion

As it has been reported that partial charges can be improperly assigned during molecular dissociation we start with plotting the charge state of particles in the octatetraene system 50 ps after a 15 keV  $C_{60}$  projectile impact. The result is shown in Fig. 2a. Although, the total charge of all atoms in the system is zero, i.e. entire system is neutral, a non-zero residual charge remains on many particles even so late after projectile impact. The problem disappears if the projectile kinetic energy is reduced below the point when molecules become fragmented. The existence of partial charges may have impact on characteristics of sputtered particles due to electrostatic interactions that should not be present. These interactions artificially enhance intermolecular bonding, which, in the ReaxFF-Ig potential, is already described by van der Waals interactions [5]. As a result, material will be less prone to sputter, as indeed observed. As it has already been indicated a more rigorous solution to this problem is not available yet. Therefore, we adopted a two-step procedure of running simulations, to minimize this deficiency. In the first step, the simulations run with a full charge equilibration up to the moment where most of chemical reactions occur. Depending on the kinetic energy of the projectile and the substrate, it usually happens within 0.5–2 ps after projectile impact. For instance, for the octatetraene system a simulation time of 0.5 ps is sufficient. The termination time cannot be, however, too long, as we want to ensure that ejection of sample material is still minimal. Otherwise, the ejection characteristics would have already been distorted by non-balanced charges on ejected particles and Coulombic interactions that should not be present. After 0.5–2 ps the simulation is terminated and a procedure based on interatomic distances and bond orders is used to identify interconnected atoms. Subsequently, each particle (interconnected atoms) is taken out of the sample and the partial charges on atoms are re-equilibrated to restore neutrality of the entire particle by using LAMMPS run in the environment, where only this particle

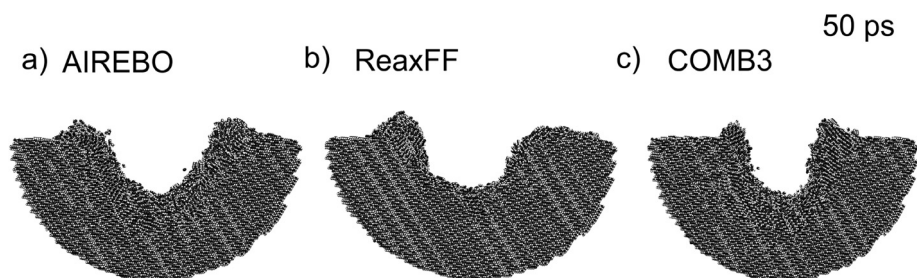


**Fig. 2.** The number of particles with particular partial charges obtained from octatetraene systems described by the ReaxFF potential at 50 ps after 15 keV  $C_{60}$  impact: a) without and b) with two-step simulation procedure described in detail in the main text.

exists. Finally, the neutral particle is reinserted into the sample at its original position. The procedure is repeated for all particles in the system. It should be pointed out, however, that partial charges still exist on individual atoms in a particle, as predicted by charge equilibration procedure, but the particle is now neutral as all. Existence of these charges is important because Coulombic interactions between atoms forming these structures, compose an important portion of the total bonding [5]. Only partial charges are modified by this procedure, while other quantities like velocities are not altered. The simulations are then restarted and we do not observe any spike in the total energy of the system. But from that moment on, they run with fixed charges, i.e. with the charge equilibration procedure disabled. Such approach, indeed, eliminates residual charges on most of particles as shown in Fig. 2b. However, the problem is not eliminated but only reduced as some particles are being still fragmented even during the second step of simulations.

While particles with non-zero charges are still present, the abundance of these particles was reduced by more than an order of magnitude. We see that the sputtering yield increases by almost 20%, when a two-step approach is used, which means that the effect of the residual charge is not negligible. Finally, it should be mentioned that the problem with charge equilibration does not occur in homogenous systems composed of identical atoms. As there is no difference in electronegativity, each atom has zero charge and there is no charge transfer during molecular fragmentation. Sputtering of such systems should, therefore, be modelled with the charge equilibration procedure disabled from the beginning to speed up simulations.

The snapshots of the system bombarded by 15 keV  $C_{60}$  projectiles taken at 50 ps are shown in Fig. 3 for AIREBO, ReaxFF-Ig and COMB3 potentials. The two-step simulation procedure is used on system where interatomic forces are described by the ReaxFF-Ig potential. In all cases large craters are formed in the solid. The shape of the craters is similar. There is, however, a significant difference in the size of craters. The craters formed in systems described by AIREBO and ReaxFF potentials are comparable in size, however, the crater formed in the system described by COMB3 is much narrower. Indeed, the calculated sputtering yield for the COMB3 system is  $71 \text{ nm}^3$ , which is more than 2 times smaller than  $181 \text{ nm}^3$  calculated for the AIREBO sample. A closer inspection of energy redistribution pathways shows that the deposited energy is transferred out of the bombarded volume much faster for the COMB3 potential. For instance, almost 90% of initially deposited energy is already transferred outside bombarded volume and absorbed by the stochastic zone at 10 ps for COMB3, whereas barely 16% is absorbed by this zone for AIREBO or ReaxFF at the same time. We do not know the reason for such behavior. We suspect that it has to be associated with conditions present during cluster bombardment, as successful simulations were reported for systems bombarded by atomic projectiles. As it seems that there is some important issue with the COMB3 potential we decided not to include results obtained with this force field in further analysis. Mass spectra gathered after a 50 ps simulation with utilization of AIREBO and ReaxFF-Ig potentials are shown in Fig. 4. Ignoring ejection of H and  $H_2$  atoms ejection of intact molecules dominates the spectrum. There are many molecular fragments with masses lower than the mass of intact molecule and much fewer molecular complexes heavier than octatetraene. There is virtually no difference in the shape of polar angle distributions of intact octatetraene molecules ejected from both investigated systems as shown in Fig. 5. The statistics obtained with a single impact does not allow us to plot kinetic energy distributions, but the average kinetic energy of intact octatetraene molecules ejected from AIREBO and ReaxFF-Ig systems is 0.9 eV and 1.3 eV, respectively.



