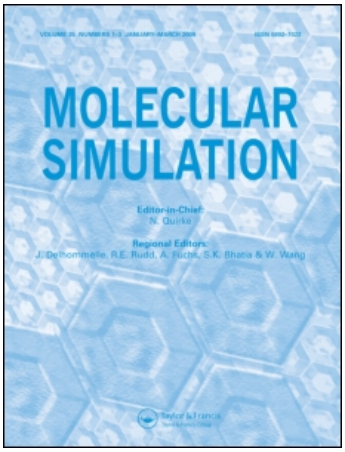

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Impact-induced desorption of large molecular structures from graphitic substrates

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Impact-induced desorption of large molecular structures from graphitic substrates

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We use molecular dynamics computer simulation to show how the impact of a C_{60} molecule on a graphite surface can cause an acoustic wave across the surface of the substrate that is strong enough to desorb a neighbouring C_{60} molecule that has already been adsorbed. This could have potential implications for experimentalists attempting to grow fullerene-based structures on graphite-like materials using an energetic deposition technique. It suggests that unlike normal growth conditions, where sticking probabilities are the principle concern, an extra problem of deposition induced desorption may further slow a growth process.

Keywords: Computer simulation; Fullerene deposition; Graphite; Growth process

1. Introduction

The phenomenon of sputtering has been well known and understood for over a century now and has been put to good uses in areas such as secondary ion mass spectrometry (SIMS) and focussed ion beam (FIB) lithography. It has been the cause of some minor technological problems in employing ion beams by causing premature saturation effects in implantation and through undesired surface morphology changes in many other applications. In the majority of cases these problems have been overcome relatively simply.

Currently many new applications are being considered that involve the positioning of large fullerene-based objects on surfaces to create both active and passive devices. The investigation presented here uses molecular dynamics computer simulation [1] to highlight a potential pit-fall that might cause some initial problems when attempting to build these systems using an energetic deposition mechanism, particularly if the substrate material is a layered material such as graphite.

We have employed full many-body potentials with an additional long range component to model the Van der Waals forces [2] to demonstrate the behaviour of the surrounding surface after a relatively gentle impact of fullerenes (single cage fullerenes, C_{60}, have been used as well as multiple cage, C_{300} and C_{840}) onto a graphite (hopg) surface. It is seen in figure 1 that the impact, whilst leaving the molecule intact, can cause an acoustic wave on the surface of the graphite. Previous work [3] has shown that this acoustic wave can cause substantial ejection of benzene molecules adsorbed onto the surface of the substrate. Here we use the same computational model and general technique and show that this acoustic wave can cause desorption of a large molecules as well.

2. Simulation method

The precise details of the computer simulation technique used in this investigation have been given elsewhere [1,4], hence only a brief summary outlining the important components will be given here. The classical molecular dynamics simulation technique is employed solving Newton's Laws of Motion for many thousands of atoms obeying a realistic many-body interaction potential. The interaction potential used is the Brenner hydrocarbon potential [5,6] with an additional long range term as described by Smith and Beardmore [2]. In this paper the authors describe how the long range pairwise interactions in carbon systems can be included with short range many-body potentials in such a way that the bulk crystal properties predicted by the covalent potential functions are unaltered [2]. A brief description of the technique is given

