

Coarse-grained molecular dynamics studies of cluster-bombarded benzene crystals

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Abstract

As high-energy cluster projectile beams become standard analysis probes for SIMS, simulating larger crystals is now a requirement for the modeling community due to the large sputtering yields. As crystals get larger, computer resources become a limitation. Even though computer technology has evolved to include large memory systems and fast processors, there are still issues with having sufficient resources to run a calculation. This manuscript reports a method of studying a full crystal of benzene after impact with a 500 eV C₆₀ projectile using a coarse-grained model. The potentials developed for this model incorporate the C–H bond of benzene into a single coarse-grained bead. This coarse-grained method has several advantages over atomistic models—the amount of time to perform these calculations has been drastically reduced and the potentials for this sample are pair-wise additive potentials. A discussion is made as to how these results compare to those obtained with fully atomistic calculations using the AIREBO potential.

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1. Introduction

In order to develop an understanding of the phenomena of cluster solid interactions, it is important to model experimental systems using theoretical calculations. However, computation time is greatly increased with sample size. With this issue, the need to develop simpler models for understanding what is happening during a sputtering event is necessary. In this paper, we describe molecular dynamics simulations using a coarse-grained method that allows one to study larger systems with simpler potentials and faster computation times. The strategy involves combining the carbon and hydrogen atom in benzene into a single coarse-grained particle interacting within the same benzene by a Morse potential. Then, by using a Lennard–Jones pair potential to describe interactions between these CH particles in different molecules, we are able to model a C₆₀ impact on benzene. The results show that the coarse-grained calculation is able to closely mimic a fully atomistic calculation

in much shorter computation time than the fully atomistic case. Although the results show some differences, the approximation allows the essential physical phenomena associated with the bombardment to be rapidly extracted.

2. Simulation method

The classical method of molecular dynamics (MD) simulations used to model the particle bombardment events is described in detail elsewhere [1]. Briefly, Hamilton's equations of motion are integrated to determine the position and velocity of each atom as a function of time. Final positions and velocities are used to calculate quantities for comparison to experimental data and to analyze for microscopic motions.

An essential component of MD simulations is the interaction potential or force field among all the atoms. Traditionally, atomistic potentials have been used in modeling the particle bombardment process. Chemically accurate potentials are challenging to develop and there are only potentials available for a limited number of systems. In particular, we have used the REBO [2] and AIREBO [3] potentials for modeling particle bombardment of organic films [4] and organic substrates [5].

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Although these potentials have a high level of chemical accuracy, they do not, in fact, describe every reaction for hydrocarbon materials. Moreover, they are limited to compounds containing only carbon and hydrogen. Finally, the potentials are very time consuming to calculate because of their inherent complexity and the vast number of atoms that interact simultaneously.

As an alternative to atomistic potentials, many researchers have started reducing the computational effort in a simulation by grouping several atoms or molecules into one particle. These united atom or coarse-grained approaches have been successful for modeling a number of phenomena including self-assembled monolayers on metal substrates [6], vesicle fusion [7] and laser ablation of molecular solids [8,9]. The advantages of these coarse-grained approaches are that there are fewer particles, the potentials are simpler thus faster to calculate and the annoying H-vibration is eliminated which allows for a larger time step to be used in the integration.

In this study, we use the coarse-grained approach to model C_{60} bombardment of a benzene solid. Each benzene molecule is represented by six CH particles with a mass of 13 amu. A Lennard–Jones potential is used to describe the interactions of the CH–CH particles located on different molecules. Starting from published values of ϵ and σ [10], we adjusted the values to give the correct density of the molecular solid. The Lennard–Jones potential yields a binding energy of 0.49 eV per benzene molecule. The experimental cohesive energy, which depends on temperature, is measured to be between 0.45 [11] and 0.57 eV [12]. For the intramolecular interactions, our objective is to have a description that allows the molecule to dissociate and to accommodate some internal energy. Thus, the main interaction to include is a dissociating bond stretch term and for this we chose a Morse potential between adjacent CH particles (the 1–2 interaction) with parameters that reflect the bond strength and equilibrium distance in benzene. The other necessary interactions are between CH particles separated by one C atom (the 1–3 interaction) or by two C atoms (the 1–4 interaction). At this stage we feel that the most important consideration is to have a pair potential that allows the particles to interact if the molecule is dissociated. Thus, we include Morse potentials for these terms with small well depths. In the future we will include angle bend terms although as conventionally used they do not allow for dissociation. The REBO potential is used to describe the C–C interaction of the C_{60} [2]. Finally, a weak Lennard–Jones potential is used between the C atoms of the fullerene and the CH particles of the coarse-grained benzene molecule. The parameters for the Lennard–Jones and Morse interactions are given in Tables 1 and 2, respectively.

Table 1
Lennard–Jones interaction parameters

| Interaction | ϵ (eV) | σ (Å) | r_{cut} (Å) |
|-------------|-----------------|--------------|----------------------|
| CH–CH | 0.0052 | 3.70 | 7.65 |
| CH–C | 0.004 | 3.70 | 7.65 |

A 12-6 Lennard–Jones potential is used.

