

Crossover in energy redistribution during $C_{60}@Xe_{144}$ surface impact

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Molecular-dynamics simulations are performed to study heterogeneous cluster-Si (111) surface impact dynamics. A transition in energy redistribution is observed as the initial velocity of the cluster complex increases. The Xe_{442} outerlayer plays a role as a cushion to soft-land a C_{60} molecule at a lower velocity (5 km/s) and becomes a hammer to break the molecule at a higher velocity (10 km/s). Detailed studies indicate that the transition in the behavior of the xenon layers occurs at $v=7-8$ km/s. Issues such as penetration depth, deformation, fragmentation, and surface modification are addressed.

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Cluster-surface impact has attracted attention from many research groups since the early 1990s.¹⁻⁴ The motivation for studying such processes lies in controlling the growth of nanostructure materials^{5,6} and searching for chemical reaction channels.^{7,8} In the past several years, the combined efforts from both experimental measurements and molecular-dynamics simulations have achieved great success in understanding the energetics, dynamics, and thermodynamics of many complex systems during collision processes. Among the systems studied, the fullerenes^{9,10} have been used extensively in surface collision experiments because of their unique properties and the promise of important roles in future nanotechnologies.

More recently, a growing interest has developed in cluster science to prepare heterogeneous fullerene complexes¹¹ via doping, coating, and other techniques. The emergence of these systems raises questions and problems in current nanoscience research. While efforts have been made to understand the structure, electronic structure, and mechanical and optical properties of clusters, the interaction between heterogeneous clusters and surfaces remains largely unexplored. Many fundamental issues related to the dynamic behavior of such processes are yet to be addressed.

In a 1993 simulation³ of controlled deposition and soft-landing of a cluster in a liquid-surface collision, rare-gas Ne and Ar films were used to illustrate soft-landing vs glassification, respectively. The study suggested that rare-gas films could be used to reduce or to increase the damage of a $Na_{36}Cl_{36}$ cluster. One can control the outcome by using films that have different mass densities. The authors in this work suggested a promising method to soft-land a nanocrystal and/or to make a nanoglassy particle. The theoretical predictions were verified later by experimental measurements.¹² The focus of these earlier studies was on homogeneous, single nanocrystals. In the middle 1990s, scientists began to study molecules embedded in a cluster environment. This work led to so-called cluster-surface impact chemistry.^{7,8,13} The idea was first suggested in 1992 as a result of the discovery of nanoshockwaves during cluster-solid surface collisions. Simulations suggested that the shock wave and the extreme conditions during impact can be used to induce chemical reaction pathways. This idea was followed by a number of theoretical and experimental studies.^{7,8,13} Among these activities, a prototype system was chosen to demon-

strate the impact-induced dissociation of I_2 in $I_2@Xe_n$ surface collisions. In contrast, in the collisions between a Na_4Cl_4 cluster coated with Ar_n and a NaCl surface, no evidence was observed for fragmentation or isomerization of the salt cluster.¹⁴

Inspired by the recent experimental developments in the area of heterogeneous clusters, the unanswered questions remaining in previous studies, as well as the urgent needs for theoretical insights in heterogeneous systems, we performed a series of large-scale simulations to study cluster-surface impact phenomena systematically. This paper reports the results of our investigations of collision processes between C_{60} and a Si(111) surface for three different conditions. The Si(111) surface was prepared at 300 K with a static substrate at the bottom of the surface. The surface layer was approximately $250 \times 250 \times 250 a_o$ in size with periodic boundary conditions in the x - y directions. The C_{60} clusters were prepared at two temperatures and in three environments: A bare C_{60} and a $C_{60}@C_{240}$ were preheated to 300 K, and a C_{60} that was embedded in the center of a Xe_{442} cluster was held at 40 K. In all cases, thermodynamic equilibrium was achieved for the clusters and surfaces before collision. The initial velocities of the clusters ranged from 1–10 km/s perpendicular to the surface. The corresponding energies per C_{60} molecule range from 3.72 to 372 eV and 0.3 to 30.4 keV for the $Xe_{442}C_{60}$ complex. The interaction functions used for the Si-Si, Si-C, and C interactions are Tersoff potentials, which have been used in numbers of previous molecular-dynamic simulations.¹⁰ For the Xe-Si and Xe-C interactions, we adopted Lennard-Jones functions for large interatomic separations and modified the energy function using density-functional theory for the short-distance interactions.¹⁵ This modification provides a much better description for close contact between Si, C, and Xe atoms, which is important for collisions at high energy. The molecular-dynamics step size varies between 0.1 and 0.4 fs, depending on the incident velocity. Between the surface and the static substrate, temperature control is applied to absorb the energy carried by the lattice vibration.

