

Molecular simulation of the fullerene (Buckyball) to different sizes

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Abstract

In this study, we perform molecular dynamics simulations of the spherical fullerene (buckyball) nanomaterial at different sizes to verify how its physicochemical properties change with the number of atoms in its structure, which is proportional to the diameter of this molecule. The molecular dynamics simulations were performed with the following nanostructures: C₂₀, C₆₀, C₈₀, C₁₈₀, C₂₄₀, and C₅₆₀, assuming a simulation time of 4 nanoseconds at standard temperature and pressure. The graphical results of the simulations show that the specific heat at constant volume and the molar entropy of the molecules tend to stabilize according to a logarithmic curve as a function of the number of atoms. These functions were fitted by numerical interpolation and are presented in this text. At the same time, the classical mechanical energies were obtained from the simulations, and they variations were analyzed. Was observed that kinetic energy increases linearly with the number of atoms. On the other hand, the potential energies of intramolecular interactions don't present this linear behavior, showing a predominantly dependence on van de Waals interactions, which is described by the Lennard-Jones potential. In addition, the heat dissipated of the spherical fullerenes were estimated, showing that the friction between its atoms increase with de molecular size.

Keywords: buckyball; fullerene; molecular dynamics; nanomaterials; thermodynamics.

1. INTRODUCTION

Fullerenes are a group of molecules consisting of carbon atoms linked by single and double bonds. Their geometries are hollow and can be spherical, ellipsoidal or

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cylindrical. In spherical fullerenes, also called buckyballs, their structure has hexagonal and pentagonal faces, similar to a soccer-ball (Mateo-Alonso *et al.* 2006). This nanostructure, discovered in 1985, originally contained 60 carbon atoms (C60). However, thanks to technological progress, a considerable variety of this molecule is now known, present in different amounts of atoms (C20, C70, C72, C74, ...) (Meija, 2006).

Besides to attracting attention for its high molecular symmetry, Fullerene has been the subject of numerous researches around the world due its very different physicochemical properties, enabling several applications, especially in the biomedical area. In the review paper by Bhakta and Barthunia (2020), for example, the authors cite several researches and applications in the field of photovoltaic energy or in biomedical fields as antiviral agent, antioxidant, neuroprotective activities or even as X-ray contrast agent.

For the development of these applications, it is important to know the physicochemical properties of these nanostructures. Therefore, research has also been carried out to characterize the properties and obtain models to predict them. For example, in the study by Dinadayalane and Leszczynski (2017), the authors discuss some structural, electronic, and chemical properties of various carbon nanostructures.

Therefore, this study presents results on how some properties and physicochemical quantities of fullerenes depend on the size of their nanostructure. The study was carried out using computer simulations of classical molecular dynamics, where their energies and some thermodynamic quantities could be calculated.

2. METHODOLOGY

For the development of the research, DM simulations were performed to study the changes in the properties and physicochemical characteristics of the fullerene molecule when the size of the nanostructure is increased. The simulations were performed for the following structures: C20, C60, C80, C180, C240, and C540. To model the systems, five molecular structures of fullerene were first constructed (see Figures 1.a - 1.e). Then, an energy optimization calculation was performed for each nanostructure. In the optimization calculations, the Polak-Ribière algorithm was used to converge the energies, which allowed for better performance in the DM simulations (Arouche *et al.* 2020; Neto *et al.* 2010; Neto *et al.* 2014; Santos *et al.* 2014; Silva *et al.* 2011).

Simulations were performed using Hyperchem 8.0 software (HYPERCHEM (TM)), with a simulation time of 4000ps (picoseconds) in vacuum. The calculations were performed with a step time of 10^{-4} ps, using molecular mechanics + (MM+) as the theory level and with the system heat bath to stabilize the temperature of each simulation at 300K (Aires *et al.* 2017).

The following physicochemical quantities were calculated: Kinetic energy, potential energy and total energy, also specific heat at constant volume (C_v), entropy and heat loss. In addition, the C_v and entropy curves were calculated as functions of the number of carbon atoms in the fullerene. These calculations were performed by numerical interpolation, which allows the prediction of these properties for larger nanostructures.