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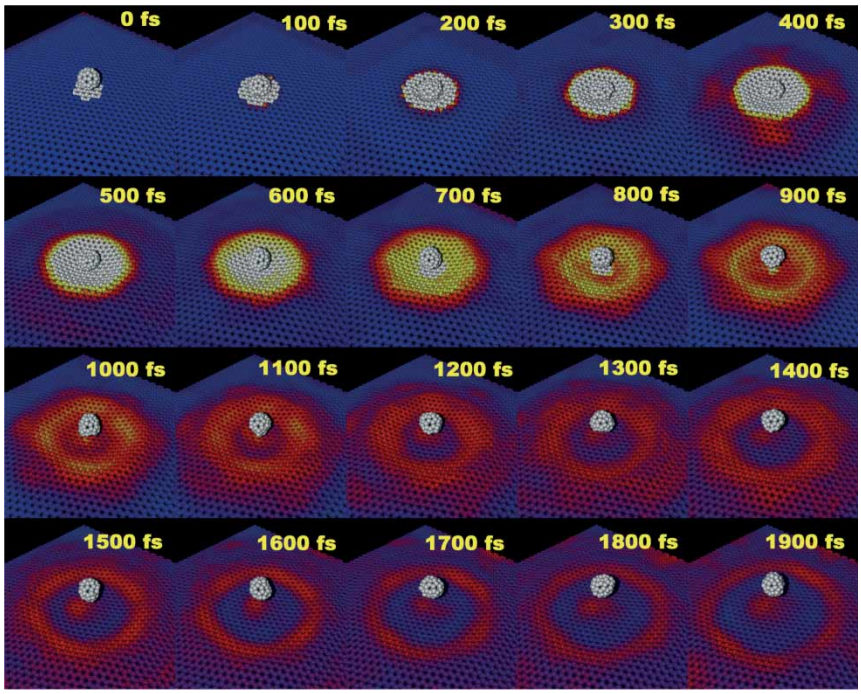

Figure 1. Impact of low energy (250 eV) fullerene on a graphite surface can cause a substantial acoustic wave.

here. The implementation requires the use of separate neighbour lists for the long-range and short-range interactions. The basic form of the long-range interaction is a Lennard–Jones potential of the form

$$V = V_e[(r_e/r)^{12} - 2(r_e/r)^6]$$

For graphite, the authors [2] have set $V_e = 0.0037$ eV and $r_e = 3.85$

The long-range interactions are smoothly joined to the short-range covalent bonding Brenner potential. We use the parameters from the Brenner 1 formulation as this gives a good description of both graphite and fullerene as described in detail in Ref. [2]. The Brenner potential employs a short-range cut-off function which takes the form:

$$f_c(r) = \begin{cases} 1 & r \le R_i \\ \frac{1}{2} - \frac{1}{2}\sin[\pi(r-R)/(R_0 - R_i)]. . . & R_i \le r \le R_0 \\ 0 & r \ge R_0 \end{cases}$$

and $R = (R_0 + R_i)/2$

The long-range interaction between the two atoms is cut-off smoothly by a function dependant upon the co-ordination of the atoms via the covalent bonds. The short-range neighbour list is used to see if the two atoms are connected by three or fewer covalent bonds by the function:

$$f_c^{lr}(r) = \begin{cases} 1 & w_{ij} \le 0 \\ \frac{1}{2} + \frac{1}{2}\cos(\pi w_{ij}). . . & 0 \le w_{ij} \le 1 \\ 0 & w_{ij} \ge 1 \end{cases}$$

where,

$$w_{ij} = f_c(r_{ij}) + \sum_{k \ne i,j} f_c(r_{ik}) f_c(r_{kj}) + \sum_{k \ne i,j \ldots l \ne i,j,k} f_c(r_{ik}) f_c(r_{kl}) f_c(r_{ij})$$

and $f_c(r)$ is the short range cut-off as above. The long-range interaction thus cuts smoothly to zero if atoms are sufficiently close to sp^2 or sp^3 co-ordination.

The elastic properties of this potential have been investigated more fully by Smith and Christopher [7] in a simulation of nano-indentation for diamond, graphite and fullerite films. In their simulations they find good agreement with experiment. In the results presented here the elastic behaviour of the graphite surface is key in determining the exact results and so it is important that this behaviour is modelled well. However, it can be expected that the phenomenon discussed here is likely to occur in any layered material, like graphite, to a lesser or greater extent.

