Thermal road for fullerene annealing

P.A. Marcos, M.J. López, A. Rubio, J.A. Alonso

Departamento de Física Teórica, Universidad de Valladolid, E-47011 Valladolid, Spain

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Abstract

The Stone–Wales transformation has been proposed as a basic process for ring rearrangement in a fullerene cage and, consequently, for annealing fullerene structures down to the ground state. We present a new, thermally activated, mechanism for the Stone–Wales transformation. This mechanism, found in dynamical simulations of C_{60}, involves a multi-step isomerization transition process in contrast with the commonly assumed single-step mechanism. The step-to-step energy barriers found in the multistep process are much lower than the reported ones for a single-step process. We also present a dynamical simulation of the thermal fullerene-to-graphite reconstruction of C_{60} of relevance to the growth of fullerenes. The two thermal processes presented open new roads for investigating the formation and annealing mechanisms of different carbon structures.

The preferential formation of C_{60} buckminster fullerene (BF) molecules (under the right experimental conditions [1]) has not been explained so far. The difficulty stems from the fact that the production of BF does not take place under thermal equilibrium conditions but rather it involves a kinetics-controlled process. Several growth models have been proposed in the literature, e.g. the pentagon road model, the fullerene road model or the cycloaddition model. All these models require, in the last stages of BF formation, an annealing mechanism (involving the rearrangement of pentagons and hexagons) driving C_{60} from one of the 1812 possible fullerene structures (hollow cages formed by 12 pentagons and 20 hexagons) into the most stable BF structure, the only fullerene having I_h symmetry and no adjacent pentagons. Even this last process of annealing the fullerene structures down to BF is not well understood.

The basic transformation for ring rearrangement in a fullerene cage, proposed by Stone and Wales [2], has been shown to have quite high activation barriers that could prevent the Stone–Wales (SW) transformation from being an efficient annealing mechanism for fullerenes. We have found (through dynamical simulations) a thermally activated mechanism for the SW transformation. This mechanism involves isomerization transitions through intermediate isomers which connect the BF structure with the C_{60} fullerene isomer obtained via an SW transformation of BF (this isomer, containing two pairs of adjacent pentagons, is the necessary last step in the annealing of fullerenes before reaching BF [3]). A multi-step process, as the dynamically driven mechanism presented here for the SW transformation, was completely unexpected on the grounds of the structural optimizations performed by other authors [4–6]. On the other hand, this new mechanism may help to understand the kinetics of the annealing process.

In this work we have performed extensive con-
Fig. 1. Low energy path for the SW transformation of BF. The reaction coordinate between each two successive isomers, I and F, with coordinates $X^I$ and $X^F$, respectively, is defined as $X = (1 - \alpha)X^I + \alpha X^F$ ($\alpha = 0 - 1$). Between isomers III and IV an intermediate configuration (indicated by the arrow in the figure) has been considered. This configuration, suggested by the dynamical process, is obtained by a 20 degrees rotation of the C2 handle in isomer III. The geometries of the isomers involved in the multi-step isomerization transition are also shown.

stant energy molecular dynamics (MD) simulations to investigate the structural transformations that C$_{60}$ may undergo as a function of temperature. We use the Tersoff [7] interatomic potential to mimic the covalent bond between carbon atoms in C$_{60}$. A smooth Fermi-type cut-off function [8] is used to cut the interactions between first and second nearest neighbors. The Tersoff potential is based on bond order considerations and incorporates explicit dependence on both coordination and bond angles which makes it reliable for describing the structural features and the energetics of carbon over a wide range of configurations including real and hypothetical carbon polytypes (i.e. diatomic molecule, diamond, graphite, and simple cubic, body centered cubic and face centered cubic lattices). This potential also describes the elastic and defective properties of diamond and graphite. Newton’s equations of motion are integrated numerically using the velocity version of the Verlet algorithm with a time step of 0.2 fs which guarantees conservation of the total energy within 0.01% for trajectories lasting $10^5$ time steps.

Starting from the minimum energy structure (BF) of C$_{60}$ at $T = 0$ K we heat up the C$_{60}$ fullerene until break up of the cage occurs ($T \sim 5000$ K). The temperature is stepwise increased ($\Delta T \sim 50$ K) by scaling up the velocities of all the atoms between successive MD runs of 20 ps each. The BF structure remains intact (the carbon atoms just oscillate around the equilibrium positions) up to a temperature of about 2500 K. At higher temperatures C$_{60}$ undergoes structural changes, i.e. isomerization transitions between BF and fullerene-like isomers having one or several open windows (OW) in the cage (a window

Notice that the Tersoff potential gives a melting temperature for carbon of about 6000 K whereas the experimental value is about 4300 K. Therefore, when comparing to experiments, the present temperatures should be rescaled.
opens when a carbon–carbon bond of the cage is broken). A window mechanism has been proposed for explaining the formation of endohedral fullerenes [9]. Our simulations show that the OW structures are metastable states of C$_{60}$ with a finite lifetime that provides further support for that mechanism.

