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Modeling Interactions of Iron Atoms Encapsulated in Nanotubes

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Abstract: The behavior and electronic structure of the carbon and boron nitride nanotubes that interact with the iron atom were studied using the Lennard–Jones potential and hybrid discrete-continuum approach. The iron-filled nanotubes were explored by means of classical applied mathematics in order to develop an understanding of the underlying mechanisms of the encapsulation of metal atoms inside nanotubes. Herein, we examined the suction energy and then the equilibrium offset positions of the iron atoms inside zigzag and armchair single-walled nanotubes, to obtain the optimal radii of the tubes and encapsulate the iron atom by determining the radii that provide the minimum interaction energies. Our observations indicate that the encapsulation behaviour depends on the radii of the nanotubes, and we predict that it is less likely for an iron atom to be enclosed inside the nanotubes when the value of the tube radius is less than \( \approx 2.5 \text{ Å} \). The optimal nanotube necessary to fully enclose the iron atom has a radius of \( \approx 4.2 \text{ Å} \) for both carbon and boron nitride nanotubes, which approximately corresponds to the interaction energies of \(-1.8 \text{ kcal/mol}\). In its entirety, this work presents an approach that might further the understanding of the encapsulation of metal atoms inside nanotubes.

Keywords: iron atom; nanotube; mathematical modeling; hybrid discrete-continuum; Lennard–Jones potential

1. Introduction

Carbon nanotube (CNT) and boron nitride nanotube (BNNT) have a one-dimensional structure, and they share the same honeycomb lattice geometry. Nanotubes can form a hollow cylinder, configured by rolling up a sheet in a cylindrical shape \([1,2]\). They may be uniquely described by a chiral vector in terms of their two integers \((u, v)\). The tubes with \(v = 0\) are referred to as the zigzag single-walled nanotubes, and those with \(u = v\) are called armchair single-walled nanotubes. The nanotube radii can be determined from \(c = a \sqrt{3(u^2 + v^2 + uv)} / 2\pi\), where \(a\) is the bond length in the C–C bonds in graphene sheet \((a = 1.42 \text{ Å})\), and B–N bonds in hexagonal boron nitride sheet \((a = 1.45 \text{ Å})\) \([3,4]\). Recently, semiconductor nanotubes (NTs) have elicited increasing interest due to their exceptional properties, such as their large surface area and superior electrical conductivity, and they have several potential applications in nanoengineering, for example, optoelectronic devices in the ultraviolet \([5–7]\). The mechanical behavior of metals filled nanotubes and their properties have been analyzed and have been the focus of extensive research for applied scientists, due to their applicability as very-large-scale integration interconnects, and their fundamental and technological interest \([8–12]\). In particular, the potential of iron (Fe) atom-filled nanotubes can provide a great performance as a nanoscale soldering device, which is the subject of special interest, and the encapsulation of Fe inside NTs might assist in preventing degeneration of the magnetic and electronic properties due to the weak interaction with the NTs \([5,12,13]\). Some theoretical studies showed that the interactions of the encapsulation of Co and Ni atoms inside NTs are weak, and have no effect on their electromagnetic properties, Fe atoms encapsulated into NTs may also have these advantages and they have the most stable phase structure into the NTs, as it an important electromagnetic material \([5,14]\). The encapsulation of the Fe inside carbon and boron...
nitride nanotubes has been investigated experimentally and simulated theoretically in a number of studies. Wang et al. used the first-principles with the density functional theory (DFT) calculations to investigate encapsulation of the Fe atoms inside \((u, 0)\) zigzag BNNTs \((8 \leq u \leq 15)\); they found that the \((8, 0)\) is the only tube formed endothermically. The other tubes are formed exothermically, and the optimal BNNT to wrap the Fe nanowire is a \((13, 0)\) tube, with the lowest formation energy of \(-1.848\) eV \([13]\). Xie et al. studied the magnetic properties and electronic structures of Fe nanowires into a zigzag \((12, 0)\) BNNTs using first-principle calculations, and they showed that the Fe nanowires might be endothermically inserted inside zigzag \((12, 0)\) BNNT \([14]\). Moreover, Zhang et al. applied DFT methods to enhance the sensitivity of boron nitride nanotubes to nitrogen dioxide using the encapsulation of a Fe atom into \((10, 0)\) BNNT \([5]\), and this indicated that the encapsulation of the single Fe atom inside is energetically favorable. The electronic and magnetic properties of a chain of iron atoms have been investigated inside armchair \((u, u)\) BNNTs \((4 \leq u \leq 6)\) using DFT by Fathalian et al.; their results suggested that the \((6, 6)\) BNNT is the optimal tube for use in the magnetic nanodevices \([15]\). Koi et al. studied the Fe nanowire encapsulated in BNNTs; their results showed that the Fe nanowires were parallel to the BN nanotube axis \([16]\). In addition, by using molecular dynamics (MD) simulations, Munizaga et al. simulated the formation of CNT–metal contacts by iron-filled CNTs; they observed that this constitutes a possible tool to repair CNT break-ups in future CNT-based nanoelectronic devices \([6]\). Horga et al. performed DFT calculations of the electronic structure of the electronic structure of the Fe12 inside \((11, 0)\) and \((10, 0)\) CNTs; their results showed that the encapsulation of Fe atoms inside CNTs is energetically favorable, and because the edges are very active, the atoms are preferentially located near the nanotube edges compared to places deeper inside the tube \([12]\). Munizaga et al. investigated the deformation of Fe atom-filled CNT using classical MD; they observed that the deformation process of the Fe inside CNTs is influenced by temperature and the direction of Fe atoms along the tube axis \([8]\). Wang et al. examined the electronic properties of Fe atoms encapsulated inside armchair \((u, u)\) CNTs \((2 \leq u \leq 6)\) by using first-principles within DFT; they showed that the \((6, 6)\) CNT is the ideal tube to wrap a Fe atom, especially on the tube center axis \([17]\). The purpose of this work is the application of fundamental mechanical principles and applied mathematical modeling to obtain the behavior and the electronic structure of the encapsulation of the iron atoms inside carbon and boron nitride nanotubes. The issue of iron-filled nanotubes is fundamental, particularly for applications in magnetic data storage, magnetic resonance imaging and electromagnetic wave-absorbing. In the present work, we carried out the Lennard–Jones potential and hybrid discrete-continuum approach calculations to determine the interactions of an iron atom with zigzag and armchair single-walled CNTs and BNNTs.