The long-range term provides the interlayer bonding term for graphite and the Van der Waals attraction of molecules to the graphite surface. The binding energy of clusters to the graphite surface is calculated by moving the particle close to the surface and away to beyond the cut-off of the long range potential. The potential energy of a fullerene C_{60} molecule is plotted as a function of distance from the surface and shown in figure 2. The binding energy is found to be 0.275 eV to the graphite surface at an equilibrium distance of 6.3 Å above the surface, the distance being measured from the centre of the cage structure. Previous simulations [8] of binding and

equilibrium distances of benzene molecules in this way have found good agreement with experimental values. Estimates, based on measurements of the sublimation energy and cohesive energy of bulk C_{60} to be about 0.85 eV [9]. The values are not in great agreement here, but the estimated value is not based on direct measurement of the C_{60} binding to graphite and could be in error. However, the simulations presented here are meant as a guide to demonstrate the behaviour of loosely bound molecules to layered surfaces after impact close by from a similar molecule so that the actual details are less critical. A further investigation is underway to determine the effect of the strength of the binding energy of the adsorbate.

Similar results are found for C_{300} structures with a binding energy of 0.47 eV at 10 Å above the surface. Cell sizes contain about 100,000 atoms depending upon the over-layer and projectile simulated. The lateral edges of the simulation cell are treated as periodic but the surface and bottom are treated as free boundaries. The simulations are run for typically 4 ps, if they run for much longer then reflections from the periodic boundaries can cause noticeable effects to the results.

3. Results

The simulations have been run to observe the effects of the impact from a fullerene molecule on a graphite surface on which a fullerene molecule has been adsorbed. As described above the impact at energies of 200 eV (that is an equivalent energy of 3.33 eV per atom) can cause the propagation of acoustic waves across the surface that have sufficient energy to cause the ejection of small benzene molecules that have previously been adsorbed to the surface. Can the same mechanism cause the ejection of larger adsorbed molecules?

Figure 3 above shows that an energetic impact of a C_{60} molecule can cause desorption of a neighbouring C_{60} molecule. The figure shows the ejection of a nearby adsorbed C_{60} molecule (dark grey) caused by the impact of a 4 keV C_{60}^{+} molecule (light grey). In the initial frame the "dark grey" C_{60} is bound to the surface and the impacting "light grey" C_{60} is about to make impact with the surface. In this figure the atoms between the "viewing point" and the impact point have been removed from the drawing, but are present in the simulation, to allow the observer a clearer view as to what happens at the impact site and close to the desorbed molecule. In each frame the time after the start of the simulation in femtoseconds is shown. It can be seen that the energetic C_{60} impacts the surface and breaks through the surface of the graphite and destroys itself and causes an acoustic wave to propagate across the surface from the impact site. This wave then interacts with the adsorbed C_{60} giving it enough energy (at about 2400 fs) to overcome the binding between it and the surface. In figure 4 we show a similar set of results for a similar energy impact, but this time near a C_{300} adsorbed cluster. The effect is very similar despite the increased mass of the cluster and the higher binding. The impacting C_{60} creates an acoustic wave in the surface of the graphite with enough strength to cause the C_{300} cluster to be desorbed from the surface. The mechanisms are very similar; the initial impact causes the surface to move downwards—away from the adsorbed molecule—pulling it with it. The surface then recovers and springs back, hitting the adsorbed molecule and giving it enough energy to escape the surface binding potential.

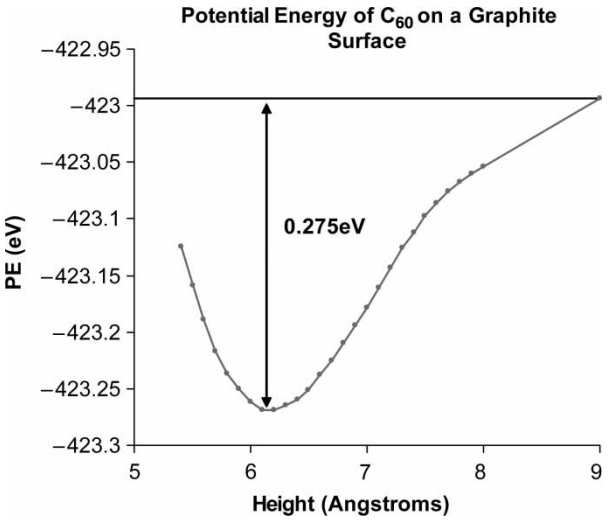

Figure 2. Potential Energy of C_{60} as a function of height above graphite surface.