At a temperature of about 3900 K we were able to identify the Stone–Wales transformation of BF. A detailed analysis of the trajectory reveals that the SW transformation involves a new multi-step isomerization transition process, in contrast with the commonly assumed single-step mechanism. The isomers involved in the SW transformation were identified using the thermal quenching procedure. In this procedure, the high energy configurations of C$_{60}$ along the dynamical trajectory are cooled down to the closest local minimum of the potential energy surface. The mechanism of the SW transformation found in our simulations proceeds through the following isomers (see Fig. 1): (1) a window opens between a pentagon and a hexagon, (2) a second window opens next to the first one; these two windows share a C$_2$ handle which lies about 10% outwards of the fullerene cage, (3) the C$_2$ handle rotates and recloses one of the windows changing the relative positions of the pentagon and the hexagon which formed that window, (4) the second window recloses also changing the relative positions of the corresponding pentagon and hexagon and producing, consequently, the SW isomer. We have generated a continuous low energy path on the potential energy surface connecting the BF and SW structures of C$_{60}$ through those isomers (see Fig. 1). Between each two successive isomers, I and F, with coordinates $X^I$ and $X^F$, respectively, the reaction coordinate is defined as $X = (1 - \alpha) \ X^I + \alpha \ X^F$ (with $\alpha$ ranging from 0 to 1). The highest barrier along this path is found between isomers III and IV and lies 6.89 eV above the ground state of C$_{60}$. This barrier height can be significantly reduced, down to 5.58 eV above the ground state of C$_{60}$, by considering an intermediate configuration between isomers III and IV obtained by a 20° rotation of the C$_2$ handle in isomer III. This intermediate configuration is suggested by the dynamical pathway of the SW transformation and is indicated by the arrow in Fig. 1. The value of the barrier height between the BF and the SW structures obtained here is somewhat lower than the activation energies (6–7 eV) found by other theoretical methods for a direct (one-step) SW transformation. What is probably more noticeable about the multi-step mechanism proposed here is that the step-to-step isomerization transition barriers are substantially reduced (none of them exceeds 2.6 eV) with respect to the one for the global process. As a consequence the intermediate metastable isomers connecting two fullerene structures may play an important role in defining the kinetics of the annealing process without relying on an autocatalysis mechanism [6].

In order to complete the picture of the thermal behaviour of C$_{60}$ we present in Fig. 2 a few representative snapshots, extracted from the simulations, of the C$_{60}$ structure at several temperatures. As we have mentioned above, up to a temperature of about 2500 K the fullerene cage remains intact (Fig. 2A) and at higher temperatures (up to about 4000 K) the

![Fig. 2. Representative snapshot of the structure of C$_{60}$ at several temperatures. (A) $T = 2500$ K, (B) $T = 3800$ K, (C) $T = 4200$ K, (D) $T = 4600$ K, (E) $T = 4900$ K [9]. These geometries have been extracted from the dynamical simulation runs. Before atom evaporation occurs, C$_{60}$ undergoes a structural transformation to a planar (2D) graphitic-like structure.](image-url)
structure changes locally only, through the open-window mechanism, while the rest of the fullerene is unchanged (Fig. 2B). At still higher temperatures \(C_{60}\) experiences much more significant structural transformations. Big holes open in the fullerene cage (Fig. 2C) which finally completely destroy the cage structure of \(C_{60}\) (Fig. 2D). In this temperature range (above 4000 K) bond-breaking and bond-forming becomes a fast process within the timescale of our simulation runs. In the particular simulation shown here bond-breaking leads to a weakly bound tubular-like structure (Fig. 2D) that by slightly further heating opens up forming an “almost perfect” graphitic sheet (Fig. 2E) before the system starts to evaporate atoms. This is the first time that a fullerene-to-graphite reconstruction has been observed in computer simulations and, in conjunction with the proposed multi-step-isomerization-annealing process, opens a new road for theoretical investigations on the formation mechanisms of different carbon structures including fullerenes, onions or nanotubes from a hot carbon-plasma or cluster coalescence.

As a final remark we wish to indicate that only those processes with a lifetime of the order of or smaller than the simulation time will be observed in a MD run. On the other hand, since the reaction rates (inverse of the lifetime) increase with energy, the temperature at which a certain process is observed in a simulation is largely determined by the simulation time. The clear implication is that since the timescale of our simulation runs, \(\sim 0.1\) \(\mu\)s (although quite extensive for present-day standards) is shorter by several orders of magnitude than the experimental timescale, the structural transformations of \(C_{60}\) will be present in the experiments at much lower temperatures than the ones reported here.

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