2. Computational Details

We performed calculations of the interactions between the iron atom with nanotubes using the van der Waals correlation functional. We used the Lennard–Jones potential to model the van der Waals interaction energy between two atoms at a distance of \(l\) apart, which is given by

\[
P(l) = -\frac{A}{l^6} + \frac{B}{l^{12}},
\]

where \(A\) and \(B\) are the attractive and repulsive constants, respectively; they can be calculated from the empirical combining rules \(\sigma_{mn} = \sigma_m + \sigma_n / 2\) and \(\epsilon_{mn} = \sqrt{\epsilon_m \epsilon_n}\), where \(A = 4 \sigma^6\) and \(B = 4 \sigma^{12}\), and are listed in Table 1. The values of the van der Waals diameters \(\sigma\) and well-depths \(\epsilon\) for C, B, N, and Fe atoms are taken from Rappi et al. \([18]\).
Herein, we use the hybrid discrete-continuum approach to derive the interactions of the Fe atom with nanotubes, and this is given by

\[ E = \sum_j h \int P(l_j) dS, \]

(1)

where \( P(l_j) \) denotes the potential function, \( h \) is the surface density of atoms on the molecule surface, and \( l \) is the distance from the surface of the molecule to the atom \( j \), which is modeled as a summation over each of its atoms and a typical surface element \( dS \) on the continuously modeled molecule. In this paper, the atomic surface densities of the molecules (carbon and boron nitride nanotubes) are given as \( h_g = 0.3821 \text{ Å}^{-2} \) and \( h_{bn} = 0.3682 \text{ Å}^{-2} \), respectively [19]. First, by assuming that the iron atom is placed on the z-axis and near the open end of a semi-infinite tube, we study the suction energy of the atom entering the nanotube, as shown in Figure 1a. In addition, we calculate the equilibrium offset positions of the iron atom, which are assumed to be located in the nanotube with reference to the cross section of the nanotubes, as shown in Figure 1b.

Figure 1. Schematic illustration of a Fe atom interacting with nanotube: (a) entering a nanotube and (b) inside a nanotube.

Table 1. Approximate values of the attractive and repulsive constants.

| Interaction | A (Å⁶ kcal/mol) | B (Å¹² kcal/mol) |
|-------------|-----------------|-----------------|
| C-Fe        | 230.724747      | 360,215,204700  |
| BN-Fe       | 242.024836      | 384,731,550600  |

2.1. Suction Energy of Fe Atom Entering Nanotube

Here, we determine the interaction energy of an iron atom as it enters CNT and BNNT; the tubes are assumed to be in a semi-infinite cylinder. With reference to the Cartesian coordinate system \((x, y, z)\), the tube of radius \( c \) has the coordinates \((c \cos \eta, c \sin \eta, z)\), where \(-\pi \leq \eta \leq \pi\) and \(-\infty < z < \infty\), and the coordinates of the Fe atom are given as \((0, 0, K)\). Thus, the distance \( l \) between the atom and a typical point on the tube is given by

\[ l^2 = c^2 + (z - K)^2, \]

and the total interaction of the Fe atom entering the tube is given by

\[ E = c h_t \int_{-\pi}^{\pi} \int_0^\infty \left( -\frac{A}{l^6} + \frac{B}{l^{12}} \right) dz d\eta = h_t (-AG_3 + BG_6), \]