These examples have been modelled at a higher energy (4 keV for the C_{60} or 66.67 eV per atom) than would be used in a deposition system, and it does demonstrate a potential problem of such a technique. Also, whilst the overall energy is relatively high the energy per incoming atom is lower than is often used in a deposition system. It should also be noted that fullerene impacts of 250 eV, which are enough to "soft-land" a fullerene on the surface, also create acoustic waves [10]. We have investigated a number of impacts at 250 eV at a range of distances away from the adsorbed fullerene molecule and the general results can be compared in figure 5 below.

Figure 5 shows the mean perpendicular velocity of all the atoms in the adsorbed molecule (either a C_{300} cluster of a C_{60} molecule) as a function of time during the simulation. The same effect can be seen here as were described above from the atom positions. Looking at the curve labelled with triangles on the figure (the 4 keV C_{60} impact near an adsorbed C_{60}), the perpendicular velocity of the adsorbed molecule shows that the molecule is first pulled towards the surface (+ve direction) and then pushed away from the surface (− ve direction), this is repeated with more energy and at about 2400 fs the molecule is given enough energy to escape the surface, which it eventually done at about 3 ps. A very similar effect is seen (curve labelled with circles) when the energy of the impacting molecule is dropped to 500 eV (8.3 eV per atom). This has been repeated for initial energies of 400 eV (not shown) with the same result.

