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Zigzag and spiral configurations for fullerenes in carbon nanotubes

Duangkamon Baowan, Ngamta Thamwattana and James M Hill

Nanomechanics Group, School of Mathematics and Applied Statistics, University of Wollongong, NSW 2522, Australia

E-mail: db898@uow.edu.au, ngamta@uow.edu.au and jhill@uow.edu.au

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Abstract

The success or otherwise of nanoscale devices hinges on a correct understanding of the physical effects at this scale. Research in nanotechnology is predominantly through either experimentation using electron and atomic force microscopy or through large-scale computation using molecular dynamics simulation. In this paper, we employ elementary mechanical principles and classical modelling procedures to investigate the packing of C_{60} fullerene chains inside a single-walled carbon nanotube by utilizing the Lennard–Jones potential function and the continuum approximation. Such assemblies are often referred to as nanopeapods. We examine both zigzag and spiral chain configurations inside (10, 10), (16, 16) and (20, 20) carbon nanotubes and we obtain analytical expressions in terms of hypergeometric functions for the potential energy for such configurations. We find that for a (10, 10) tube, the C_{60} fullerene chain is formed linearly along the tube axis. In the case of both (16, 16) and (20, 20) tubes, both zigzag and spiral configurations are more clearly evident along the tube. In particular, the resulting pattern obtained for the zigzag chain is entirely consistent with a specific angular spacing for the spiral pattern.

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1. Introduction

Although classical applied mathematical modelling has been widely used for solving many wide-ranging problems, it has received less usage in the field of nanotechnology which is dominated by experiments and molecular dynamics simulations. A significant outcome obtained from the use of mathematical modelling is an improved insight and understanding into the basic physical concepts of the problem. Recently, nanodevices and nanostructures have received much attention scientifically due to their underlying unique physical properties arising from the van der Waals interaction force and the large surface to volume ratio, which

do not occur to the same extent at the micro-scale. However, there is a practical size limit at which equipment can operate, and this leads to difficulties studying nano-scale objects. As such, mathematical modelling techniques provide an alternative approach to investigate the special properties. The aim of this paper is to exploit conventional applied mathematical modelling and fundamental mechanical principles to describe the energy behaviour of certain configurations of fullerenes inside carbon nanotubes, which are sometimes referred to as nanopeapods. In particular, we examine the inter-atomic energy for both zigzag and spiral chains of C_{60} fullerenes inside a single-walled carbon nanotube by utilizing the Lennard–Jones potential function and the continuum approximation.

Nowadays, carbon nanostructures, such as C_{60} fullerenes, carbon nanotubes and nanopeapods, are being examined as components in many potential applications [1]. One particular proposed application is the use of carbon nanotubes as nanocarriers for drug delivery. Single-walled carbon nanotubes filled with C_{60} fullerenes, commonly called nanopeapods, have a unique morphology such that the space inside the tube can be considered as the nano-container and the C_{60} molecules can be considered as the drug [2]. Nanopeapods have been previously observed by Smith *et al* [3, 4], who use high-resolution transmission electron microscopy to show that self-assembly of C_{60} fullerene chains occurs inside carbon nanotubes. While the actual formation mechanisms of nanopeapods are unknown, a number of studies propose that a C_{60} molecule is either being sucked in through the tube open ends or being adsorbed through a large defect on the nanotube wall. By using molecular dynamics simulations, Berber *et al* [5] claim that the encapsulation of C_{60} molecules either in an isolated or bundled single-walled carbon nanotubes is most likely to occur through a large opening in the tube wall. For bundled tubes, or rope, the result of Berber *et al* [5] contradicts the prediction of Ulbricht and Hertel [6] and Ulbricht *et al* [7] that encapsulations through tube ends are more likely than encapsulations through defect openings on the side wall of carbon nanotubes. For the suction of C_{60} fullerenes through the open end of a carbon nanotube, molecular dynamics studies of Qian *et al* [8] suggest that (9, 9) and (10, 10) nanotubes will accept a C_{60} molecule from rest, but an (8, 8) nanotube will not. Furthermore, from the study of the energetics and electronic structures of nanopeapods, Okada *et al* [9] propose that the smallest radii of nanotubes which can encapsulate a C_{60} molecule is approximately 6.4 Å. This result agrees with Hodak and Girifalco [10] who determine that a nanotube with a radius less than 6.27 Å cannot be filled with C_{60} molecules, and the continuum model of Cox *et al* [11] which predicts that a nanotube with radius smaller than 6.338 Å will not accept C_{60} fullerenes by the van der Waals' suction force alone. After being accepted into the tube, the C_{60} molecule is likely to locate itself in a position with an inter-atomic distance away from the tube wall so that the inter-atomic potential energy is a minimum. In [12], a mathematical expression is obtained to determine the preferred position of the C_{60} molecule inside the nanotube. Their results show that in a (10, 10) nanotube the preferred position of the C_{60} is on the tube axis, whereas this position tends to be offset further away from the tube axis as the tube radius becomes larger. The above results of Hodak and Girifalco [10] and Cox *et al* [11, 12] confirm the findings of Okada *et al* [9] that the incorporation of a C_{60} molecule into a (10, 10) nanotube is energetically favourable, whereas this is not the case for (8, 8) and (9, 9) nanotubes due to large structural deformation of both the tubes and fullerenes.

