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A comparison between fullerene and single atom impacts on graphite

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Abstract

Recent experimental measurements of craters/defects caused by energetic C_{60} impacts on graphite have shown how the penetration depth of the C_{60} increases as a function of velocity. We show here Molecular Dynamics Simulations of C_{60} , C_{70} , C_{76} , C_{78} and C_{84} impacts on graphite which are in very close agreement with the experimental findings. By comparison with single atom impacts on the same surface and study of the early cascade propagation we obtain an evidence of long time co-operative, non-linear, effects of the molecular surface interaction which give rise to greater displacement of target atoms than would be expected by just scaling up results from single atom interactions. There is little difference found between different impact sites for the molecules, unlike the single atom impact behaviour.

1. Introduction

The stopping of energetic ions and clusters in solids is a topic of growing interest because of the increasing use of both ion and cluster beams in the materials processing. For a number of years now the interactions of energetic fullerenes with surfaces have been studied via both experiments [1–5] and simulations [6–8]. Much of the earlier work has concentrated on lower energy collisions with the graphite surface, when the fullerene bounces from the surface, leaving the graphite intact only propagating an acoustic wave. For molecular energies in excess of 500 eV it has been found [5,8] that the fullerene will penetrate the surface, causing some surface disruption.

The interaction of single particles (atoms) with solids has been much studied over the years and the subject might well be considered to be mature, in that most of the phenomena of implantation are readily predicted by theory and simulation. In the case of a typical implantation situation an ion is of sufficient energy to penetrate the surface, may initiate a collision cascade, cause some of the constituent target atoms to be sputtered and some to be displaced from their normal resting places causing radiation damage. In many cases these effects can be modelled well using a linear model of energy deposition.

In the case of molecular impact on surfaces it is less clear that this linear treatment of energy propagation will

be as reliable as we are now depositing energy in much higher density than is the case for single particle implantation.

The purposes of the work presented here are: (i) to demonstrate that the simulations and experimental observations of these higher energy phenomena are in good agreement; (ii) to observe the effects of the interactions of the higher fullerenes with a graphite surface and, hence, determine the parameters which effect the experimentally observable features; and (iii) to contrast the behaviour of molecular impacts with those of single atom impacts.

2. Simulation method

The Molecular Dynamics model used in this work has been described in detail in the past [8,9] and so only a brief description will be given here. The Tersoff many-body carbon potential [10] is used to model the interactions between the C atoms in both the graphite and fullerenes. This potential has been used extensively in the past to model dynamical processes in graphite [8,11] as the potential gives the correct cohesive energy of carbon in the graphite and diamond structures. It also gives stable structures for the fullerenes used in this work. The targets used here were typically 11.7 nm × 11.7 nm containing 46720 atoms in 8 layers to a depth of 2.7 nm for the lower energies and up to 12 layers for the higher energies. Free boundaries were used throughout and the effects of inelastic energy losses due to direct interaction with the electronic system were ignored. Free boundaries were employed to avoid any unnecessary damping forces, choos-

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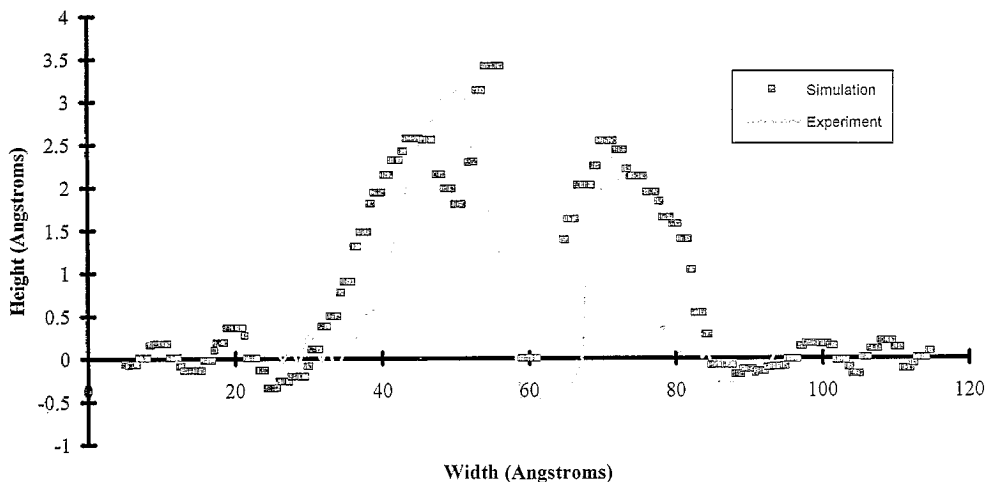