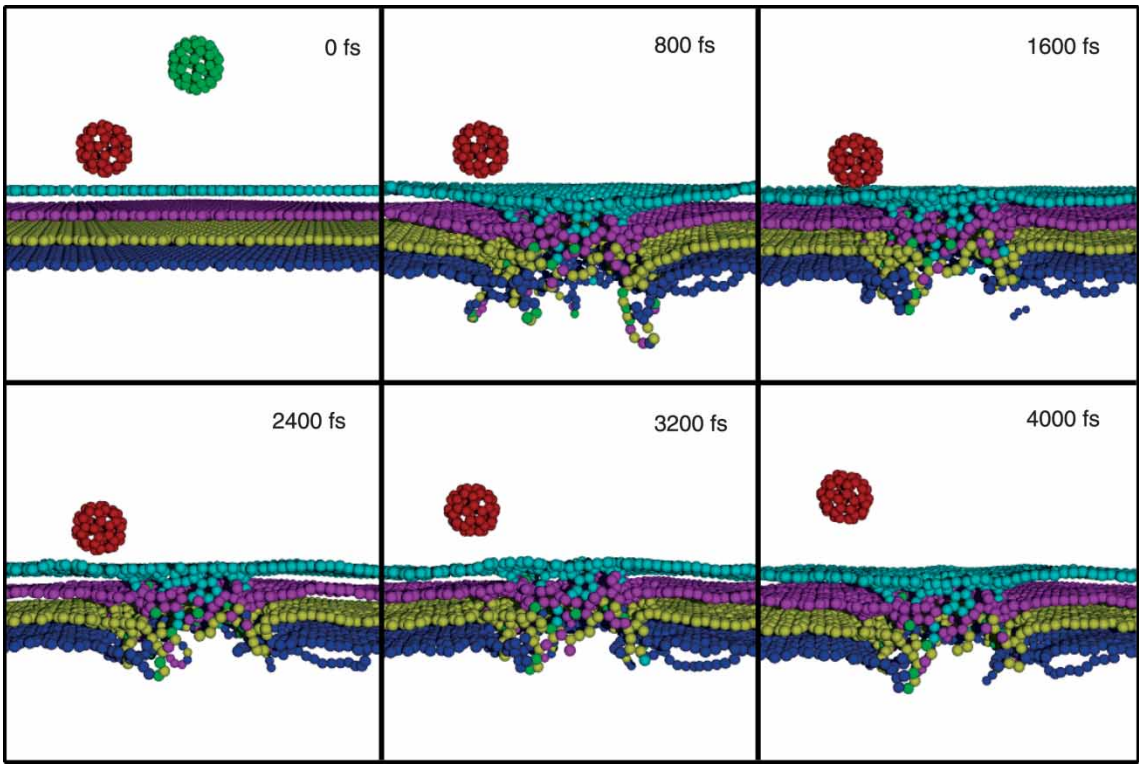

Figure 3. The energetic impact of a 4 keV C_{60} on a graphite surface—see text for discussion.

When the adsorbed molecule is changed for a C_{300} cluster (curve labelled with diamonds) then the story is very similar but the velocities are lower. If we change the impacting particle to a C_{300} cluster as well then the adsorbed cluster is desorbed from the surface with the first vibration of the surface (see the curve labelled with squares) suggesting that the effect is even more pronounced. However, in the case of the impact by a

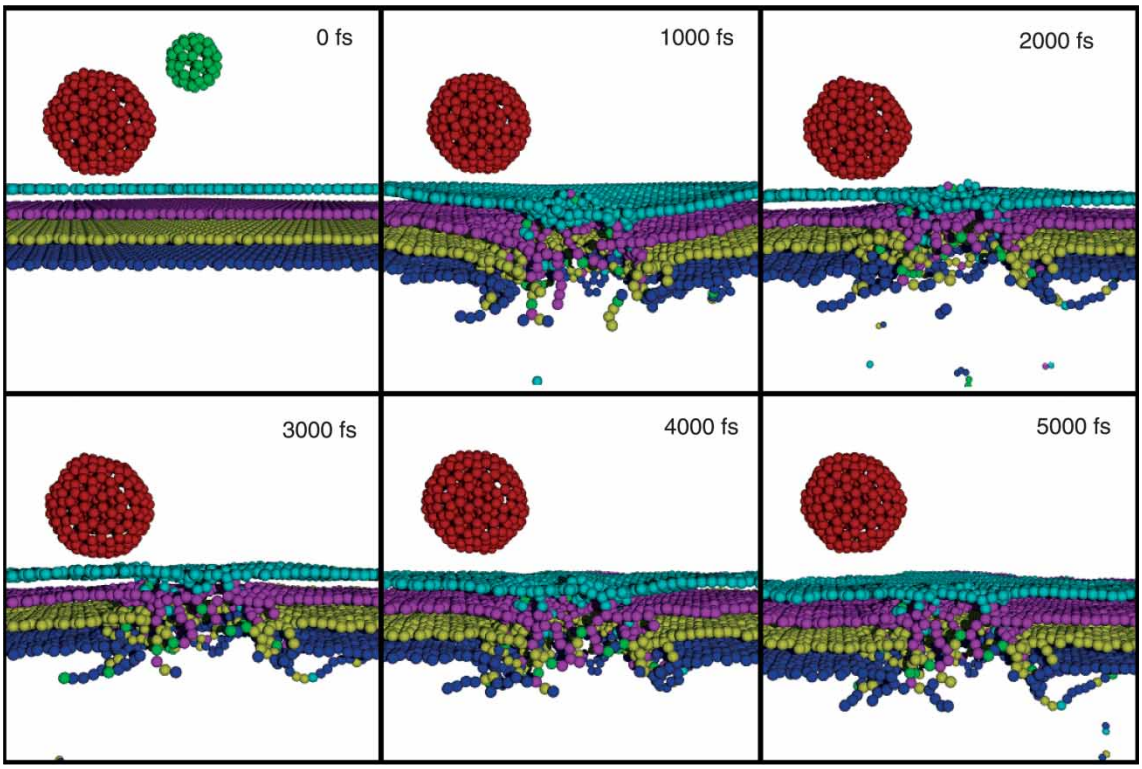

Figure 4. The energetic impact of a 4 keV C_{60} near a C_{300} adsorbed molecule.