Table 2
Morse interaction parameters

| CH–CH interaction | D_e (eV) | r_e (Å) | α | r_c (Å) |
|-------------------|------------|-----------|----------|-----------|
| 1–2 | 5.41 | 1.42 | 2 | 5.0 |
| 1–3 | 0.01 | 2.42 | 2 | 5.0 |
| 1–4 | 0.01 | 2.84 | 2 | 5.0 |

The 1–2 interactions are defined as the nearest neighbor interactions in benzene, the 1–3 are the next nearest neighbor and the 1–4 are the across the molecule interactions.

The system investigated is a benzene crystal, represented by 139,104 coarse-grained CH–CH particles arranged in 28 layers of 828 molecules each. Positions of the benzene molecules are determined by heating the crystal at the experimental configuration to 300 K, with all six sides of the crystal having a rigid boundary to prevent evaporation, then quenching to 0 K using an algorithm based on the generalized Langevin equation [13,14]. The top rigid layers are removed and the crystal is equilibrated at 0 K for approximately 4 ps. Each trajectory begins with a C_{60} cluster projectile with 500 eV of kinetic energy bombarding the surface at normal incidence.

An atomistic simulation under the same conditions is evaluated using the AIREBO [3] potential for all the interactions. In this case, the sample has 30 layers of 828 molecules each or a total of 298,080 atoms.

3. Results and discussion

Snapshots of the cross-sectional view of the temporal evolution of a collision event due to 500 eV C_{60} bombardment for coarse-grained and atomistic benzene are shown in Fig. 1. Both the coarse-grained and atomistic calculations indicate that after impact, the C_{60} projectile stays intact albeit a couple bonds are broken in the coarse-grained case. After impact, a crater is formed in the solid. A crater depth of 2.7 nm deep is found for the coarse-grained calculation, which is in good agreement of 3.0 nm in the atomistic case. The overall trend for both the coarse-grained system and atomistic systems are similar, although not every detail such as the swelling of the surface at about 6 ps is identical. The more accurate, full reaction, atomistic calculation takes approximately 6 months to complete a 25 ps calculation. On the other hand, our coarse-grained system, takes approximately 4 days to complete a calculation of the same time. We estimate that to model C_{60} bombardment at 5–10 keV on a benzene solid that 252,000 benzene molecules will be required. This calculation is not computationally feasible with the atomistic simulation, thus we explore further the details of the comparison between the atomistic and coarse-grained simulations.

The coarse-grained calculation yields 13 sputtered benzene molecules, which is in good agreement of 12.4 in the atomistic case. All 13 ejected atoms are complete, intact benzene molecules. The total number of broken benzenes do differ significantly, but this can be accounted for by the stronger bonding of the 1–2 CH–CH interaction in benzene.