From Hodak and Girifalco [10], Okada *et al* [9] and others [2, 13–16], it is confirmed that the encapsulation energy of the nanopeapods depends only on the tube radius, and that it is independent of the tube chirality [15]. As shown by Hodak and Girifalco [10, 17], Khlobystov *et al* [18], Okada *et al* [9] and Dubay and Kresse [19], in (10, 10) and (11, 11), the C_{60} molecules form a quasi one-dimensional system, and the energy is close to a one-dimensional system of C_{60} molecules to which the interaction energy with the tube is added. However, a

phase transition occurs when the tube radius becomes larger, resulting in an increase in the dimensionality of the C_{60} fullerenes inside the tube. From a Monte Carlo study, Hodak and Girifalco [10] report a zigzag structure of C_{60} molecules inside a (15, 15) nanotube. To obtain the interaction energy, in a quasi one-dimensional system (e.g. C_{60} fullerenes in a (10,10) tube), only three nearest neighbour interactions are taken into account, while in three-dimensional N molecules, Hodak and Girifalco [10] assume that the potential energy consists of two parts. These comprise, first, the nearest neighbour interactions between molecules which depend on the inter-molecular distance measured along the axial direction, and second, the contribution from the energy that depends on the offset distance of each molecule from the tube central axis.

In the present paper, we adopt this assumption together with the Lennard–Jones potential and the continuum approximation to predict the structure of a chain of C_{60} fullerenes inside a single-walled carbon nanotube. Our approach provides an explicit analytical result for the potential energy, which upon minimizing gives rise to the precise structure of the chain. Using this technique, we determine zigzag and spiral configurations of C_{60} fullerene chains inside nanotubes with radii in the range 6.784–13.557 Å. Our results agree with Hodak and Girifalco [17] who use a simulated annealing method to study the minimum energy configurations of C_{60} fullerenes inside carbon nanotubes with radii from 6.27 to 19.68 Å [17]. They predict that ten different packing arrangements occur for C_{60} molecules inside nanotubes within this size range. Each arrangement depends strongly on the size of the tube radius, and as such each arrangement exists only in certain sizes of carbon nanotubes.

In this paper, we employ the continuum approximation, for which the discrete carbon atoms are assumed to be replaced by an average atomic distribution over each surface, and the Lennard–Jones potential function, to determine the potential energy of a nanopeapod, which is assumed to form either a zigzag or a spiral configuration. The analysis for zigzag nanopeapods comprising $(2k + 1)$ C_{60} molecules is then presented in section 3. Furthermore, the investigation for nanopeapods with a spiral configuration and comprising k C_{60} molecules is presented in section 4. For both cases we obtain analytical expressions and we determine the minimum energy configurations. A concluding summary is presented in section 5. In appendix A, analytical expressions for the interaction energies between a carbon atom and a C_{60} molecule and between two C_{60} molecules are presented. Finally in appendix B, we present certain details for the derivation of the total potential energy for the zigzag and the spiral nanopeapods which are in the form of the hypergeometric functions.

2. Interaction energy

The widely used Lennard–Jones potential (see, for example, [10–12, 20]) is adopted here to determine the potential energy for a chain of C_{60} fullerenes inside a single-walled carbon nanotube. The classical Lennard–Jones potential for a pair of atoms at a distance ρ apart is given by

$$E(\rho) = -\frac{A}{\rho^6} + \frac{B}{\rho^{12}}, \quad (1)$$

where A and B are the attractive and the repulsive constants, respectively. Equation (1) can also be written in the form

$$E(\rho) = 4\epsilon \left[-\left(\frac{\sigma}{\rho}\right)^6 + \left(\frac{\sigma}{\rho}\right)^{12} \right],$$

where σ is the van der Waals diameter and the well depth $\epsilon = A^2/4B$. The equilibrium distance ρ_0 is given by $\rho_0 = 2^{1/6}\sigma = (2B/A)^{1/6}$. For carbon–carbon atom interactions, the

their contributions to the total energy. We comment that the van der Waals force is a short-range force so that, for example, for two interacting C_{60} fullerenes it operates at the van der Waals diameter of 8.9424 \AA , and since the nearest neighbour approximation involves a distance between fullerene centres of at least 10.0375 \AA , only a single nearest neighbour interaction needs to be considered. We assume that the distance in the z direction between centres of adjacent molecules is Z . Then the centre of the upper j th C_{60} molecule ($j = 1, 2, \dots, k+1$) is located at position $2(j-1)Z$, while the centre of the lower i th C_{60} molecule ($i = 1, 2, \dots, k$) is located at position $Z + 2(i-1)Z = (2i-1)Z$.

With reference to a rectangular Cartesian coordinate system (x, y, z) , a typical point on the surface of the tube has the coordinates $(b \cos \theta, b \sin \theta, z)$ where b is the radius of the tube. The length of the tube is assumed to be $2L$ where L may tend to infinity. Similarly, with reference to a rectangular Cartesian coordinate system (x, y, z) with the origin located at the centre of the most left C_{60} molecule, centres of the upper j th C_{60} molecules have coordinates $(\varepsilon, 0, 2Z(j-1))$ ($j = 1, 2, \dots, (k+1)$) and centres of the lower i th C_{60} molecules have coordinates $(-\varepsilon, 0, Z(2i-1))$ ($i = 1, 2, \dots, k$), where Z is the distance between centres of adjacent C_{60} fullerenes and ε is the offset position from the centre of the tube to the centre of the C_{60} fullerene in the x direction, as illustrated in figure 1. Then from (2) the total potential energy is obtained by

$$E^{\text{tot}} = \sum_{i=1}^k E_i(\rho_i) + \sum_{j=1}^{k+1} E_j(\rho_j) + (2k-1)E^{**}(d_1) + 2kE^{**}(d_2),$$

where d_1 and d_2 are the distances between the centres of C_{60} fullerenes as shown in figure 1, and $d_1^2 = 4Z^2$ and $d_2^2 = 4\varepsilon^2 + Z^2$. The potential functions $E^{**}(d_1)$ and $E^{**}(d_2)$ arise from the type I and type II interactions between a pair of C_{60} molecules, respectively, and are defined by (A.4). The potential functions E_i and E_j represent the energy of a C_{60} fullerene interacting with the carbon nanotube which is obtained from

$$E_m = b\eta_g \int_{-\pi}^{\pi} \int_{-L}^L E^*(\rho_m) dz d\theta, \quad (m = i, j) \quad (3)$$

where η_g is the mean atomic surface density for a carbon nanotube and the length L is subsequently taken to be infinite. The potential function E^* is defined by (A.1) and ρ_m ($m = i$ and j) are given by

$$\begin{aligned} \rho_i^2 &= (b + \varepsilon)^2 - 4b\varepsilon \sin^2(\theta/2) + [z - Z(2i-1)]^2, \\ \rho_j^2 &= (b - \varepsilon)^2 + 4b\varepsilon \sin^2(\theta/2) + [z - 2Z(j-1)]^2. \end{aligned}$$