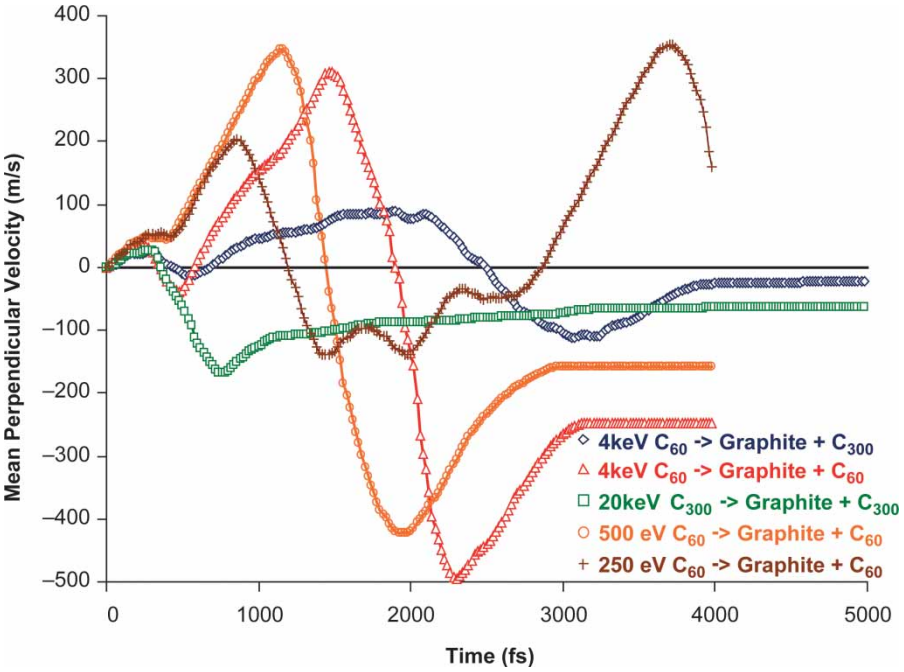

Figure 5. Perpendicular velocities of "adsorbed" molecule for various fullerene impacts.

250 eV C_{60} (curve labelled with crosses), an energy at which soft-landing occurs, it can be seen that the adsorbed molecule undergoes the same behaviour except that when the molecule is pushed away from the surface it does not acquire enough kinetic energy to escape the surface and remains bound. However, the velocity on the second bounce is substantially higher as it comes closer to the surface and at 4 ps it does appear to be about to start moving away from the surface and the curve gives a hint that in the following time-steps the molecule might well shake itself free of the surface. Unfortunately the simulation time beyond 4 ps is untrustworthy and it is possible that reflections from the boundaries could cause ejection of the molecule at this point. Simulations on larger systems are now underway to investigate if impacts at these low energies do indeed cause ejection as well or if this is just a side effect of the boundary conditions of the simulation.

These simulations have been performed for a system initially at 0K. In the real world, this would clearly not be the situation, and both the adsorbed fullerene and the graphite surface would exhibit some thermal motion. Initial thermal vibrations could affect the results in both an additive and subtractive manor, depending on the timing of the initial impact. The induced wave and original thermal vibrations will combine in either a constructive or destructive manor at the position of the adsorbate. The most likely outcome of this is that the addition of thermal vibrations to the simulation will simply blur the effect already seen. Clearly, at elevated temperatures, close to the temperature at which the adsorbate would detach anyway (the temperature at which this happens in the simulation is the subject of a further investigation), there will be an increase in the probability of ejection of the adsorbate.

5. Conclusions

Although at the present time we have not been able to observe coupling of the wave with sufficient energy to a neighbouring fullerene to cause desorption for low energy impacts it has been demonstrated that it does occur for larger energies and there is some indication from the simulations that there could well be a problem for low energies at which soft-landing occurs. It is felt that this could, therefore, potentially be a real problem and will almost certainly contribute to a reduction on the experimentally observed sticking probability in this kind of system. This investigation is very much preliminary at this stage.

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