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MODELING C\textsubscript{540}-C\textsubscript{20} FULLERENE COLLISIONS

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Abstract. Collisions of C\textsubscript{20} and C\textsubscript{540} fullerenes are studied in a wide range of velocities by means of classical molecular dynamics. The simulations show that the collision scenario strongly depends on the collision velocity of the fullerenes. At low collision energies, the fullerenes are repelled by the van der Waals forces, and after bouncing off a part of the kinetic energy of their translational motion is converted into the energy of cage vibrations. At higher collision energies, the fullerenes overcome the potential barrier of Pauli repulsion with the formation of the new chemical bonds, and a significant change in the geometry of the molecules is observed. At very high collision energies, structure of the molecules is destroyed with the formation of new carbon clusters. Analysis of collisions for fullerenes of significantly different size revealed some new features associated with their asymmetric energy exchange.

1. INTRODUCTION

The discovery of fullerenes in 1985 has opened era of carbon nano-polymorphs [1]. Fullerene molecules of different sizes possess various unique properties which opens wide possibilities of their application for fuel [2] and solar [3] cells, in biomedicine [4,5], for synthesis of fullerene reinforced composites [6,7], for designing nano-devices [8], to name a few. The possibility of application of fullerenes as the hydrogen storage cells is also considered [9-11]. It is shown that especially giant fullerenes (C\textsubscript{720}) can contain more than 6.5 wt.\% of hydrogen atoms [9]. The great interest in the investigation of fullerene molecules is connected with their high structural stability, symmetry [12], variety of shapes and non-negative Gaussian curvature everywhere [12]. Fullerene outer surface is available for chemical modification, while its inner space is available for the encapsulation of a variety of chemical elements [13]. Moreover, fullerenes are the base elements for such solid structures as fullerite [14], diamond-like phases [15-21] and they undergo phase transition to polycrystalline diamond at the pressure higher than 20 GPa [22].

It is well-known that fullerene family contains several molecules ranging from C\textsubscript{20} to C\textsubscript{960} [23-26]. The most abundant fullerenes are C\textsubscript{60} and C\textsubscript{70} which can be synthesized by evaporation of carbon, incomplete combustion of benzene in oxygen and microwave method [27-28]. Coalescence of fullerenes into large fullerenes up to C\textsubscript{900} has been observed in the gas phase and inside carbon nanotubes [29,30]. Collision-induced fusion of fullerenes has been characterized by means of first-
principle molecular dynamics simulations and it has been shown that the highest probability of fusion is observed for collision energies of 120-140 eV [31]. However, it is interesting to note that fullerene formation mechanisms are still largely unknown. Study of the interaction and collision between different fullerene molecules is of significant interest. A wealth of experiments and numerical calculations devoted to fullerene collisions have been performed in the past years [32-34] including electron capture and ionization of C_{60} [35]; fusion and fragmentation of C_{60} induced by ion impact [36,37] or collisions with surfaces [38]; fusion, fragmentation and charge transfer induced by fullerene collisions [39-42]. After the pioneering C_{60} C_{50} collision experiment [39], cluster-cluster collisions became a versatile new field of research. Collisions between highly charged Xe\textsuperscript{20+} and fullerene van der Waals clusters have been found to lead to molecular growth [32]. At the same time, a little attention is given to the collisions of fullerenes of different sizes, for example, the collision of the smallest known fullerene C\textsubscript{20} and one of the giant fullerenes C\textsubscript{540}.

Despite the study of fullerene collisions has been going on for more than twenty years, an experimental study of the dynamics of collisions remains difficult, and the results of such experiments often contradict each other [43]. Molecular dynamics (MD) simulation is a robust numerical method to address nanoscale phenomena. MD calculations can reveal the physical and chemical properties of various carbon nano-structures or can help to devise the possible formation pathways. Existing potential functions allow to simulate both covalent bonds between carbon atoms and van der Waals forces between fullerene molecules.

In this study, MD simulations of fullerene collisions are conducted at a temperature close to zero. Collision of the smallest possible fullerene C\textsubscript{20} and one of the giant fullerenes C\textsubscript{540} is considered in a wide range of velocities.

2. SIMULATION DETAILS

Fig. 1 illustrates the simulation setup for equilibrium fullerenes C\textsubscript{540} and C\textsubscript{20} with the initial distance between their centers of mass equal to 30 Å. At this distance the closest carbon atoms of fullerenes are far from each other and do not interact. The centers of mass of the fullerenes are on the x-axis and they move toward each other with the initial velocities $V_{C_{540}}=-V_{C_{20}}/27$ keeping the center of mass of the whole system at rest, since C\textsubscript{540} is 27 times heavier than C\textsubscript{20}. The dimensions of the simulation box are 10000x55x55 Å with the periodic boundary conditions applied along all three directions.

All the simulations are carried out using the LAMMPS platform [44] with the well-known AIREBO potential [45].