According to equations (A.2), (A.3) and (3), we need to evaluate

$$G_m = \int_{-\pi}^{\pi} \int_{-\infty}^{\infty} \frac{1}{(\rho_m^2 - a^2)^n} dz d\theta, \quad (4)$$

where n is an integer. The details for evaluating (4) are presented in appendix B and we may deduce

$$G_m = \frac{\pi^2}{2^{2n-3}(\alpha_m + \beta_m)^{n-1/2}} \binom{2(n-1)}{n-1} F\left(n - \frac{1}{2}, \frac{1}{2}; 1; 1 - \gamma_m\right),$$

where $F(a, b; c; z)$ denotes the usual hypergeometric function, $\binom{x}{y}$ represents the usual binomial coefficient, $\gamma_m = \alpha_m/(\alpha_m + \beta_m)$ ($m = i$ and j), $\alpha_i = (b + \varepsilon)^2 - a^2$, $\beta_i = -4b\varepsilon$, $\alpha_j = (b - \varepsilon)^2 - a^2$ and $\beta_j = 4b\varepsilon$.

Table 1. Values of various constants.

Parameters	Values
Radius of C ₆₀ (<i>a</i>)	3.55 Å
Radius of (10, 10) (<i>b</i>)	6.784 Å
Radius of (16, 16) (<i>b</i>)	10.846 Å
Radius of (20, 20) (<i>b</i>)	13.557 Å
Attractive constant—C ₆₀ –C ₆₀ (<i>A</i>)	20.0 eV Å ⁶ ^a
Repulsive constant—C ₆₀ –C ₆₀ (<i>B</i>)	34.8 × 10 ³ eV Å ¹² ^a
Attractive constant—C ₆₀ –graphene (<i>A</i>)	17.4 eV Å ⁶ ^a
Repulsive constant—C ₆₀ –graphene (<i>B</i>)	29.0 × 10 ³ eV Å ¹² ^a
Mean surface density of C ₆₀ (η_f)	0.3789 Å ⁻²
Mean surface density of carbon nanotube (η_g)	0.3812 Å ⁻²

^a Data taken from [20].

Table 2. Equilibrium distance *Z* (Å), offset location ε (Å) and total potential energy of the system E^{tot} (eV) for each pair of C₆₀ fullerenes in a zigzag configuration nanopeapod comprising $(2k + 1)$ C₆₀ molecules.

<i>k</i>	(10, 10)			(16, 16)			(20, 20)		
	<i>Z</i>	ε	E^{tot}	<i>Z</i>	ε	E^{tot}	<i>Z</i>	ε	E^{tot}
1	10.0375	0	-6.8099	5.1838	4.2977	2.7516	0	7.0200	2.1063
2	10.0362	0	-13.9535	5.0281	4.3193	6.4709	5.0177	7.0207	4.8644
3	10.0359	0	-21.0971	5.0262	4.3207	-10.1929	5.0179	7.0202	7.6325
4	10.0358	0	-28.2407	5.0255	4.3213	-13.9148	5.0180	7.0200	-10.4006
5	10.0358	0	-35.3843	5.0252	4.3216	-17.6368	5.0180	7.0198	-13.1687
10	10.0356	0	-71.1023	5.0246	4.3223	-36.2468	5.0180	7.0195	-27.0092
15	10.0356	0	-106.8203	5.0245	4.3225	-54.8568	5.0180	7.0194	-40.8498
20	10.0356	0	-142.5384	5.0244	4.3226	-73.4669	5.0180	7.0193	-54.6903
25	10.0356	0	-178.2564	5.0243	4.3227	-92.0769	5.0181	7.0193	-68.5308
50	10.0356	0	-356.8464	5.0243	4.3228	-185.1270	5.0181	7.0192	-137.7335
100	10.0356	0	-714.0267	5.0242	4.3223	-371.2273	5.0181	7.0192	-276.1387

3.1. Numerical solutions for zigzag nanopeapods

By minimizing the total energy of the system we determine the offset location ε from the centre of the tube to the centre of the C₆₀ fullerene and an equilibrium distance *Z* between centres of a pair of C₆₀ molecules for zigzag nanopeapods. The total potential energy consists of two nearest neighbour interactions of two C₆₀ fullerenes and one interaction between the C₆₀ fullerene and the carbon nanotube. We examine an infinite length carbon nanotube which comprises $(2k + 1)$ C₆₀ molecules inside (10, 10), (16, 16) and (20, 20) carbon nanotubes. Using the algebraic computer package MAPLE together with the parameter values in table 1, the numerical values for the offset location ε , the equilibrium distance *Z* and the total potential energy E^{tot} are as shown in table 2. We note that the global minimum energy location of the system is first graphed to ensure a genuine global minimum and the optimization package in MAPLE is then utilized to find the optimum values for each parameter at this location.