Fig. 1. A cross-sectional scan through center of a typical irradiation induced hillock generated by a 4 keV C_{60} impact, both simulated and from STM measurements.

ing, instead, to make the boundaries sufficiently far away to have little effect on the calculations.

3. Comparison with experiment

Experimental observation of energetic fullerene (C_{60}^+)/graphite interaction has been made previously [5] in which an HOPG target was irradiated by a range of energetic C_{60}^+ molecules (from 500 eV to 23 keV). An STM was used in these experiments to image the surface after irradiation. Hillocks of between 30–50 Å in diameter and height 2–3 Å were observed. It has also been reported

previously [8] that similar hillocks have been observed in simulations of the same system. Fig. 1 shows a cross section through the centre of a typical hillock found in both the experimental and simulated irradiations. As can be seen there is very good agreement between the two. The simulation shows a wider hillock than that found experimentally, which is most likely due to the fact that the simulations have only been run out to about 1.5 ps and the hillock will probably relax on a larger timescale.

The experimental work [5], mentioned above, also measured the depth to which damage was introduced into the graphite by employing an oxidation technique which selectively etches away layers which contain defects. They

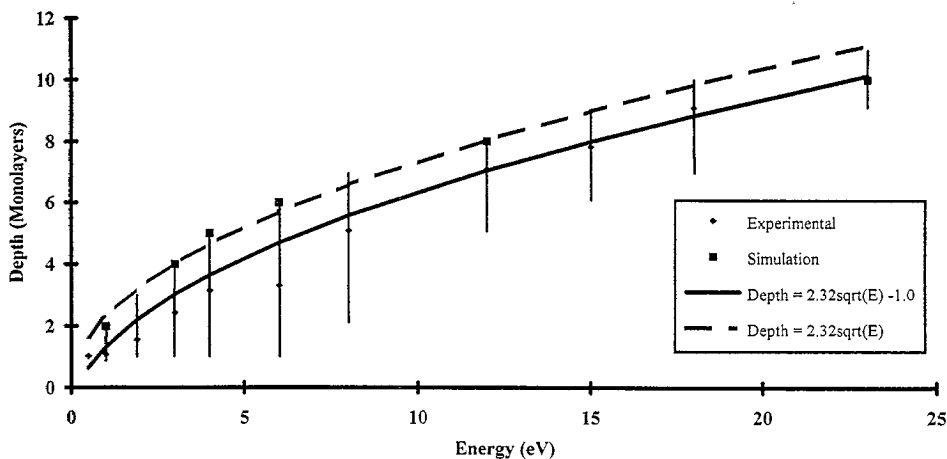


Fig. 2. Penetration depth as a function of projectile energy for C_{60} impacts on graphite, experimental and simulated results. Error bars on experimental results reflect range of crater/defect depths measured by subsequent etching.