The non-bonding interactions between fullerenes are the van der Waals forces, which are attractive, while at smaller distances repulsive Pauli interactions come into play. The most common way to describe the van der Waals interactions gives the Lenard-Jones potential which is already included into AIREBO. Proper definition of interatomic forces is one of the most essential factors in MD modeling. AIREBO potential is the member of classical bond-order family of the Tersoff-Brenner potentials which effectively manipulate covalent bonds in non-polar systems. Previously, AIREBO potential was successfully used for the similar studies, for example, the collision between fullerene and graphene [33], self-assembly of fullerenes and graphene [46], ion collisions with clusters of C\textsubscript{60} fullerenes [34], growth of fullerenes and nanotubes [47-49], etc.

Equilibrium atomic configurations of fullerenes are found before the collision simulation. The equilibration is conducted at temperature close to 0K and the canonical ensemble (NVT) is employed. A time step of 0.5 fs is taken for the simulation. After the equilibrium positions were found, the initial velocities are introduced along the line connecting fullerenes’ centers of mass, which coincides with x-axis. For these simulations the NVE ensemble is used. Thermal fluctuations at initial moment are absent. The velocity of the smaller fullerene ($V_{C_{20}}$) is chosen as a control parameter and collisions are simulated within a broad range of its values, from 1 to 150 Å/ps.
3. RESULTS AND DISCUSSION

The obtained results suggest that the fullerene collisions follow three different regimes depending on the initial velocity $V_{C20}$.

For the velocity of $V_{C20}<87$ Å/ps, two fullerenes after collision move away from each other without any recombination of chemical bonds with the absolute velocities less than before the collision, since a part of the kinetic energy of their translational motion is transformed into the energy of cage oscillations. The repulsion of two fullerenes took place because of the Pauli interaction and elasticity of the cages. Typical picture of the fullerene collision at relatively small velocity is presented in Fig. 2 for $V_{C20}<25$ Å/ps. Here and further, atoms are colored in accordance with their kinetic energy. As it can be seen, at first (Fig. 2a) all the atoms of C$_{20}$ have highest kinetic energy, while C$_{540}$ atoms have much smaller energy due to the large difference in their initial velocities. During the collision, kinetic energy of fullerenes is partly transformed into elastic deformation energy of cages but after the fullerenes bounce off, a part of the elastic energy returns into the energy of translational motion.

In order to quantify the energy flow in the system, in Fig. 3 kinetic energy per atom (blue lines) and kinetic energy of the center of mass per atom (red curves) for (a) C$_{20}$ and (b) C$_{540}$ colliding at the initial velocity $V_{C20}=25$ Å/ps is plotted. Recall that total energy (kinetic plus potential) is conserved in

![Fig. 2. Snapshots of the fullerene collision at the initial velocity $V_{C20}=25$ Å/ps. Similar picture is observed for fullerenes colliding at a velocity within the range $V_{C20}<83$ Å/ps. Atoms are colored in accordance with their kinetic energy.](image)

![Fig. 3. Kinetic energy per atom (blue curves) and kinetic energy of the center of mass per atom (red curves) for (a) C$_{20}$ and (b) C$_{540}$ colliding at the initial velocity $V_{C20}=25$ Å/ps. Open dots on the curves correspond to the snapshots from Fig. 2.](image)
the system. Kinetic energy of the center of mass does not include the kinetic energy related to internal motion of molecules and reflects only their translational motion. Open dots in Fig. 3 correspond to the snapshots from Fig. 2. As it can be seen, for both fullerenes before the collision the kinetic energy is equal to the kinetic energy of the center of mass because internal vibrational modes are not excited. At the moment of collision ($t=0.8$ ps), the kinetic energy of the system is redistributed due to the excitation of the internal vibrational modes of each fullerene. The collision lasts for approximately 0.3 ps, when the kinetic energy of the fullerenes’ centers of mass is close to zero. For the considered collision velocity $V_{C_{20}}=25$ Å/ps, the kinetic energy of the centers of mass of the fullerenes after collision is less than half the initial value. Within the velocity range $V_{C_{20}}<83$ Å/ps, the higher $V_{C_{20}}$, the greater portion of the translational energy of fullerenes goes into their internal vibrations. It should be noted, that the large difference in the fullerene size causes the asymmetry in the energy exchange between them. Most of the translational energy of $C_{20}$ is expended to the heating of $C_{540}$. Indeed, after the collision, the kinetic energy per atom of $C_{540}$ oscillates at the level of 0.004 eV, while the energy of its translational motion is an order of magnitude smaller. On the other hand, most of the kinetic energy of $C_{20}$ after collision remains in the form of translational energy. This can be explained by the fact that $C_{540}$ fullerene has a larger number of normal vibrational modes, the excitation of which occurs during the collision.