Figure 1 depicts the energetics of C_{60} molecules during impact at an incident velocity of 5 km/s. The translational kinetic energy (KE) of the C_{60} decreases during the collision in very different fashions for $C_{60}@Xe_{442}$ compared to a bare

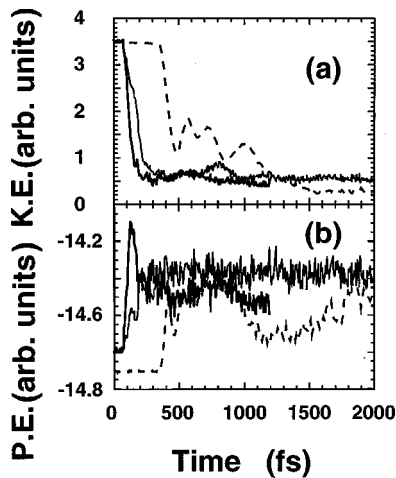


FIG. 1. Energy redistribution during the collision between a C_{60} molecule and an Si surface with an initial velocity of 5 km/s. (a) shows the kinetic energy of the center of mass of the bare molecule (thick solid line) inside a C_{240} cage (thin solid line) and embedded in a Xe_{442} cluster (dashed line). (b) shows the total potential energy of the three systems.

C_{60} or a bucky onion (fullerenes with two or more concentric shells, e.g., a C_{60} inside a C_{240}). A delay in time of the KE decrease is observed followed by a shallower dip and then an oscillatory pattern. The potential energy (PE) of a C_{60} in Xe_{442} lies below the curves of the bare C_{60} and the bucky onion. The initial difference of ~ 1.3 eV is due to the Xe_{442} - C_{60} interaction. Note that we assign atom i and atom j each with one half of the potential energy from a pair interaction V_{ij} . Each of the three-body terms V_{ijk} is divided and assigned to atoms i , j , and k equally. Thus, the potential energy of a subsystem can be obtained by adding up the energy that is associated with each atom, which provides a measure of energy deviation from the equilibrium structure. The peak in the PE upon collision is substantially higher for the bare C_{60} compared to the embedded molecules. The PE decreases quickly for the bare C_{60} in about 50 fs and then oscillates around a constant value that is ~ 5.5 -eV higher than a gas phase C_{60} . Note that at this time the molecule is bonded to the Si surface that forms a SiC complex region in the surface. The z component of the center of the mass of the bare C_{60} is about $6.2a_o$ above the top layer of the Si (111) surface. Another quantity that reflects the internal energy increase of C_{60} molecules is the temperature jump during the collision (Fig. 2). It should be mentioned that this temperature is defined as a measure of the average kinetic energy of each degree of freedom of the system or a subsystem. It is clear that the internal kinetic-energy increase (~ 900 K) is much smaller for the C_{60} embedded in Xe_{442} than in the other two cases (~ 1500 K). This fact indicates that the Xe_{442} provides protection to the C_{60} in the center at 5 km/s. The C_{60} has been soft-landed and impinged in the Si surface. Note that the center of mass of the C_{60} is $40a_o$ below the top surface layer at $t=2$ ps. Meanwhile, there is very little difference in the energetics between the bare C_{60} and the C_{60} in the bucky onion.