**Fig. 3.** Cross sectional view of octatetraene bombarded by 15 keV  $C_{60}$  at normal incidence obtained at 50 ps for systems with a) AIREBO, b) ReaxFF-Ig and c) COMB3 interatomic potentials. A slice 2 nm wide of the system centred at the impact point is shown.

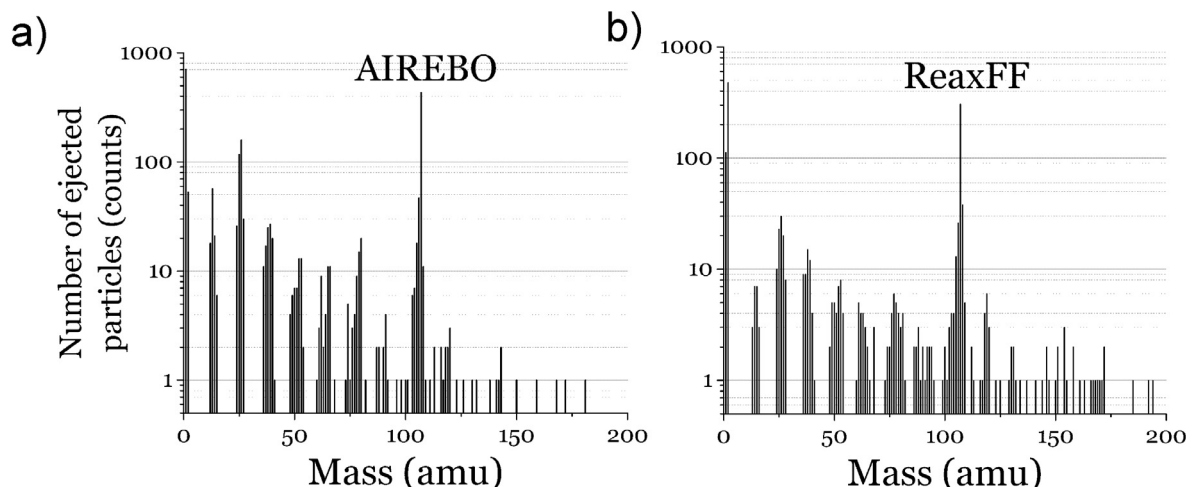


Fig. 4. Mass spectrum of particles ejected by 15 keV  $C_{60}$  from octatetraene with a) AIREBO and b) ReaxFF-Ig interactions.

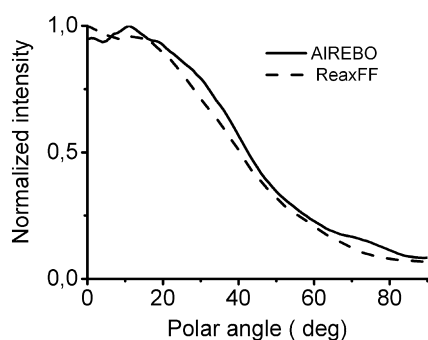


Fig. 5. The peak-normalized polar angle distributions of intact molecules sputtered by 15 keV  $C_{60}$  from octatetraene with AIREBO (solid line) and ReaxFF-Ig (dashed line) interatomic potentials.

While there are no major differences between the behavior of octatetraene systems described by the AIREBO and ReaxFF-Ig potentials, there is, however, a large difference in the time required to complete simulation. Around 180 h are needed for program running in a parallel mode on 49 processor cores to complete 50 ps simulation, when forces are described with the AIREBO potential. Almost 380 h are needed when ReaxFF-Ig is used with a two-step simulation procedure. The longest time of 450 h is needed for COMB3 potential. This difference is caused by a much more complex mathematical form of ReaxFF and COMB3 potentials.

#### 4. Conclusions

Molecular dynamics computer simulations have been performed to study the effect of interatomic potentials on sputtering of octatetraene system by 15 keV  $C_{60}$ . It has been found that care should be taken when simulating particles ejection from nonhomogeneous systems that undergo significant fragmentation described by the ReaxFF. In this case, the charge state of many ejected particles can be improper, due to inadequate procedure used to calculate partial charges on atoms when molecules undergo dissociation. The two-step simulation approach is proposed to partially circumvent this deficiency. The results obtained with this procedure indicate that both the ReaxFF-Ig potential and the AIREBO potential are giving similar results on the octatetraene system. There are some issues with the COMB3 potential, as it gives much lower sputtering yield compared to other potentials.

This difference is caused by a much faster transfer of the deposited energy out of the sputtered volume. This deficiency must be associated with conditions present during cluster bombardment, as successful simulations of sputtering for atomic projectiles are reported [22,23]. The AIREBO potential seems to be the best choice for simulations of cluster sputtering of pure hydrocarbon samples as it gives results similar to the ReaxFF potential in more than 2 times shorter time. The main advantage of ReaxFF is availability of a large number of parametrizations that allow to model systems composed of elements other than H and C. Furthermore, parametrizations for new systems are continuously being developed.

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