The pre-critical behavior of the fullerenes is shown in Fig. 4 for $V_{C_{20}}=75$ Å/ps. Atoms are colored in accordance with their kinetic energy. As it can be seen, during the collision, considerable deformation of the giant fullerene takes place, however after the collision its quasi-spherical structure is restored being perturbed by intrinsic oscillations.

For the collision velocity range $83< V_{C_{20}}<140$ Å/ps, fullerenes have enough energy to overcome the Pauli repulsion barrier, and formation of new chemical bonds between two fullerenes occurs. The interaction dynamics for representative velocity $V_{C_{20}}=85$ Å/ps is illustrated in Fig. 5. It should be noted, that the hybridization of the atoms participating in the formation of new bonds changes which leads to the local change in the fullerene geometry. From Fig. 6, where the example of the new covalent bond formation is presented, the appearance of a sharp ledge can be seen. It is found that a lower potential energy of the system can be achieved if one more covalent bond is formed. Under this structural transformation, the appearance of the concave region on $C_{540}$ fullerene is beneficial due to van der Waals forces acting between two molecules.

In Fig. 7 the same as in Fig. 3 but for the collision velocity $V_{C_{20}}=85$ Å/ps is presented. It can be seen, that even after the collision the kinetic energy of the centers of mass of two bonded fullerenes drops to zero, since the total momentum of the sys-
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Fig. 5. Snapshots of the fullerene collision at the initial velocity $V_{C_{20}} = 85$ Å/ps. Similar picture is observed for collision velocities in the range $83 < V_{C_{20}} < 140$ Å/ps.

(a) The formation of one new covalent bond and (b) formation of the second covalent bond, which is beneficial due to the strong geometrical transformation of the fullerenes.

Fig. 6. Snapshots of the fullerene collision for the initial velocity $V_{C_{20}} = 85$ Å/ps. Similar scenario is observed for collision velocities within the range $83 < V_{C_{20}} < 140$ Å/ps. (a) The formation of one new covalent bond and (b) formation of the second covalent bond, which is beneficial due to the strong geometrical transformation of the fullerenes.

Fig. 7. Same as in Fig. 3 but for $V_{C_{20}} = 85$ Å/ps. Open dots on the curves correspond to the snapshots from Fig. 5.
tem is zero. Thus, the entire energy of the translational motion of the fullerenes goes into their internal vibrational modes and for creation of new valence bonds. In Fig. 7, a temporary increase in the kinetic energy of the mass centers of fullerenes is observed for 1.1<t<1.8 ps. Within this interval, two molecules connected by a single covalent bond move away after a maximum approach, but being unable to break a newly created bond, they again come together to create the second bond. The molecule merging process takes about 1.5 ps.

For the initial velocity greater than 140 Å/ps another scenario is observed: the collision of two fullerenes causes the destruction of one or both molecules. Example of such dynamics is presented in Fig. 8. As the result of collision C$_{20}$ is destroyed and a cluster of four carbon atoms is separated and moves away.

4. CONCLUSIONS

Collision of a giant fullerene C$_{540}$ with the smallest fullerene C$_{20}$ is investigated by molecular dynamics simulation for various collision velocities. Three main scenarios of fullerene collision are found depending on the collision velocity within the range 0<V$_{C20}$<150 Å/ps (V$_{C540}$=V$_{C20}$/27).

For relatively slow collisions, V$_{C20}$<83 Å/ps, fullerenes retain initial structure and move apart with the absolute velocities less than initial ones, since a part of their kinetic energy of the translational motion transforms into the energy of internal oscillations. The asymmetry of the energy redistribution, caused by the difference in the sizes of the interacting molecules, leads to the energy of the translational motion of the small fullerene being spent to heat the large one. This is explained by the fact that a large fullerene has a greater number of vibrational degrees of freedom, which are excited during the collision.

For the velocity range 83<V$_{C20}$<140 Å/ps, the two fullerenes have energy high enough to overcome the Pauli repulsion, and formation of the new chemical bonds occurs. The center of gravity of the new structure after the collision is at rest and the entire energy of the translational motion of the molecules is spent for creation of the new valence bonds and for excitation of internal oscillations. Bonding of the two fullerenes leads to the appearance of a concave region on C$_{540}$ due to the action of Pauli repulsive forces between them.

High-energy collisions at V$_{C20}$>140 Å/ps, are accompanied by the destruction of one or both fullerenes and formation of new carbon clusters. Collisions of different fullerenes can be observed in detonation chambers during their synthesis or in a mixture of gases of various fullerenes [29,36].

In the present work, a set of regimes for fullerene head-on collisions has been identified, but further details, such as effect of the fullerene size, slash collision, etc. require extensive investigations, which will be pursued in future studies. It is also important
to address the effect of defects on the collision outcomes [50-54]. Such studies are of high importance for understanding the collision behavior and fullerene formation in technological processes.

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