

# Computational Simulations of Carbon Materials

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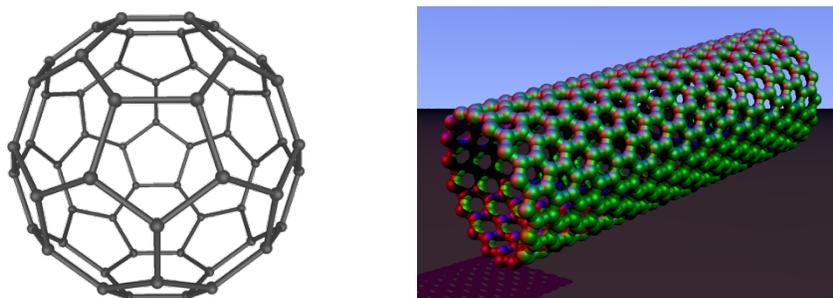
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**Abstract**

Carbon materials and nanostructures (fullerenes, nanotubes) are promising building blocks of nanotechnology. Potential applications include optical and electronic devices, sensors, and nano-scale machines. The controlled growth of single-walled carbon nanotubes and furthermore the ability to control the assembling of smaller carbon nano-blocks into larger units with specific physico-chemical properties is a major challenge in nanotechnology for material science and carbon nano-tube research [1]. Our computational efforts concern on improving understanding of processes related to the fabrication of carbon nano-materials, especially focusing on the possibility of reactions between nano-particles. We investigate collision induced coalescence of carbon nanostructures by means of direct molecular dynamics in which electrons are treated quantum mechanically via the self-consistent-charge density-functional tight-binding (SCC-DFTB) method [2]. We particularly focus on explaining a mystery of very high stability and low reactivity of the  $C_{60}$  fullerene comparing to the  $C_{70}$  fullerene [3,4].

## Introduction

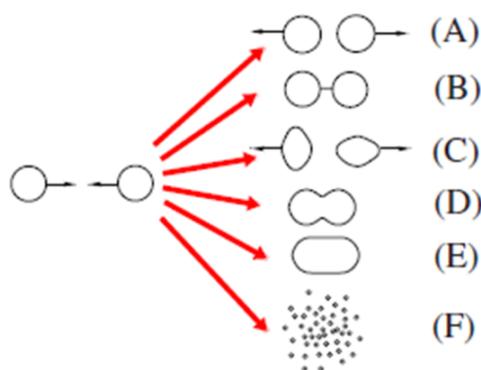
The idea of using carbon materials as building blocks for larger carbon structures has long been of interest to the scientific community. This is due largely to the potential applications it could have in the field of nanotechnology, including optical and electronic devices, sensors, and nano-scale machines. The method behind this idea is to involve these carbon materials in collisions under certain conditions and hopefully achieve coalescence. However, this science is complex in its nature due to the resistance of some carbon materials that are involved in collision to fuse.



**Figure 1.** Members of the fullerene family:  $C_{60}$  and a carbon nanotube [5].

The image on the left in figure 1 represents a  $C_{60}$  fullerene, or a buckminsterfullerene, commonly known as a “buckyball.” Carbon fullerenes are hollow spherical structures made entirely of carbon atoms. This  $C_{60}$  fullerene, of course, is made up of 60 carbon atoms. The image on the right in figure 1 is a carbon nanotube, much like a carbon fullerene, but cylindrical in shape.

Carbon fullerenes  $C_{60}$  and  $C_{70}$  are the main focus of this paper and the subjects of the controlled collisions that are being simulated. Several different competing collision paths that carbon fullerenes may take have been recognized [4]. A short description of these collision paths is presented below.