(2)

where \( t \in \{ g, bn \} \). We start to calculate the integral \( G_n \) \((n = 3, 6)\) as follows:

\[ G_n = c \int_{-\pi}^{\pi} \int_0^\infty \frac{1}{[c^2 + (z - K)^2]^{n/2}} dz d\eta = 2\pi c \int_0^\infty \frac{1}{[a^2 + (z - Z)^2]^{n/2}} dz. \]
Now, we evaluate this integral over $z$ by using the substitution $r = z - K$, and we obtain

$$G_n = 2\pi \int_{-K}^{\infty} \frac{1}{(c^2 + r^2)\pi} dr.$$ 

Making the change in variable $r = c \tan \phi$, the integral $G_n$ becomes

$$G_n = 2\pi c^{1-2n} \int_{\tan^{-1}(-K/c)}^{\pi/2} \sec^{2-2n} \phi \, d\phi = 2\pi c^{1-2n} \int_{\tan^{-1}(-K/c)}^{\pi/2} \cos^{2n-2} \phi \, d\phi.$$ 

To evaluate the above integral, we use the formula from in [20] ($f$ 2.512(2)); therefore, for the values of $n = 3$ and 6, the integral $G_n$ can be expanded as

$$G_3 = \pi c^{-5} \left[ \frac{3\pi}{8} + \frac{3}{4} \tan^{-1} \left( \frac{K}{c} \right) + \frac{3Kc}{4(c^2 + K^2)} + \frac{Kc^3}{2(c^2 + K^2)^2} \right],$$

and

$$G_6 = \pi c^{-11} \left[ \frac{9\pi}{3840} + \frac{3}{640} \tan^{-1} \left( \frac{K}{c} \right) + \frac{Kc^9}{5(c^2 + K^2)^5} + \frac{9Kc^7}{40(c^2 + K^2)^4} + \frac{7Kc^5}{60(c^2 + K^2)^3} + \frac{Kc^3}{16(c^2 + K^2)^2} + \frac{3Kc}{80(c^2 + K^2)} \right],$$

and these expressions complete Equation (2).

### 2.2. An Equilibrium Offset Position of Fe Atom Inside Nanotube

With reference to Figure 1b, which shows that the Fe atom is assumed to be located inside the tube, we determine the interaction energy of the equilibrium offset position for the Fe atom into the CNT and BNNT. To calculate the optimal position of an iron atom inside the tube, we determine the interaction energy of the equilibrium offset position for

$$E = c h_1 \int_{-\pi}^{\pi} \int_{-\infty}^{\infty} \left( -\frac{A}{r^2} + \frac{B}{r^2} \right) dzd\eta = c h_1 (-A J_3 + B J_6).$$

To evaluate these integrals, we calculate the integral $J_n$ ($n = 3, 6$) as follows:

$$J_n = c \int_{-\pi}^{\pi} \int_{-\infty}^{\infty} \frac{1}{[(c - \omega)^2 + 4c\omega \sin^2(\eta/2) + z^2]^{n/2}} dzd\eta.$$ 

By letting $\delta^2 = (c - \omega)^2 + 4c\omega \sin^2(\eta/2)$ and making the change in variable $z = \delta \tan \psi$, which gives

$$J_n = c \int_{-\pi/2}^{\pi/2} \cos^{2n-2} \phi \, d\phi \int_{-\pi}^{\pi} \frac{1}{\delta^{2n-1}} \, d\eta.$$ 

$$J_n = c B(n - 1/2, 1/2) \int_{-\pi}^{\pi} \frac{1}{\delta^{2n-1}} \, d\eta,$$
where $B(p, q)$ denotes the beta function. Allowing $\lambda = \sin^2(\eta/2)$ yields

$$J_n = \frac{2c}{(c-\delta)^{2n-1}} B(n-1/2, 1/2)$$

$$\times \int_0^1 \lambda^{-1/2} (1 - \lambda)^{-1/2} \left[ 1 + 4c\omega/(c - \omega)^2 \right]^{1/2-n} d\lambda.$$ 

We might solve this integral using the Euler form

$$J_n = \frac{2\pi c}{(c-\delta)^{2n-1}} B(n-1/2, 1/2)$$

$$\times F\left(n-1/2, 1/2; 1/2; 1; 4c\omega/(c - \omega)^2\right),$$

where $F(a^*, b^*; c^*, z^*)$ is the usual hypergeometric function, and by using the quadratic transformation from in [21], $J_n$ becomes

$$J_n = \frac{2\pi c}{(c-\delta)^{2n-2}} B(n-1/2, 1/2)$$

$$\times F\left(n-1/2, n-1/2; 1/2; 1; \omega^2/c^2\right).$$

3. Numerical Results and Discussion

In this section, using the algebraic computer package MAPLE with the aforementioned constant values, we describe the interaction energies of the iron atom with CNTs and BNNTs. First, for various CNT and BNNT sizes, we determine the interaction energies of the iron atom entering these tubes. Then, we calculate the equilibrium offset of the Fe atom inside the tubes to obtain the preferred positions of the iron atom in the tubes.