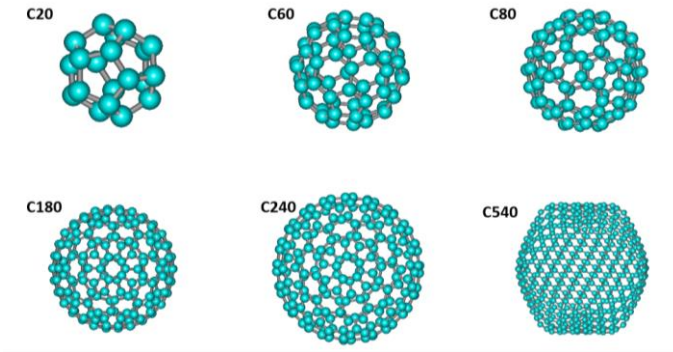


Figure 1: Simulated fullerene molecules C20, C60, C80, C180, C240 and C540.

The geometry optimization and DM calculations were performed based on the kinetic energy and classical interactions of the particles that make up the molecules, so that the Hamiltonian (\hat{H}) of each system can be represented by Equation 1 below:

$$\hat{H} = \sum_i^{n_{atoms}} \frac{P_i^2}{2m_i} + \sum_i^{n_{bonds}} b_i(r_i - r_{i,eq})^2 + \sum_i^{n_{angles}} a_i(\theta_i - \theta_{i,eq})^2 + \sum_i^{n_{diedrals}} \sum_n^{n_{lmax}} \left(\frac{V_{i,n}}{2}\right) [1 + \cos(n\phi_i - \gamma_{i,n})] + \sum_{\langle i,j \rangle}^{n_{atoms}} \left(\frac{A_{ij}}{r_{ij}^{12}} - \frac{B_{ij}}{r_{ij}^6}\right) + \sum_{\langle i,j \rangle}^{n_{atoms}} \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \quad (1)$$

Therefore, in Eq. 1, the energies calculated during the simulations are shown below:

$$\sum_i^{n_{atoms}} \frac{P_i^2}{2m_i} \quad (2)$$

In Eq. 2 we have the kinetic energy of the atoms, being P_i and m_i the linear momentum and the mass of the i -th particle, respectively.

$$\sum_i^{n_{bonds}} b_i(r_i - r_{i,eq})^2 \quad (3)$$

In Eq. 3 we have the stretching energy of chemical bonds when treated as classical springs, where $r_i - r_{i,eq}$ corresponds to the stretching of the i -th bond, and b_i represents its spring constant.

$$\sum_i^{n_{angles}} a_i(\theta_i - \theta_{i,eq})^2 \quad (4)$$

In Eq. 4 we have the rotation energy of chemical bonds, where $\theta_i - \theta_{i,eq}$ is the angular change of the i -th bond, and a_i is the spring constant for rotations;

$$\sum_i^{n_{diedrals}} \sum_n^{n_{lmax}} \left(\frac{V_{i,n}}{2}\right) [1 + \cos(n\phi_i - \gamma_{i,n})] \quad (5)$$

In Eq. 5 we have the torsional energy of the chemical bonds.

$$\sum_{\langle i,j \rangle}^{n_{atoms}} \left(\frac{A_{ij}}{r_{ij}^{12}} - \frac{B_{ij}}{r_{ij}^6}\right) \quad (6)$$

In Eq. 6 we have the van der Waals potential energy, represented by the Lennard-Jones potential and which describes the interactions of induced dipoles during the simulations.

$$\sum_{\langle i,j \rangle}^{n_{atoms}} \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \quad (7)$$

And Eq. 7 which corresponds to electrostatic potential energy for atomic interactions.

The simulations made it possible to determine the energies of the fullerenes, so that the following quantities were calculated: Kinetic energy (E_C), potential energy (E_P), total energy (E_{TOT}), specific heat at constant volume (C_V), and entropy.

3. RESULTS AND DISCUSSION

3.1 Classical energies of the fullerene

Using the simulations from MD, it was possible to verify how the fullerene energy changes as a function of time and the increase in the number of carbon atoms. In this way, the calculations performed on the basis of the MM + force field provided the energy values that treat the molecular structures as classical systems.

First, the results were determined in terms of the kinetic energy of the fullerenes, taking into account the translational, rotational, and vibrational motions of the individual nanostructures. Figure 2.a shows the variation of the kinetic energy during the 4ns of the simulation, observing that their values are proportional to the number of atoms in the molecule. Thus, the energy curves are arranged in descending order according to the following relation - E_{KIN} : C540 > C240 > C180 > C80 > C60 > C20. It is important to note that for each curve in Figure 2.a, the largest E_{KIN} changes occur in the first moments of the simulation, corresponding to the thermalization time of the molecules. It can be concluded that the fullerene exhibits a linear increase in thermalization time, which is due to the growth of its structure. Moreover, Figure 2.b shows the comparison between the average E_{KIN} and the number of atoms of each nanostructure, so the linear relationship between these quantities can be observed according to the following linear equation: E_{KIN} (kcal/mol) = $8.94 \times 10^{-3} \times N_C + 6 \times 10^{-3}$.