**Figure 2.** Schematic outcomes of collision between fullerene-like structures [4].

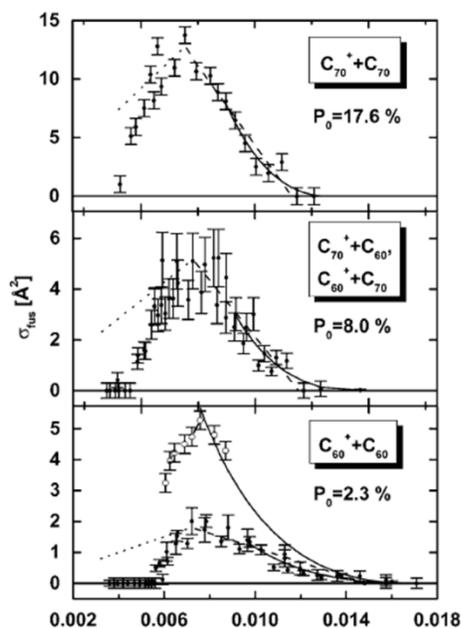
In figure 2, path (A) represents nonreactive elastic scattering, path (B) shows dimerization/polymerization, path (C) depicts inelastic scattering with collision-induced internal reorganization, path (D) represents partial coalescence, path (E) shows full coalescence, and path (F) depicts fragmentation [4]. It was found that nonreactive elastic scattering occurred most often when the energy was less than 10 electron volts (eV) (path A), that collision energies between 10 and 60 eV resulted most often in dimerization/polymerization (path B), and that collision-induced internal reorganization/inelastic scattering usually occurred at energies between 60 and 100 eV (path C) [4]. Paths D and E both represent coalescence, which occurs typically when collision energies are between 100 and 140 eV, and at energies greater than 140 eV fragmentation usually occurs (path F) [4]. The goal is to observe optimal conditions to achieve coalescence (paths D and E) when the fullerenes are involved in collision. Figure 2 represents results for a non-polarized case, so our efforts involve finding results for the polarized case.

In our current work we analyze the relation between polarizabilities of fullerenes and the relative cross section for collision induced fusion of  $C_{60}$  and  $C_{70}$  fullerenes. The difference in the interaction between colliding species affects the probability of reactive collisions. In the

experimental settings, one of the species (projectile) is always ionized while the target molecule remains neutral. The external electric field is used to accelerate the projectile cation. The leading long-range term for the interaction between colliding fullerenes is Coulomb interaction between projectile cation and the induced dipole moment of the neutral target molecule. The temperature of the species is about 2000 K for the projectile and 500 K for the target molecule. High temperature may lead to energy transfer between electronic and nuclear degrees of freedom. Electronic excitations are also involved and affect the collision outcome.

## Methods

We are attempting to see if there is a correlation between dipole polarizability of  $C_{60}$  and  $C_{70}$  fullerenes and the relative cross section. The experimental cross sections are shown in figure 3.



**Figure 3.** Absolute fusion cross section as a function of the inverse collision energy for the three collision systems indicated in the figure [3].

Campbell et al has observed a significantly larger value for fusion probability for  $C_{70}$  than for  $C_{60}$  [3]. We are also interested in how polarizability changes when approximate electronic excitation is accounted for, as well as the dynamics of the structure.

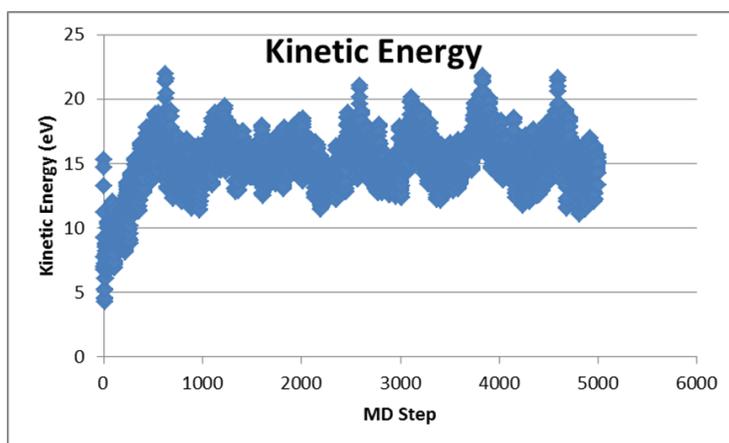
First we performed canonical ensemble molecular dynamics (MD) simulation of isolated fullerene molecules at temperature 2000 K to generate a set of randomized structures that correspond to experimental conditions. Nose-Hoover thermostat was employed. Then the finite difference method was used with DFTB level of theory to calculate the dipole polarizabilities of the fullerenes [2]. The electronic excitations were approximated via electronic temperature.

## Procedures

Our simulations were performed using electronic structures which were computed within the framework of the self-consistent-charge density functional tight-binding (SCC-DFTB) theory using the program, DFTB+ on the super computer, Kraken. DFTB is an approximate density functional theory that employs Slater type orbitals rather than the Gaussian type orbitals that one would typically see in a chemistry code. Its basis set is minimal, and only the valence electrons are treated, so the core electrons as well as the nuclei are described through pairwise repulsion potential. The accuracy of DFTB+ can be compared to that of Beck, 3-parameter, Lee-Yang-Parr (B3LYP) functional of density functional theory (DFT), but DFTB+ is between 2 and 3 orders of magnitude faster. We wrote several codes using bash scripting and, in order to run simulations on Kraken, we wrote a PBS script and became familiar with the queuing system for Kraken. Due to the nature of our research, we did mostly serial scripting rather than parallel.