In the case of the (10, 10) carbon nanotube, we obtain an offset position $\varepsilon = 0$ which is equivalent to a distance 3.234 Å from the tube wall to the nearest atom on the C₆₀ molecule and compares well with Okada *et al* [9]. The equilibrium distance is shown to be $Z = 10.0375$ Å for three C₆₀ molecules inside the tube which is in excellent agreement with

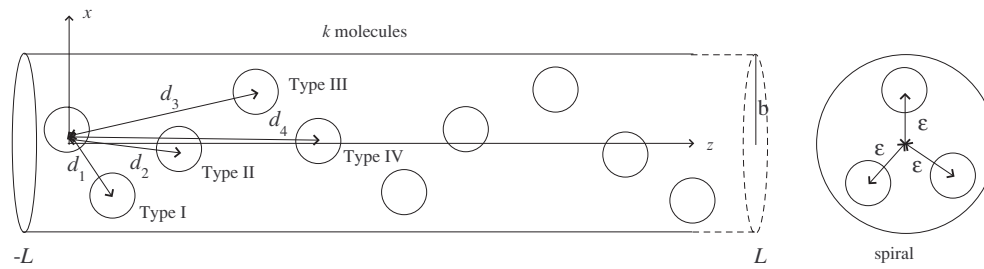


Figure 2. Spiral configuration for k C_{60} molecules inside a carbon nanotube.

Rocheffort [13]. As a result, all C_{60} fullerenes inside the (10, 10) tube are likely to align and form a linear chain along the tube axis. The equilibrium distance decreases slightly as the number of the C_{60} molecules is increased due to the packing of the molecules. Moreover, the C_{60} fullerenes move closer to the wall as the radius of the tube increase. We obtain the offset positions of $\varepsilon = 4.30 \text{ \AA}$ and $\varepsilon = 7.02 \text{ \AA}$ and the equilibrium distances of $Z = 5.024 \text{ \AA}$ and $Z = 5.018 \text{ \AA}$ for the (16, 16) and (20, 20) carbon nanotubes, respectively. For these two cases, the zigzag pattern is more clearly evident along the tube. However, for the three C_{60} fullerenes inside the (20, 20) carbon nanotube, the equilibrium distance is $Z = 0$ which means that although a zigzag pattern exists, all three of the C_{60} molecules are in the same plane. This is because there is a sufficient amount of space for the three C_{60} molecules to align themselves due to the large circumference of tube. This result is related to the investigation made by Hodak and Girifalco [17]. Furthermore, upon considering C_{60} fullerenes inside a (15, 15) nanotube, our results suggest $\varepsilon \simeq 3.6 \text{ \AA}$ and $Z \simeq 6.9 \text{ \AA}$ which agree well with Hodak and Girifalco [10].

We find that the offset locations for all three nanopeapod configurations in this investigation are in a very good agreement with Cox *et al* [11] for a single C_{60} fullerene inside a single-walled carbon nanotube. Moreover, we observe that the interaction energy between the C_{60} fullerenes has more effect in forming the chain conformation than the interaction energy between the tube and the C_{60} fullerene. For example, we obtain an equilibrium distance of 10.036 \AA for (10, 10) nanopeapod, which is comparable to the equilibrium distance between two C_{60} molecules as determined in appendix A. We further observe that the number of C_{60} molecules in the system makes only a minor contribution to the alignment of the molecules as shown in table 2.

4. Spiral nanopeapod comprising k C_{60} molecules

In this section, a spiral configuration is assumed for k C_{60} fullerenes, which are located inside a single-walled carbon nanotube, as shown in figure 2. We minimize the energy of the system and we determine the angular spacing α , the longitudinal spacing β and the offset location ε for a spiral pattern. We assume that the total potential energy of the system comprises

- (i) k C_{60} fullerenes each interacting with all the carbon atoms of the carbon nanotube;
- (ii) $2(k - 1)$ type I interactions, comprising two for each $i = 2, 3, \dots, k - 1$ and one for each of $i = 1$ and $i = k$; thus $2(k - 2) + 2 = 2(k - 1)$;
- (iii) $2(k - 2)$ type II interactions, comprising two for each $i = 3, 4, \dots, k - 2$ and one for each of $i = 1, 2$ and $i = k - 1, k$; thus $2(k - 4) + 4 = 2(k - 2)$;

- (iv) $2(k - 3)$ type III interactions, comprising two for each $i = 4, 5, \dots, k - 3$ and one for each of $i = 1, 2, 3$ and $i = k - 2, k - 1, k$; thus $2(k - 6) + 6 = 2(k - 3)$;
- (v) $2(k - 4)$ type IV interactions, comprising two for each $i = 5, 6, \dots, k - 4$ and one for each of $i = 1, 2, 3, 4$ and $i = k - 3, k - 2, k - 1, k$; thus $2(k - 8) + 8 = 2(k - 4)$,

where the four nearest neighbour interactions of types I, II, III and IV are as shown in figure 2.

With reference to a rectangular Cartesian coordinate system (x, y, z) , a typical point on the surface of the tube has the coordinates $(b \cos \theta, b \sin \theta, z)$ where b is the radius of the tube. The length of the tube is assumed to be $2L$, where L may tend to infinity. Similarly, with reference to a rectangular Cartesian coordinate system (x, y, z) with the origin located at the centre of the left most C_{60} molecule, centres of C_{60} molecules have coordinates $(\varepsilon \cos \alpha i, \varepsilon \sin \alpha i, \beta i)$ ($i = 1, 2, \dots, k$), where ε represents the offset location, α and β denote the angular and the longitudinal spacings for the spiral shape, respectively. We note that $\alpha = \pi$ gives rise to the special case of the zigzag pattern. From (2) the total potential energy is given by

$$E^{\text{tot}} = \sum_{i=1}^k E_i(\rho_i) + (k-1)E^{**}(d_1) + (k-2)E^{**}(d_2) + (k-3)E^{**}(d_3) + (k-4)E^{**}(d_4),$$

where d_ℓ ($\ell = 1, 2, 3, 4$) are the distances between centres of C_{60} fullerenes as shown in figure 2 and

$$d_\ell^2 = 4\varepsilon^2 \sin^2(\ell\alpha/2) + (\ell\beta)^2. \quad (5)$$

The potential function $E^{**}(d_\ell)$ represents types I, II, III and IV interactions which are the potential energies between a pair of C_{60} fullerenes defined by (A.4). The potential function E_i ($i = 1, 2, \dots, k$) represents the energy of a C_{60} fullerene interacting with the carbon nanotube which is obtained from (3) where in this case $m = i$ and $i = 1, 2, \dots, k$. The function E^* is defined by (A.1) and ρ_i ($i = 1, 2, \dots, k$) is given by

$$\rho_i^2 = (b - \varepsilon)^2 + 4b\varepsilon \sin^2[(\theta - \alpha i)/2] + (z - \beta i)^2.$$