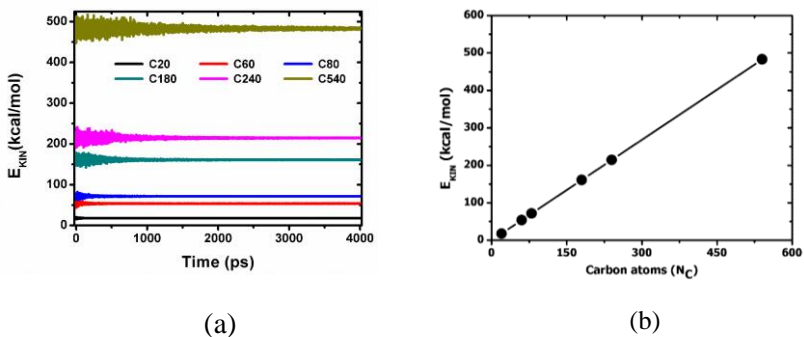


Figure 2: Kinetic energy of fullerene (C20, C60, C80, C180, C240 and C540) a) as a function of time and b) as a function of the number of carbon atoms.

The potential energy as a function of time for each fullerene was also analyzed. Unlike E_{KIN} , the E_{POT} energy did not show a linear behavior as a function of molecular structure size. Figure 3 shows that this energy behaves positively (repulsive) for smaller structures and negatively (attractive) for larger structures. This result indicates that the E_{POT} for the fullerene is mainly represented by the van der Waals interactions, whose values are given by the Lenard-Jones potential. For example, in a C20 molecule, the carbon atoms are very close to each other so that the positive

interactions predominate, so $E_{POT} > 0$. In the C60, C80 and C180 fullerenes, the carbon atoms become more numerous, which increases the E_{POT} of the nanostructures. However, as the number of atoms increases, the distance between them also increases, resulting in decreasing energy. In C240 and C540 fullerenes, on the other hand, the energies decrease again, indicating that the negative potential begins to predominate, so that the $E_{POT} < 0$. These results indicate that fullerenes with less than 540 carbon atoms have positive classical potential energy and their atoms tend to have repulsive interactions, while fullerenes with more than 540 atoms are expected to have attractive interactions.

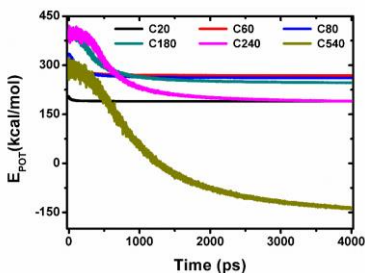


Figure 3: Potential energy of fullerene (C20, C60, C80, C180, C240 and C540) as a function of time.

Therefore, after analyzing the kinetic and potential energies of the fullerene molecules, it was found that E_{KIN} is linearly proportional to the number of atoms in the nanostructure, while E_{POT} is related to the Lennard-Jones potential (Potential Energy = $C_1 \cdot d^{-12} - C_2 \cdot d^{-6}$, being “ C_1 ” and “ C_2 ” constants and “ d ” the distance between the atoms).

Figure 4, which shows the total energy ($E_{TOT} = E_{KIN} + E_{POT}$) of the molecules, allows a comparison of the two energies. It can be seen that for C20 it is predominantly a potential energy and the nanostructure is hardly moved. However, for larger molecules E_{KIN} becomes more meaningful while E_{POT} decreases, so for C180 these energies are comparable. For C240 and C540 molecules, however, E_{POT} again predominates, but with negative values. It can be concluded that, according to the classical model for fullerene, the intramolecular interactions are stronger for C20, C60, C80, C240, and C 540. For C180, on the other hand, the interactions are less significant compared to the motion of the atoms.

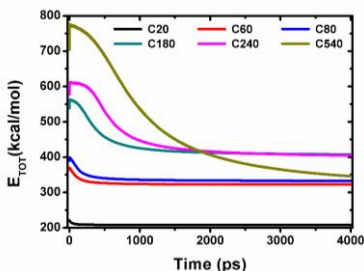


Figure 4: Total energy of fullerene (C20, C60, C80, C180, C240 and C540) as a function of time.