3.1. Suction Energy

Here, the results outline whether the iron atom would be accepted into the interior of zigzag and armchair CNTs and BNNTs with different sizes. We calculate the total interaction energy between the Fe atom entering the tubes using Equation (2). Figure 2 shows that the Fe atom is accepted for all nanotubes with various radii ($2.7 \leq c \leq 4.5$), where the interaction energies are less in the tube (positive $K$) than outside the tube (negative $K$). For the armchair $(3, 3) (c \approx 2.1 \text{ Å})$, the Fe atom is prevented from entering both CNT and BNNT, as the energy in the positive $K$ direction is bigger than the negative $K$ direction, which is outside the tube. It can be seen from the plot that in this case the tube would not accept the iron atom from the rest because the suction energy is not sufficient to overcome the barrier energy at the tube opening. Thus, it is possible for the interaction energy $E$ to exhibit two peaks (positive in the range $(K_1, K_2)$ and negative in the range $(K_2, \infty)$), as shown in Figure 2. We comment that when the curve of the energy $E$ crosses the horizontal axis at $K_2$, it becomes energetically favorable for the Fe atom to be inside the tube; thus, some additional energies are required to encapsulate the iron atom into the $(3, 3)$ nanotube or tubes with smaller radii. In addition, by minimizing the energy, the results indicate that the Fe atom might be allowed to enter with a radius bigger than $c \approx 2.5$, such that $(7, 0)$ zigzag nanotube.
Herein, the preferred positions of a Fe atom inside armchair \((u, u)\) carbon and boron nitride nanotubes \(5 \leq u \leq 8\) are determined by an evaluation of Equation (3). In Figure 3, we plot the relationship between the interaction energies \(E\) and the equilibrium distance \(\omega\) for each tube; the results show that the lowest energy for the Fe interacted inside both CNTs and BNNTs is \((6, 6)\), where the Fe lies on the tube axis, which is the same location as for the \((5, 5)\) tube. In addition, in the cases of \((7, 7)\) and \((8, 8)\) tubes, we obtain \(\omega = 1.26\ \text{Å}\) and \(\omega = 2.02\ \text{Å}\), respectively. These results are equivalent to the distance between the tube wall and the Fe atom of approximately 3.5 Å, and 3.4 Å, respectively, so we can deduce that where the minimum energy is obtained, the location of the Fe atom tends to be closer to wall of the tube as the radius of the tube becomes larger. By summarizing our results, we may deduce that the optimal radius of both BNNTs and CNTs for encapsulating the Fe atom is \((6, 6)\) \((c \approx 4.1\ \text{Å})\), which provides the lowest interaction energies. Our results are in excellent agreement with those given in [12,15,17].
Figure 3. Interaction energies of an offset Fe atom inside BNNTs and CNTs with respect to the distance $\omega$.

4. Summary

The numerical results of this study are described using the algebraic computer package MAPLE to determine the preferred radii of the CNTs and BNNTs for encapsulating the Fe atoms. In the modeling, we first studied whether the entrance of the Fe atom is accepted, which is assumed to be located outside the tube on the axis, and near an open end of a semi-infinite. The results showed that the encapsulation of the Fe atom into CNTs and BNNTs might occur for nanotubes larger than 2.5 Å. Moreover, we observed that the Fe atom confronted a large energy barrier at the (3, 3) tube opening, consequently, for the Fe atom to be encapsulated into the BNNTs and CNTs with radii in the range $(2.1 \leq c \leq 2.7)$, some additional energy is required. In addition, by assuming that the Fe atom is already accepted inside the tubes, we found the minimum energy equilibrium positions of the offset Fe atom tend to be closer to tube wall as the radius of the tube increases. The observations are compared with other works and are in excellent agreement with them [12,15,17]. Our model and calculations are a powerful tool for quickly evaluating the encapsulation of the iron atoms inside nanotubes, and thus might assist in studying and developing the search for the molecular storage of metal atoms inside nanotubes.

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**Data Availability Statement:** The data that support the findings of this study including the MAPLE package, are available from the corresponding author upon reasonable request.

**Conflicts of Interest:** The author declares that there is no conflict of interest.

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