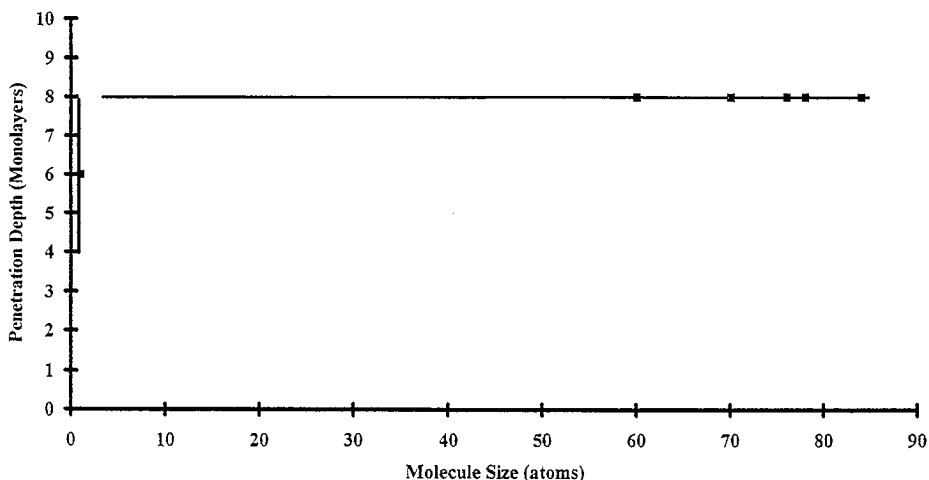


Fig. 3. Penetration depth as a function of molecule size at 200 eV/atom – constant velocity.

found that the depth to which the C_{60} created defects was a function of energy shown in Fig. 2. In this original paper the authors suggested that this may be a linear function of energy. However, further analysis of this data, additional measurements of other impact energies and comparison with the simulation results now suggest that the depth of penetration of the C_{60} can best be described as a function of velocity or $E^{0.5}$. Fig. 2 also shows a set of simulation results for the depth of penetration of the molecules. The depth of penetration in the simulation was taken as the deepest layer which was left broken by the impact. As can be seen the simulation and experiment agree very well in form although there appears to be an offset of about one monolayer between them. The most likely reason for this

is that the deepest layer may well “recover” and hence not become etched in the experiment.

4. Simulation results and discussion

The promising agreement with the experimental results demonstrated above allows us to use the simulation with confidence to investigate the interaction as a function of molecule size. In Fig. 3 we use the simulation to predict the penetration depth as a function of molecule size maintaining a constant velocity for the impinging particle (either atom or molecule). As can be seen from the figure the penetration depth does not change as a function of molecule size. The most interesting point is that even the single

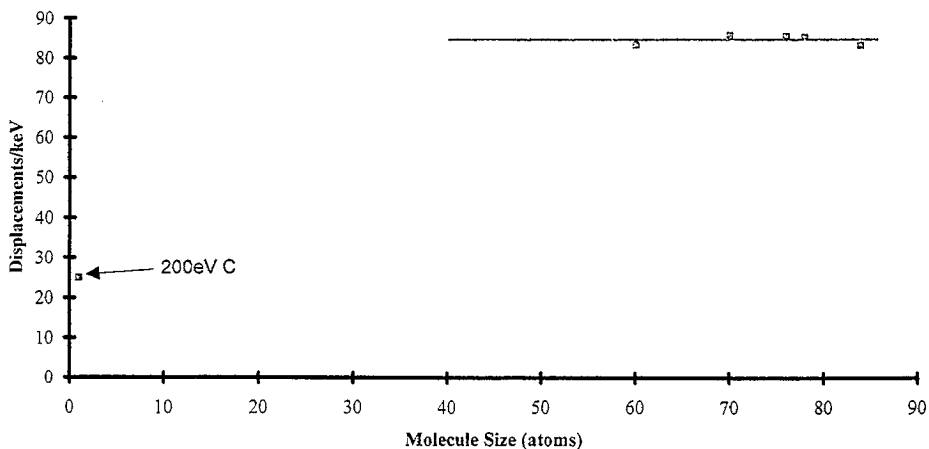


Fig. 4. Number of displaced atoms per keV as a function of molecule size at constant velocity – 200 eV/atom; collisions at 150 fs.