3.2 Thermal properties of the fullerenes

The thermodynamic properties C_v and entropy (Figure 5) were calculated as a function of the carbon number in the fullerene. In addition, the curves were interpolated and equations were generated to describe these properties. It can be seen that both thermodynamic properties grow exponentially with the number of atoms, so that the growth is more pronounced for smaller fullerenes (C20 and C180), while it applies to structures larger than C180.

After interpolating the C_v and entropy curves, it can be seen that the quantities with excellent agreement ($R_2 = 0.99$) can be described by logarithm functions, as shown in equations into the graphs. From these equation, one can derive the values of entropy and C_v for fullerenes with a number of atoms greater than 540.

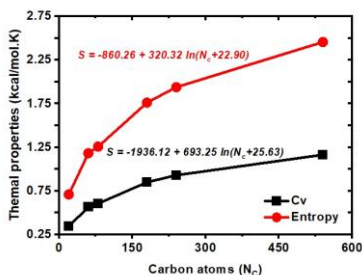


Figure 5: Specific heat at constant volume and the entropy of fullerene (C20, C60, C80, C180, C240 and C540) as a function of the number of carbon atoms.

The heat dissipated by fullerene molecules due to their intramolecular interactions can also be calculated. These quantities were estimated by considering the energy balance given by Equation 8 below:

$$\text{Heat} \left(\frac{\text{cal}}{\text{mol}} \right) = E_{TOT} - (E_{KIN} + E_{POT}) \quad (8)$$

Using this calculation, it was possible to estimate the amount of energy dissipated in the form of heat for molecules C20, C60, C80, C180, C240, and C540 (Figure 6.a). It was found that for C20 to C80, approximately the same amount of energy is dissipated, while for molecules larger than C180, the amount of heat transferred increases. This increase in dissipated energy can be interpreted as a result of the larger number of atoms in the nanostructure, which increases the degrees of freedom of the molecules, causing their surfaces to move in different directions, creating more friction and transferring more heat. To confirm this analysis, Figure 6.b shows the E_{KIN}/T ratio of statistical thermodynamics, which is proportional to the degrees of freedom of the molecules. Note that the ratio is linearly proportional to the number of carbon atoms.

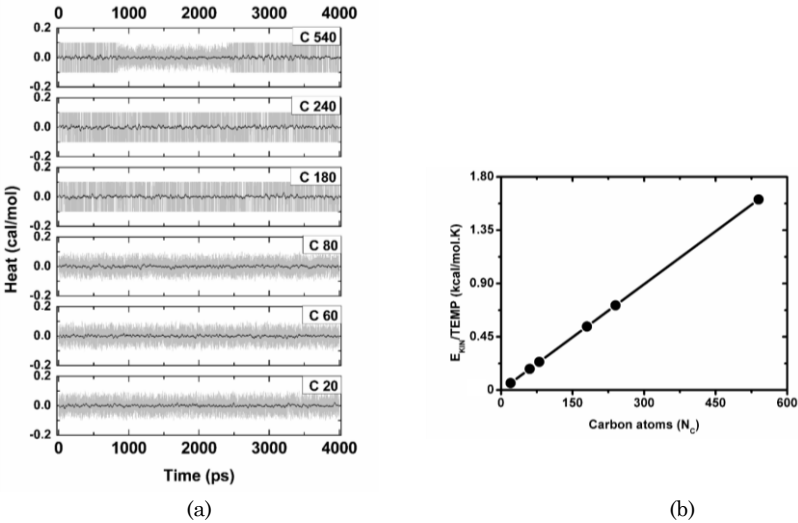


Figure 6:a) Heat release of fullerenes (C20, C60, C80, C180, C240 and C540) as function of time and b) E_{KIN}/T versus the number of carbon atoms.

4. CONCLUSION

In this study, we have investigated how the physicochemical properties of buckyball fullerenes change with the size of their structure. This is relevant investigation once these molecules have been presenting several applications. Thus, it was observed the dependence of its mechanical energy with respect to the carbon atoms amount, where the its potential energy depends mainly on the van der Waals interactions described by the Lennard-Jones potential, so that the potential energy is positive for smaller molecules and becomes negative for larger molecules due to the distance between their atoms. On the other hand, its kinetic energy is linearly proportional to this quantity.

Some thermal quantities were also observed for the fullerenes in different sizes. It can be seen that the entropy and specific heat increase proportionally to the number of atoms in the structure at constant volume, however this growth is logarithmic, and these functions were interpolated. Also, the heat dissipated of the spherical fullerenes were estimated, showing that the friction between its atoms increase with de molecular size.

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