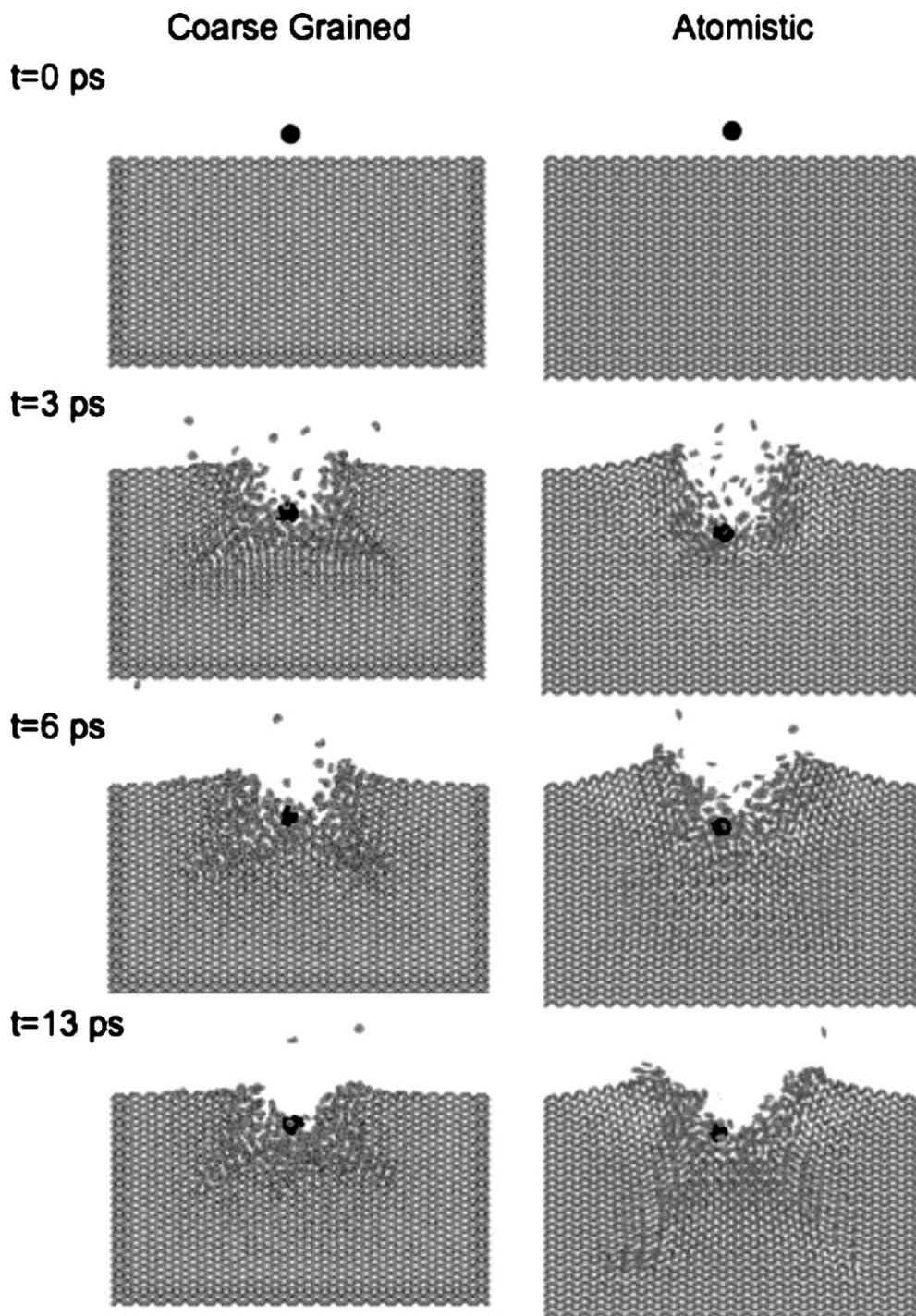


Fig. 1. Snapshots of the cross-sectional view of the temporal evolution of a collision event due to 500 eV C_{60} bombardment. The sample size for the coarse-grained calculation is $17.03 \text{ nm} \times 9.17 \text{ nm} \times 16.89 \text{ nm}$ and $17.03 \text{ nm} \times 9.86 \text{ nm} \times 16.89 \text{ nm}$ for the atomistic calculation. A slice 1.5 nm wide in the center of the system is shown. The atomistic simulation is two layers larger than the coarse-grained case, thus, the surfaces have been lined up for easier comparison.

4. Conclusions

The similarities and differences between a coarse-grained versus a fully atomistic simulation of C_{60} bombardment of benzene at 500 eV are discussed. Although the coarse-grained approach exhibits some differences from the fully atomistic approach, the essential physics is retained. The coarse-grained approach opens the door for modeling of large organic systems

with entanglement, other systems containing elements besides C and H, partial charges and larger systems bombarded by high-energy projectiles.

As a next step in our project, we plan to investigate a larger benzene crystal with impacting energies between 5 and 10 keV. We estimate a sample size of 1.5 million CH particles will be needed to properly dampen any pressure wave after the C_{60} impact. Based on the calculation just performed, this will take

approximately 40 days. The time to do this type of simulation using a fully atomistic benzene model using currently available hardware would extend to almost eternity.

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References

- [1] B.J. Garrison, in: J. C. Vickerman, D. Briggs (Eds.), *ToF-SIMS: Surface Analysis by Mass Spectrometry*, Surface Spectra, Manchester, 2001, p. 223.
- [2] D.W. Brenner, O.A. Shenderova, J.A. Harrison, S.J. Stuart, B. Ni, S.B. Sinnott, *J. Phys.: Condens. Matter* 14 (2002) 783.
- [3] S.J. Stuart, A.B. Tutein, J.A. Harrison, *J. Chem. Phys.* 112 (2000) 6472.
- [4] Z. Postawa, Czerwinski, N. Winograd, B.J. Garrison, *J. Phys. Chem. B* 109 (2005) 11973.
- [5] B.J. Garrison, A. Delcorte, K.D. Krantzman, *Acc. Chem. Res.* 33 (2000) 69.
- [6] J. Hautman, M.L. Klein, *J. Chem. Phys.* 91 (1989) 4994.
- [7] S.J. Marrink, A.E. Mark, *J. Am. Chem. Soc.* 125 (2003) 15233.
- [8] L.V. Zhigilei, E. Leveugle, B.J. Garrison, Y.G. Yingling, M.I. Zeifman, *Chem. Rev.* 103 (2003) 321.
- [9] Y.G. Yingling, B.J. Garrison, *J. Phys. Chem. B* 109 (2005) 16482.
- [10] M. Mondello, H.J. Yang, H. Furuya, R.J. Roe, *Macromolecules* 27 (1994) 3566.
- [11] E.G. Cox, D.W.J. Cruickshank, J.A.S. Smith, *Proc. R. Soc. A* 279 (1964) 98.
- [12] H.P. Steinrück, *Surf. Sci.* 218 (1989) 293.
- [13] S.A. Adelman, J.D. Doll, *J. Chem. Phys.* 61 (1974) 4242.
- [14] B.J. Garrison, P.B.S. Kodali, D. Srivastava, *Chem. Rev.* 96 (1996) 1327.