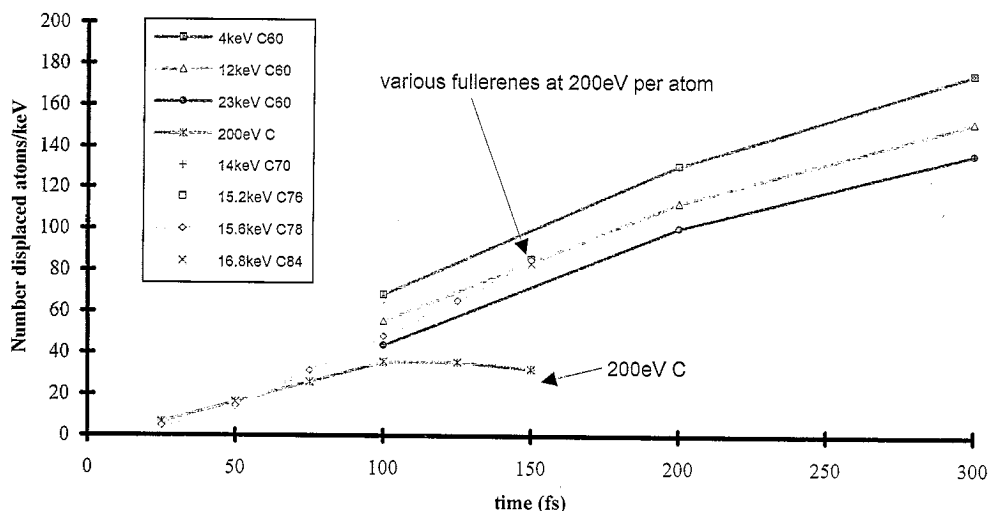


Fig. 5. Number of displaced atoms per keV as a function of time – see text for details.

atom impact can penetrate the graphite to the same depth. It is rare for the atom itself to penetrate this far but recoils can and do penetrate to this depth. It was found that changing the impact site for molecules made no difference to the depth of penetration, but for single particles the depth of penetration depended precisely where the particle struck on the surface. Thus at 200 eV per atom the single atom itself invariably ends up implanted in the second layer, initiating a small cascade of recoils. The atoms of the fullerene molecules, on the other hand, can often be implanted down to the ninth layer.

In Fig. 4 the number of defects is plotted as a function of molecule size, again for a constant velocity given by an energy of 200 eV per atom. A defect here is determined simply by counting the number of atoms not on a lattice site. We have plotted the number of defects per keV available as it is most likely that the number of defects should scale with deposited energy. Certainly the simulations predict that the number of defects increases linearly with energy in the energy regime of 1 keV to 23 keV as simulated in this work. Fig. 4 shows that the number of defects is independent of molecule size, but that the number of defects generated by a 200 eV C atom is a little lower than might be expected. The reason for this can be better appreciated by looking at the number of defects produced during the collision cascade as a function of time – see Fig. 5. For the first 100 fs the defect production rate is the same per keV available for all particles, in line with the simple predictions of the Kinchen Pease relationship [12]. At longer times the number of defects generated by the single atom impact decreases as the defects start to relax. In the case of the molecular impacts the number of defects continues to grow – even out to 1.5 ps – as the deposited energy spreads through the lattice. The results plotted in Fig. 4 were taken at 150 fs, where the single atom collision cascade has created most of its defects. However, as we

can see from Fig. 5, the cascades generated by the molecular impacts are still producing defects. Due to the long computation times involved and the need to incorporate electron-phonon coupling for such long timescales, it was not possible, at this time, to take the simulations past 1.5 ps accurately and hence allow these cascades to fully relax. This long term displacement effect is an evidence of what is often termed a Thermal Spike [5,13]. Further work is underway to look at the relaxation of these cascades.

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