We comment that because of the assumed symmetry of the tube, the term αi has no effect for the integral in (3) so formally we may let $\alpha i = 0$ and obtain

$$\rho_i^2 = (b - \varepsilon)^2 + 4b\varepsilon \sin^2(\theta/2) + (z - \beta i)^2.$$

According to equations (A.2), (A.3) and (3), in the limit as L tends to infinity we need to evaluate

$$H_i = \int_{-\pi}^{\pi} \int_{-\infty}^{\infty} \frac{1}{(\rho_i^2 - a^2)^n} dz d\theta, \quad (6)$$

where n is an integer. Using precisely the same method as the derivation of (4), it can be shown that the solution for (6) is again in the form of the hypergeometric function and we may deduce

$$H_i = \frac{\pi^2}{2^{2n-3}(\alpha_i + \beta_i)^{n-1/2}} \binom{2(n-1)}{n-1} F\left(n - \frac{1}{2}, \frac{1}{2}; 1; 1 - \gamma_i\right),$$

where as before $F(a, b; c; z)$ denotes the usual hypergeometric function, $\binom{x}{y}$ represents the usual binomial coefficient, $\alpha_i = (b - \varepsilon)^2 - a^2$, $\beta_i = 4b\varepsilon$ and $\gamma_i = [(b - \varepsilon)^2 - a^2]/[(b + \varepsilon)^2 - a^2]$.

Table 3. Angular spacing α , longitudinal spacing β , offset location ε in Å and total potential energy of the system E^{tot} (eV) for each pair of C_{60} fullerenes in a spiral configuration nanopeapod comprising k C_{60} molecules.

k	(10, 10)				(16, 16)				(20, 20)			
	α	β	ε	E^{tot}	α	β	ε	E^{tot}	α	β	ε	E^{tot}
3	0	10.0366	0	-10.3815	3.1416	5.0329	4.3174	-4.6056	1.3132	5.2127	7.0250	-3.7679
4	0	10.0361	0	-13.9542	3.1416	5.0273	4.3193	-6.4803	1.5842	0.8121	7.0235	-5.5089
5	0	10.0359	0	-17.5269	3.1416	5.0254	4.3202	-8.3551	1.5422	2.4924	7.0012	-6.9939
10	0	10.0355	0	-35.3904	3.1416	5.0230	4.3217	-17.7293	1.5594	2.5018	6.9714	-15.8494
15	0	10.0354	0	-53.2538	3.1416	5.0225	4.3221	-27.1036	1.7191	2.2893	6.9035	-26.3570
20	0	10.0353	0	-71.1173	3.1416	5.0222	4.3223	-36.4779	1.7191	2.2900	6.8997	-35.9950
25	0	10.0353	0	-88.9808	3.1416	5.0221	4.3224	-45.8522	1.7191	2.2905	6.8974	-45.6333
50	0	10.0353	0	-178.2982	3.1416	5.0218	4.3227	-92.7237	1.7191	2.2913	6.8926	-93.8261
100	0	10.0352	0	-356.9329	3.1416	5.0217	4.3228	-186.4668	1.7191	2.2918	6.8902	-190.2130

4.1. Numerical solutions for spiral nanopeapods

The energy minimization technique is employed here to determine the stable configurations of a spiral chain of C_{60} fullerenes inside a single-walled carbon nanotube. We consider nanopeapods comprising k C_{60} molecules inside infinite (10, 10), (16, 16) and (20, 20) carbon nanotubes with four possible nearest neighbour interactions for two C_{60} molecules and one interaction between the C_{60} molecule and all the atoms of the carbon nanotube. Again, using the algebraic computer package MAPLE and the parameter values in table 1, we obtain numerical values for the angular spacing α , the longitudinal spacing β , the offset location ε and the total potential energy E^{tot} for such a chain, which are shown in table 3. We note that β is analogous to the equilibrium distance Z for the zigzag configuration.

For the (10, 10) carbon nanotube, we again obtain the offset location $\varepsilon = 0$. Moreover, from (5), the angular spacing α has no effect on this configuration, and the longitudinal spacing β is found to be 10.03 Å. Subsequently, the C_{60} fullerenes form a linear chain along the tube axis. These three parameters, α , β and ε , change slightly as the number of C_{60} fullerenes in the tube increases. The angular spacing $\alpha \simeq \pi$ for the (16, 16) tube, which corresponds to the zigzag configuration, and is close to $\pi/2$ for the (20, 20) tube. For $k = 100$, we obtain $\beta = 5.0217$ Å, $\varepsilon = 4.3228$ Å and $\beta = 2.2918$ Å, $\varepsilon = 6.8902$ Å for the (16, 16) and the (20, 20) tubes, respectively. Consequently, we clearly observe spiral patterns for C_{60} fullerenes in both the (16, 16) and the (20, 20) nanotubes.

In particular, the zigzag configuration can be thought of as a special case of the spiral conformation with the angular spacing $\alpha = \pi$. We obtain comparable numerical values for the offset location ε and the longitudinal spacing β for all sizes of the tubes, and an example is shown for the case of (16, 16) carbon nanotube in table 3. Moreover, in the case of (20, 20) tube, at least four C_{60} molecules are required to form a stable spiral configuration. This observation is related to the findings of Hodak and Girifalco [17] in the sense that four molecules are required on each layer within the carbon nanotube with radius 13.5–14.05 Å.