When doing simulations using DFTB+ in which we manipulate certain conditions, the geometry of the molecule that will experience these changes must be included in the input file. In

reality, a fullerene would not constantly hold its rigid, spherical structure. There are vibrations and a natural movement within the molecule that needs to be accounted for in order to obtain accurate results. So, to obtain realistic geometries for  $C_{60}$  and  $C_{70}$ , we ran an MD simulation of both  $C_{60}$  and  $C_{70}$  for 5 ps using a Nose-Hoover thermostat at a temperature of 2000 K.



**Figure 4.** Plot of kinetic energy versus steps at 2000 K.

This simulation produced 5000 geometries for each carbon structure. We created a plot of kinetic energy versus the corresponding MD step in order to determine when the geometries stabilized, as shown in figure 4. The structures seemed to stabilize by the 1000<sup>th</sup> step, so we truncated every 50<sup>th</sup> step from 1000 to 5000. Our goal was to see how the polarizability was affected at each geometry step when the electronic temperature and the electric field were manipulated.

Method	$C_{60}$	$C_{70}$	$C_{70}/C_{60}$	References
Tight binding	77.00	91.60	1.19	[6]
TDDFT/SAOP	83.00	101.00	1.22	[7]
DFTB	56.00	67.90	1.21	Current

**Table 1.** Comparison of theoretical polarizability ( $\text{\AA}^3$ ).

Before running our code with dynamics, we calculated the optimized polarizability, which can be seen in table 1. This value was calculated with the finite difference method using the following equation:  $\vec{\mu} = \alpha \vec{E}$ , where  $\vec{\mu}$  is dipole moment,  $\alpha$  is polarizability, and  $\vec{E}$  is electric field. As is displayed in table 1, our polarizabilities are somewhat underestimated, which may be due to the minimal basis set of DFTB+.

## Results

After creating data structures within the LINUX operating system, we ran simulations on each of the geometries for electronic temperatures 0, 1000, 2000, 3000, and 10000 K for each of the following point charges: 0.0, 0.1, 0.4, 0.6, and 1.0 e. We found the isotropic polarizability for each temperature by instating each point charge in the x, y, and z directions. We then calculated the resulting polarizabilities for each of these directions, and proceeded to take an average of the polarizabilities.

Temp (K):	Polarizability: X Direction	Polarizability: Y Direction	Polarizability: Z Direction	Isotropic Polarizability
0	60.59277	60.51782	60.56739	60.55932
1000	60.62986	60.54815	60.59725	60.59176
2000	61.56756	61.41308	61.45478	61.47847
3000	63.33802	63.16380	63.17152	63.22444
10000	68.63167	68.52598	68.46683	68.54149

**Table 2.** Polarizability values in  $\text{\AA}^3$  for  $C_{60}$  at a point charge of 0.1 e.

From the data displayed in table 2, one can see that the polarizability values for  $C_{60}$  did not vary by much regardless of which direction the 0.1 e point charge was instated; x, y, or z.

Temp (K):	Polarizability: X Direction	Polarizability: Y Direction	Polarizability: Z Direction	Isotropic Polarizability
0	73.25691	73.11983	82.77998	76.38557
1000	73.30546	73.16940	82.87585	76.45024
2000	73.97528	73.87632	84.61398	77.48852
3000	74.95226	74.89785	87.34319	79.06443
10000	78.81316	78.76990	93.97554	83.85287

**Table 3.** Polarizability values in  $\text{\AA}^3$  for  $C_{70}$  at a point charge of 0.1 e.

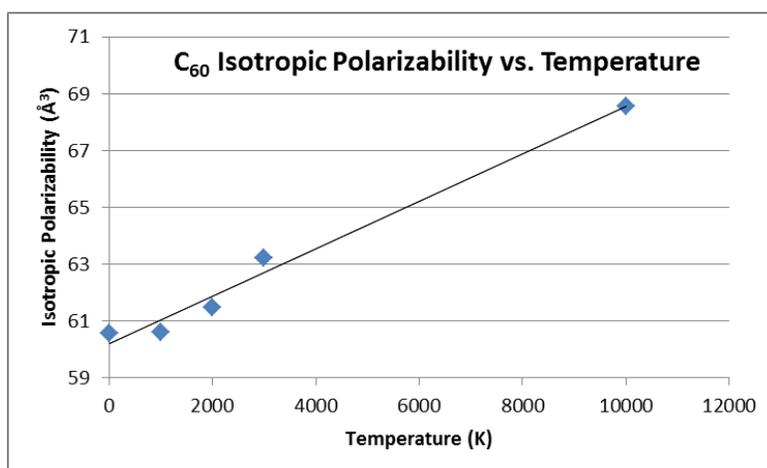
In comparison, the values for polarizability for  $C_{70}$  are consistent when a 0.1 e point charge is instated for in the x and y directions, but increases significantly when instated in the z direction, as is shown in table 3. This is most likely due to the more elliptical shape of the  $C_{70}$  fullerene as compared to the spherical shape of the  $C_{60}$  fullerene.