When the incident velocity is 10 km/s, the situation re-

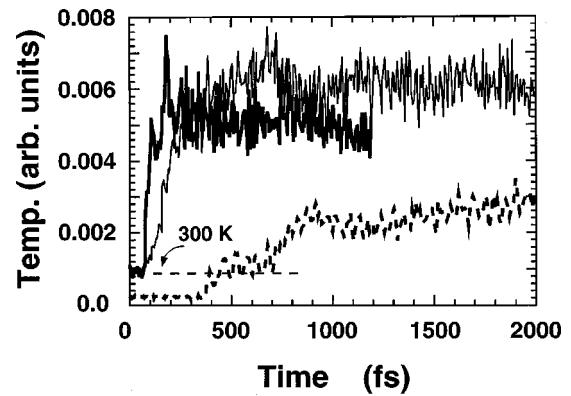


FIG. 2. Internal kinetic energy in units of temperature of C_{60} during collision with a Si surface. The thick solid line, the thin solid line, and the dashed line represent the bare C_{60} , a C_{60} inside a C_{240} cage, and a C_{60} embedded in a Xe_{442} cluster, respectively.

verses, compared to the 5-km/s case. Figure 3 depicts the same energetics as in Fig. 1, while the translational kinetic energy displays a similar pattern to that in Fig. 1. The potential energy indicates a substantial increase for the C_{60} inside Xe_{442} (~ 155 eV) compared to the bare molecule and the onion (~ 20 eV). The temperature of the molecules during the collision is displayed in Fig. 4 as functions of time. Again, the C_{60} inside the Xe_{442} cluster has a much higher increase compared to the bare molecule and the molecule inside the C_{240} cage. The total internal energy gain for the C_{60} inside the Xe cluster is approximately 207 eV. Note that at this velocity the difference between the bare C_{60} and the onion is much more visible than the difference shown in Fig. 2. The center of mass is $\sim 3.1a_o$ below the surface for the bare C_{60} , $\sim 4.6a_o$ for the molecule in the C_{240} cage, and $\sim 100a_o$ for the C_{60} with Xe_{442} coating, respectively.

The amount of energy present in this case, 207 eV (155 eV of PE and 52 eV of KE), which is about 50% of the total binding energy of a C_{60} molecule (405 eV according to the Tersoff potential and 415.5 ± 0.9 eV experimentally [see Ref.

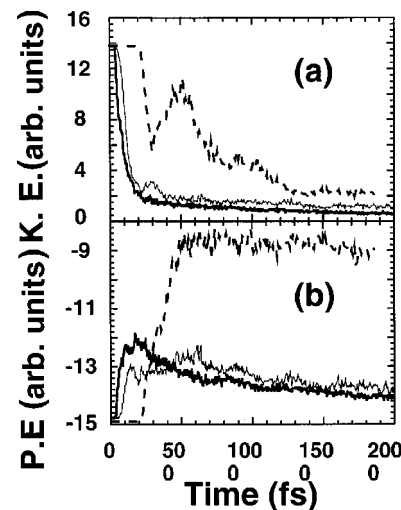


FIG. 3. Same as in Fig. 1. The initial velocity of the center of mass of the clusters is 10 km/s.

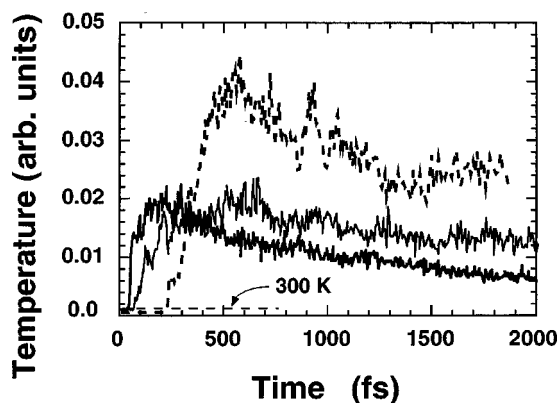


FIG. 4. Same as in Fig. 2. The center of mass of the clusters have an initial velocity of 10 km/s.