5. Summary

The major contribution of this paper is the use of elementary mechanical principles and classical applied mathematical modelling techniques to formulate explicit analytical criteria and ideal model behaviour in a nanotechnology area for which previously only experimental and molecular dynamics simulation were available. Two nonlinear patterns for a C_{60} fullerene

chain inside a single-walled carbon nanotube, which are assumed to be zigzag and spiral, are examined in this paper. We employ the Lennard–Jones potential function and the continuum approximation to obtain the energy of the system which upon minimizing gives rise to the stable structure of the system. Double surface integrals are performed to determine the potential energy which may be expressed in terms of the standard hypergeometric function. The Lennard–Jones potential energies are evaluated numerically using the algebraic computer package MAPLE.

In terms of the zigzag configuration, we consider $(2k + 1)$ C_{60} molecules inside $(10, 10)$, $(16, 16)$ and $(20, 20)$ single-walled carbon nanotubes. The offset location ε and the equilibrium distance Z are determined. The total potential energy of the system comprises the interaction energy between the C_{60} fullerenes and the tube and the two nearest neighbour interactions of the C_{60} molecules. We find that the chain of C_{60} molecules is formed linearly along the $(10, 10)$ tube axis and discernible zigzag patterns exist for both the $(16, 16)$ and $(20, 20)$ tubes. The spiral configuration comprising k C_{60} molecules is also investigated. We consider the interaction energy between the C_{60} fullerenes and the tube and the four nearest neighbour interactions between the C_{60} molecules. The angular spacing α , the longitudinal spacing β and the offset location ε are determined from minimization of the interaction energies. We also obtain a linear C_{60} fullerene chain along the $(10, 10)$ tube axis and spiral patterns for the $(16, 16)$ and $(20, 20)$ tubes. In particular, $\alpha = \pi$ gives rise to the special case of the zigzag pattern, and we obtain comparable numerical values for the zigzag configuration from the spiral configuration by setting $\alpha = \pi$.

In general, we observe that the interaction energy between the C_{60} molecules themselves dominates the energy of the system. The interaction between the C_{60} molecules determines the equilibrium position and the angular spacing of the system, whereas the interaction between the C_{60} fullerene and the carbon nanotube determines the offset position of the chain. Further, in the zigzag configuration, the number of C_{60} molecules makes a minor contribution to both the offset location and the equilibrium distance so that the assumption of periodicity made for the molecular dynamics simulations is quite reasonable. However, the periodicity assumption may not apply for the spiral configuration since as the radius of the tube increases the system requires more C_{60} molecules to maintain stability of the system. Finally, we comment that for a tube which is finite in length, we expect that the results given here also apply providing that the two fullerenes located closest to the tube ends are at a distance from the end which is at least the van der Waals radius 4.4712 \AA . If this is not the case, we might expect some small variation of the numerical values given here, since at the tube ends peak-like forces operate (see, for example, [12]) which would tend to diminish the distance between fullerene centres.

Acknowledgments

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Appendix A. Derivation of interaction energies for fullerenes

Here we summarize the derivation of the potential energy between two C_{60} molecules. To start we review the calculation of the interaction energy between a carbon atom and a C_{60}

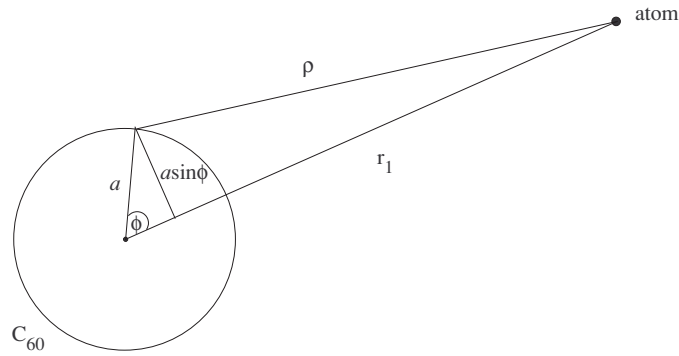


Figure A1. Atom interacting with C_{60} fullerene.

fullerene, utilizing the Lennard–Jones potential function and the continuum approximation. Subsequently, the potential energy between the two C_{60} fullerenes is obtained by performing another surface integral of a spherical fullerene.

The derivation of the potential energy between a carbon atom and a C_{60} fullerene was first given by Mahanty and Ninham [23] and Ruoff and Hickman [24] and then later adopted by Cox *et al* [11]. As shown in figure A1, with the carbon atom located outside the spherical fullerene, the distance between the atom and a typical atom on the C_{60} fullerene ρ is given by $\rho^2 = a^2 + r_1^2 - 2ar_1 \cos \phi$, where a is a radius of a C_{60} fullerene. The potential energy for a carbon atom interacting with the spherical fullerene is obtained by $E^* = -Q_6 + Q_{12}$, where Q_n ($n = 6, 12$) are defined by

$$Q_n = C_n \eta_f \int_{\Sigma} \frac{1}{\rho^n} d\Sigma,$$

where ρ denotes the distance from a carbon atom to a typical surface element of the spherical molecule $d\Sigma$. The constants C_6 and C_{12} are the Lennard–Jones potential constants A and B , respectively, and η_f represents the atomic surface density of a C_{60} fullerene. Therefore, the interaction energy between the carbon atom and the C_{60} fullerene is given by

$$E^*(r_1) = \frac{\pi a \eta_f}{r_1} \left[\frac{A}{2} \left(\frac{1}{(r_1 + a)^4} - \frac{1}{(r_1 - a)^4} \right) - \frac{B}{5} \left(\frac{1}{(r_1 + a)^{10}} - \frac{1}{(r_1 - a)^{10}} \right) \right]. \quad (\text{A.1})$$