Charge (e) / Temp (K)	$C_{60}$				$C_{70}$				$C_{70}/C_{60}$ 0.1 - 1.0
	0.1	0.4	0.6	1.0	0.1	0.4	0.6	1.0	
<b>0</b>	60.55932	60.55934	60.55934	60.55935	76.38557	76.38557	76.38558	76.38558	1.26
<b>1000</b>	60.59176	60.59178	60.59178	60.59178	76.45024	76.45024	76.45024	76.45024	1.26
<b>2000</b>	61.47847	61.47846	61.47845	61.47845	77.48852	77.48850	77.48849	77.48847	1.26
<b>3000</b>	63.22444	63.22445	63.22445	63.22444	79.06443	79.06443	79.06442	79.06441	1.25
<b>10000</b>	68.54149	68.54149	68.54149	68.54149	83.85287	83.85286	83.85286	83.85285	1.22

**Table 4.** Isotropic polarizabilities of  $C_{60}$  and  $C_{70}$  for varying temperature and charge.

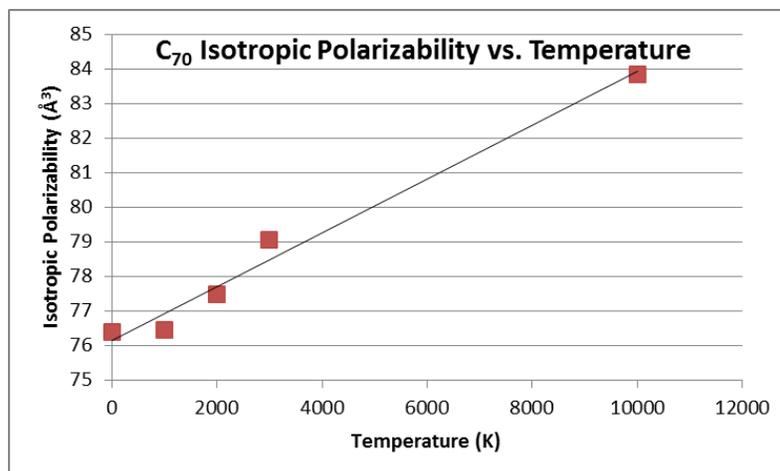
As can be seen in table 4, although there is an increase in isotropic polarizability as the temperature increases, there is very little change in isotropic polarizability as the point charge changes. The isotropic polarizability values are larger for  $C_{70}$  than for  $C_{60}$ , and the average isotropic polarizability ratio for  $C_{70}/C_{60}$  over all temperatures is approximately 1.25. As is displayed in table 4, the ratio gradually decreases with increase in temperature but does not vary significantly with charge.

The trend for each charge is similar and is exemplified by figure 5, which shows an increase in isotropic polarizability as temperature increases for a charge of 0.1 e for the  $C_{60}$  fullerene.



**Figure 5.** Isotropic polarizability versus temperature change for  $C_{60}$  at a charge of 0.1 e.

Similar to the plot of  $C_{60}$  is the plot shown in figure 6, which shows the relationship between temperature and isotropic polarizability for the  $C_{70}$  fullerene at a charge of 0.1 e.



**Figure 6.** Isotropic polarizability versus temperature change for  $C_{70}$  at a charge of 0.1 e.

It too shows a steady increase in isotropic polarizability with increasing temperature and, once again, the isotropic polarizabilities are generally larger than those for  $C_{60}$ .

## Conclusions

The values for isotropic polarizability were found to be consistently larger for  $C_{70}$  than for  $C_{60}$  at each temperature and at each point charge that was instated, just as we had hoped. The increased polarizability of  $C_{70}$  over  $C_{60}$  leads to increased attraction between two  $C_{70}$  units. This additional attraction, combined with the larger size of the  $C_{70}$  fullerenes, effectively leads to a higher probability of collision for  $C_{70}$  units than  $C_{60}$  units and, consequently, increased cross section for reaction.

## **Acknowledgments**

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## References

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