10, and references therein]), is sufficient to destroy the molecule during the collision. Figure 5 is a snapshot of the C_{60} surface system at 1.8 ps. The fragments (right) included 13 monomers, five dimers, one C_4 , one C_7 , and a C_{26} cluster, indicating that the system favors a highly nonuniform distribution of fragments. Analysis also shows that during fragmentation, some of the monomers and dimers rejoin to larger fragments due to the confined geometric conditions, while the system continues to fragment. This recombination of fragments is quite significant. It clearly suggests that the geometric confinement provides a unique channel for final products which cannot be achieved via conventional chemical means.

The energy transfer from Xe atoms as well as from the translational energy of C_{60} to the internal energy of the C_{60} ΔE is velocity dependent when one compares with the internal energy gain $\Delta E'$ of a bare C_{60} (in which $\Delta E'$ comes only from the translational energy of the C_{60}). The internal energy gains, ΔE and $\Delta E'$, ultimately determine the final state of the molecule in each situation. At 5 km/s (initial velocity), $\Delta E < \Delta E'$, and at 10 km/s, $\Delta E > \Delta E'$. This reverse suggests the existence of an intermediate velocity or a velocity range at which a bare C_{60} gains an equal amount of internal energy during the collision as the one that is embed-

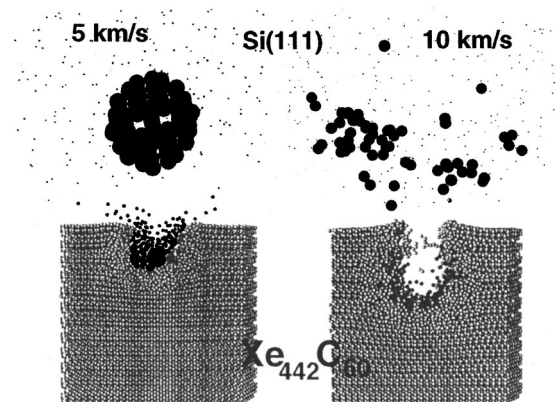


FIG. 5. Snapshots of the cluster surface after surface impact. The left is the result of a collision with an initial cluster velocity of 5 and the right is at 10 km/s.

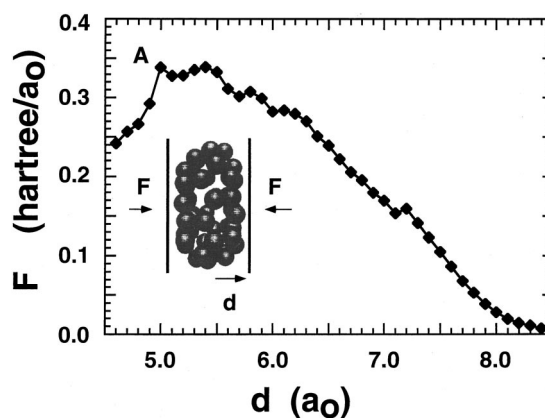


FIG. 6. Force on C_{60} versus distance between compression plates.