Following the work of Cox *et al* [11], we place the fractions over common denominators, expand and reduce to fractions in terms of powers of $(r_1^2 - a^2)$, and then it can be shown that

$$\frac{A}{2r_1} \left(\frac{1}{(r_1 + a)^4} - \frac{1}{(r_1 - a)^4} \right) = -4aA \left(\frac{1}{(r_1^2 - a^2)^3} + \frac{2a^2}{(r_1^2 - a^2)^4} \right), \quad (\text{A.2})$$

and

$$\begin{aligned} \frac{B}{5r_1} \left(\frac{1}{(r_1 + a)^{10}} - \frac{1}{(r_1 - a)^{10}} \right) &= -\frac{4aB}{5} \left(\frac{5}{(r_1^2 - a^2)^6} + \frac{80a^2}{(r_1^2 - a^2)^7} \right. \\ &\quad \left. + \frac{336a^4}{(r_1^2 - a^2)^8} + \frac{512a^6}{(r_1^2 - a^2)^9} + \frac{256a^8}{(r_1^2 - a^2)^{10}} \right). \end{aligned} \quad (\text{A.3})$$

For full details of the derivation of (A.1), we refer the reader to [11].

To determine the interaction between two spherical fullerenes, with their centres at a distance r apart, we need to perform a surface integral of (A.1) over another spherical fullerene,

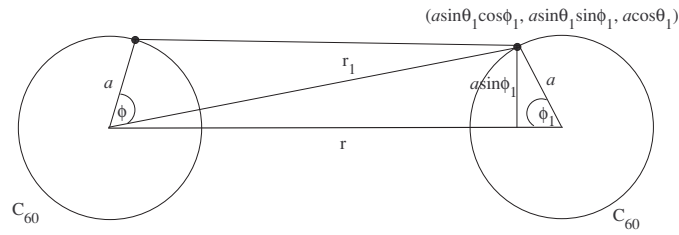


Figure A2. Two interacting C_{60} fullerenes.

which has the parametric equation $(x_1, y_1, z_1) = (a \sin \theta_1 \cos \phi_1, a \sin \theta_1 \sin \phi_1, a \cos \theta_1)$. Here the distance r_1 , as illustrated in figure A2, is given by $r_1^2 = a^2 + r^2 - 2ar \cos \phi_1$. Thus, the potential energy between two spherical fullerenes is obtained from $E^{**} = -P_6 + P_{12}$, where P_n ($n = 6, 12$) are defined by

$$P_n = \eta_f \int_0^{2\pi} \int_0^\pi Q_n a^2 \sin \phi_1 d\phi_1 d\theta_1.$$

By using appropriate substitutions and integrations, we may deduce

$$P_n = \frac{4\pi^2 a^2 C_n \eta_f^2}{r(2-n)(3-n)} \left(\frac{1}{(2a+r)^{n-3}} + \frac{1}{r^{n-3}} - \frac{1}{(2a-r)^{n-3}} - \frac{1}{(-r)^{n-3}} \right), \quad (\text{A.4})$$

for which n even simplifies to yield

$$P_n = \frac{4\pi^2 a^2 C_n \eta_f^2}{r(2-n)(3-n)} \left(\frac{1}{(2a+r)^{n-3}} - \frac{1}{(2a-r)^{n-3}} + \frac{2}{r^{n-3}} \right),$$

a formula which is also given in [21]. Using the constant values given in table 1, we find that the equilibrium distance for two C_{60} fullerenes is given by $r_0 = 10.0375 \text{ \AA}$.

Appendix B. Evaluation of the integral (4)

The integral (4) is evaluated here. On letting $\lambda_i^2 = (b + \varepsilon)^2 - 4b\varepsilon \sin^2(\theta/2) - a^2$ and $\lambda_j^2 = (b - \varepsilon)^2 + 4b\varepsilon \sin^2(\theta/2) - a^2$, we obtain

$$G_m = \int_\pi^{-\pi} \int_{-L}^L \frac{1}{[\lambda_m^2 + (z + Z_m)^2]^n} dz d\theta \quad (m = i, j),$$

where $Z_i = Z(2i - 1)$ ($i = 1, 2, \dots, k$) and $Z_j = 2Z(j - 1)$ ($j = 1, 2, \dots, k + 1$). Upon making the substitution $x_m = z + Z_m$, we may deduce

$$G_m = \int_\pi^{-\pi} \int_{Z_m-L}^{Z_m+L} \frac{1}{(\lambda_m^2 + x_m^2)^n} dx_m d\theta = \int_{-\pi}^\pi \int_{-\pi/2}^{\pi/2} \frac{\lambda_m \sec^2 \psi}{\lambda_m^{2n} \sec^{2n} \psi} d\psi d\theta,$$

where the final line is obtained by substituting $x_m = \lambda_m \tan \psi$ and letting L tend to infinity. Finally, we have

$$G_m = \frac{1}{\lambda_m^{2p+1}} \int_{-\pi}^\pi \int_{-\pi/2}^{\pi/2} \cos^{2p} \psi d\psi d\theta, \quad (\text{B.1})$$

where $p = n - 1$. The solution for (B.1) can be found in [25] (p. 149, no 2.513, 3) for which we may deduce

$$\int \cos^{2p} \psi d\psi = \frac{1}{2^{2p}} \left[\binom{2p}{p} \psi + \sum_{\ell=0}^{p-1} \binom{2p}{\ell} \frac{\sin[2(p-\ell)\psi]}{p-\ell} \right], \quad (\text{B.2})$$

where $\binom{x}{y}$ is the usual binomial coefficients. By evaluating (B.2) at $\psi = \pi/2$ and $\psi = -\pi/2$ and using the fact that $\sin 2x = 2 \sin x \cos x$, we may deduce