ded inside a Xe cluster. To pinpoint the transition in energy redistribution, we performed simulations with initial incident velocities of 6–9 km/s. The results show that the percentage of energy that flows into internal vibrational degrees of freedom of C_{60} reaches similar values for the molecules in both environments (bare and embedded in Xe_{442}) in the velocity range 7–8 km/s. During the collisions, the energy redistribution is governed by two competing mechanisms. First, the Xe atoms below the C_{60} protect the molecule by clearing the way into the Si surface such that a large portion of translational energy of C_{60} is transferred to the surface and Xe atoms below. Second, the Xe atoms above the C_{60} hammer it with their momentum and deliver energies to the C_{60} molecule. Clearly, the transition occurs when the two mechanisms reach a balance. In a simulation of cluster-surface collision with 8-km/s initial velocity, the C_{60} molecule inside the Xe cluster is highly excited but does not fragment at 1.8 ps. The total internal energy gain in this case is ~ 76 eV, with temperatures exceeding 4000 K. However, the molecule maintains a cage structure with only local disorders. At this energy, we do not observe the pretzel transformation which has been proposed as a result of melting of C_{60} in the gas phase.¹⁶ Simulations were performed on an isolated C_{60} at the same temperature for longer times to verify this point. We found that a Tersoff C_{60} cluster maintains its solidlike structure at 4000 K. As the initial velocity of the cluster increases, both the absolute value of ΔE and its ratio to $\Delta E'$ increase, which leads to fragmentation of the C_{60} molecule.

To understand the resilience of the C_{60} molecule, we performed a model simulation in which a C_{60} is placed between two hard plates. As the distance between the two plates decreases slowly, the repulsion between C_{60} and the wall increases. The repulsive force reaches a maximum and is followed by a steep decline (see Fig. 6). This drop in force indicates a transition from the reversible to the irreversible. At point A in the figure, the molecule recovers its original ground-state structure, while at points beyond A, the fullerene remains in a disordered (broken) state when the plates are removed. The estimated pressure to break the molecule is ~ 100 GPa, which is of the same order of magnitude as the pressure found in the cluster-surface collision with an initial velocity of 10 km/s. Once the molecule is broken, it is

easier to transfer additional translational kinetic energy to the C_{60} from the Xe atoms that are above the C_{60} molecule. Consequently, the significant energy transfer is observed (Fig. 3).

The simulations indicate that the impact-induced surface modification is significant. Nanoscale craters are formed when the Xe_nC_{60} complex collides with the surface at sufficiently high velocities. The precise size of the crater is determined by the initial incident velocity and the total mass of the clusters. At a given total mass, we find a linear dependence between the velocity and the depth of the crater. Nevertheless, the dependence of the depth on the mass of the clusters is not a linear function for these heterogeneous clusters, although the depth does increase as the total mass increases. Near the craters, amorphous nanostructures are formed. The energetic clusters displace a significant amount of Si atoms from their positions. Because of the nature of Si covalent bonding, the energy in the disordered region is localized. The shapes of these amorphous regions are very regular compared to those created via single-particle surface collisions.¹⁷⁻¹⁹

In summary, heterogeneous cluster-surface impact provides an opportunity to observe physical phenomena in complex processes in which unexpected results are often obtained. This study clarifies inconsistent conclusions seen in earlier studies^{8,14} in which the roles of the inert-gas coating layer were only partially understood. Our study suggests sev-

eral principles that control the dynamical outcome of cluster-surface collisions via speed selected experiments. The transition in the form of the distribution of energy deposition is the main message of this paper. The rare-gas outerlayer can be used for soft-landing or bond breaking, depending on the initial velocities of the clusters. These results provide insights for controlling the growth of nanophase materials as well as cluster-impact chemical reactions. Based on the principles of energy redistribution, we suggest experiments on the cluster-surface (semiconductors, metals, etc.) collisions using the C_{60} and the C_{60} coated with rare-gas atoms. Specifically, velocity-dependent studies can be conducted to verify our conclusions. The experiment can also be extended to other nanocrystals such as $(NaCl)_n@X_m$ ($X = Ar, Xe, Ne$). Finally, while the detailed chemical pathways of fragmentation of C_{60} molecules is yet to be described by first-principles calculations, qualitative and statistical information via studies based on model potentials are crucial for further progress. Detailed analysis of our observations of the surface modification is underway which also provides important information for possible experiments.

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