$$G_m = \frac{\pi}{2^{2p}} \binom{2p}{p} \int_{-\pi}^{\pi} \frac{1}{\lambda_m^{2p+1}} d\theta = \frac{4\pi}{2^{2p}} \binom{2p}{p} \int_0^{\pi/2} \frac{1}{\lambda_m^{2p+1}} dx,$$

where $x = \theta/2$ and then $\lambda_i^2 = (b + \varepsilon)^2 - 4b\varepsilon \sin^2 x - a^2$ and $\lambda_j^2 = (b - \varepsilon)^2 + 4b\varepsilon \sin^2 x - a^2$. First, we consider

$$J_m = \int_0^{\pi/2} \frac{dx}{(\alpha_m + \beta_m \sin^2 x)^{p+1/2}},$$

where $\alpha_i = (b + \varepsilon)^2 - a^2$, $\alpha_j = (b - \varepsilon)^2 - a^2$, $\beta_i = -4b\varepsilon$ and $\beta_j = 4b\varepsilon$. Making the substitution $t = \cot x$ and letting $\gamma_m = \alpha_m/(\alpha_m + \beta_m)$, we obtain

$$\begin{aligned} J_m &= \int_0^{\infty} \frac{(1+t^2)^{p-1/2}}{[\alpha_m(1+t^2) + \beta_m]^{p+1/2}} dt \\ &= \frac{1}{(\alpha_m + \beta_m)^{p+1/2}} \int_0^{\infty} \frac{(1+t^2)^{p-1/2}}{(1-\gamma_m t^2)^{p+1/2}} dt. \end{aligned}$$

Now on writing the integral in the form

$$J_m = \frac{1}{(\alpha_m + \beta_m)^{p+1/2}} \int_0^{\infty} \frac{(1+t^2)^{-1} dt}{[1 - (1-\gamma_m)t^2/(1+t^2)]^{p+1/2}},$$

we are led to make the substitution $z = t/\sqrt{1+t^2}$ and following we make the further substitution $u = z^2$, so that

$$J_m = \frac{1}{2(\alpha_m + \beta_m)^{p+1/2}} \int_0^1 \frac{u^{-1/2}(1-u)^{-1/2}}{[1 - (1-\gamma_m)u]^{p+1/2}} du.$$

From [25] (p. 995, no 9.111) we may deduce

$$J_m = \frac{\pi}{2(\alpha_m + \beta_m)^{p+1/2}} F\left(p + \frac{1}{2}, \frac{1}{2}; 1; 1 - \gamma_m\right),$$

where $F(a, b; c; Z)$ denotes a hypergeometric function. Finally, we obtain

$$G_m = \frac{\pi^2}{2^{2n-3}(\alpha_m + \beta_m)^{n-1/2}} \binom{2(n-1)}{n-1} F\left(n - \frac{1}{2}, \frac{1}{2}; 1; 1 - \gamma_m\right).$$

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Corrigendum

Zigzag and spiral configurations for fullerenes in carbon nanotubes

D Baowan, N Thamwattana and J M Hill 2007 *J. Phys. A: Math. Theor.* **40** 7543–7556

There is a minor error in equation (A.4) and in the equation following (A.4). The correct form of (A.4) reads,

$$P_n = \frac{4\pi^2 a^2 C_n \eta_f^2}{r(2-n)(3-n)} \left(\frac{1}{(2a+r)^{n-3}} + \frac{1}{(-r)^{n-3}} - \frac{1}{(2a-r)^{n-3}} - \frac{1}{r^{n-3}} \right), \quad (\text{A.4})$$

and for n even the correct simplification of this equation becomes

$$P_n = \frac{4\pi^2 a^2 C_n \eta_f^2}{r(2-n)(3-n)} \left(\frac{1}{(2a+r)^{n-3}} - \frac{1}{(2a-r)^{n-3}} - \frac{2}{r^{n-3}} \right).$$

This change has a small effect on numerical values presented in the original tables 2 and 3. The corrected revised tables 2 and 3 are given below. The authors are grateful to Dr. Barry Cox for pointing out this error.

Table 2. Equilibrium distance Z (Å), offset location ε (Å) and total potential energy of the system E^{tot} (eV) for each pair of C_{60} fullerenes in a zigzag configuration nanopeapod comprising $(2k + 1)$ C_{60} molecules.

k	(10,10)			(16,16)			(20,20)		
	Z	ε	E^{tot}	Z	ε	E^{tot}	Z	ε	E^{tot}
1	10.0550	0	-6.7632	5.2176	4.2977	-2.7048	0	7.0213	-2.0941
2	10.0543	0	-13.8074	5.0390	4.3216	-6.2354	5.0267	7.0220	-4.7420
3	10.0542	0	-20.8516	5.0366	4.3232	-9.7692	5.0269	7.0217	-7.3973
4	10.0542	0	-27.8958	5.0358	4.3239	-13.3031	5.0269	7.0215	-10.0526
5	10.0541	0	-34.9400	5.0354	4.3244	-16.8370	5.0269	7.0214	-12.7079
10	10.0541	0	-70.1612	5.0347	4.3251	-34.5067	5.0270	7.0212	-25.9845
15	10.0540	0	-105.3823	5.0345	4.3255	-52.1764	5.0270	7.0211	-39.2611
20	10.0540	0	-140.6034	5.0344	4.3255	-69.8460	5.0270	7.0211	-52.5377
25	10.0540	0	-175.8245	5.0344	4.3256	-87.5157	5.0270	7.0210	-65.8143
50	10.0540	0	-351.9301	5.0343	4.3257	-175.8641	5.0270	7.0210	-132.1973
100	10.0540	0	-704.1413	5.0342	4.3258	-352.5610	5.0270	7.0210	-274.9634

