Restricted three body problems at the nanoscale

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Abstract

In this paper, we investigate some of the classical restricted three body problems at the nanoscale, such as the circular planar restricted problem for three C\textsubscript{60} fullerenes, and a carbon atom and two C\textsubscript{60} fullerenes. We model the van der Waals forces between the fullerenes by the Lennard-Jones potential. In particular, the pairwise potential energies between the carbon atoms on the fullerenes are approximated by the continuous approach, so that the total molecular energy between two fullerenes can be determined analytically. Since we assume that such interactions between the molecules occur at sufficiently large distance, the classical three body problems analysis is legitimate to determine the collective angular velocity of the two and three C\textsubscript{60} fullerenes at the nanoscale. We find that the maximum angular frequency of the two and three fullerenes systems reach the terahertz range and we determine the stationary points and the points which have maximum velocity for the carbon atom for the carbon atom and the two fullerenes system.

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1 Introduction

In 1966, Jones [15] suggested in the New Scientist under the name of Daedalus that the hollow all-carbon cage molecules were possible. However, it was not until two decades later that Kroto [18] experimentally discovered C\textsubscript{60} and C\textsubscript{70} fullerenes by analyzing the resulting mass spectrometry. The dominant peak represents C\textsubscript{60} fullerene followed by a second peak representing C\textsubscript{70} fullerene. In particular, C\textsubscript{60} fullerene has I\textsubscript{h} symmetry, which has a spheroidal shape.

Various nanoscale gigahertz oscillators have been proposed in the recent literature including the oscillation of a C\textsubscript{60} fullerene or a closed carbon nanotube inside an open ended carbon nanotube. Such oscillators have also been confirmed by experiments on multi-walled carbon nanotubes. Cumings and Zettl [8] remove the cap from one end of the outer shell and attach a moveable nanomanipulator to the core of a multi-walled

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nanotube through a high-resolution transmission electron microscope. They observe that the extruded core, after release, quickly and fully retracts inside the outer shell due to the restoring force resulting from the van der Waals interactions acting on the extruded core. This experimental result lead to the molecular dynamics studies of Zheng and Jiang [29] who show that the oscillating of the inner shell between the open ends of the outer shell of a multi-walled carbon nanotube generates a gigahertz frequency. Molecular dynamics simulations on gigahertz oscillators have also been undertaken by Legoas et al. [19] and Rivera et al. [24, 25]. In terms of mathematical modelling, Baowan and Hill [1] investigate the force distribution for a double-walled carbon nanotube oscillator by adopting the continuous approach for the Lennard-Jones potential together with Newton’s second law, assuming a frictionless environment, to investigate the associated mechanics. They obtain an analytical expression for the interaction force and their model also predicts the gigahertz oscillatory behavior for the double-walled carbon nanotube oscillators.

Based on the molecular dynamics simulations of various nano gigahertz oscillators, Cox et al. [4, 5] develop an accurate mathematical model employing fundamental mechanical principles and classical applied mathematical techniques to determine an acceptance condition and the suction energies of a C_{60} fullerene entering a nanotube. They then determine the minimum radius of a carbon nanotube for which the C_{60} fullerene will be accepted from rest and the maximum total kinetic energy once the C_{60} molecule is sucked inside the nanotube by the van der Waals forces. In addition, Cox et al. [4, 5] show that the gigahertz oscillatory behavior arises from the two peak-like forces operating at the nanotube’s open ends. The analytical model of Cox et al. [4, 5] is also extended to examine some more complicated structures of the gigahertz oscillators, including the nanotube bundle oscillators, for which a single nanotube or a C_{60} fullerene oscillates inside the bundle [6, 7]. For other types of nanoscale oscillators, Hilder and Hill [13, 14] find that the gigahertz frequencies can also be obtained from a sector of a nanotube orbiting inside a carbon nanotorus and an atom and a C_{60} fullerene orbiting inside a nanotorus.

Chan et al. [2] have investigated various two body problem, namely fullerene-fullerene, fullerene-carbon nanotube at the nanoscale. In this paper, we investigate some of the classical restricted three body problems at the nanoscale. In particular, we consider three C_{60} fullerenes interacting with each other and initially located at the vertices of an equilateral triangle. The van der Waals interaction energy is modelled using the 6-12 Lennard-Jones potential and the continuous approach for which we assume a uniform distribution of carbon atoms on the surfaces of the carbon nanotube and the fullerenes. We determine the motion of the interacting molecules as they move relatively with respect to each other under the influence of their mutual centripetal force. For the case under consideration, the circular orbiting frequencies reach the gigahertz range. We comment that this paper ignores any thermal fluctuations arising from the environment.

In section 2, we develop the mathematical model for the restricted three body problems at the nanoscale. In section 3, we discuss the restricted problem for the three fullerenes system. In section 4, we investigate the capture of a carbon atom by two fullerenes and we present some conclusions in the final section.

2 Theory

In this section, we derive the theoretical basis for the study of the three body problems, namely that of three C_{60} fullerenes at the nanoscale (see Fig. 1 for details). Since we only
consider the residual molecular interactions between molecules, it is valid to examine the classical three body problems to investigate the same problem at the nanoscale \[3, 10, 12, 21, 22, 23, 27\]. We model the residual molecular interactions by van der Waals forces, and in particular the Lennard-Jones potential \[16\], which is given by

$$V(\rho) = 4\varepsilon \left( \frac{\sigma}{\rho} \right)^{12} - \left( \frac{\sigma}{\rho} \right)^{6} = -\frac{A}{\rho^6} + \frac{B}{\rho^{12}},$$

(1)

where $\rho$, $\varepsilon$ and $\sigma$ denote the distance between two arbitrary carbon atoms, the potential well depth of two carbon atoms and the parameter that is determined by the equilibrium distance respectively. In addition, $A$ and $B$ denote the attractive and the repulsive constants respectively. We assume that the carbon atoms are evenly distributed over the surfaces of the molecules such that the pairwise molecular energy between two fullerenes, i.e. $\sum_k \sum_j V(\rho_{kj})$ can be approximated by the continuous approach, which has been previously used by Cox et al. \[4, 5\]. That is,

$$V(r) = n_f^2 \int_{S_1} \int_{S_2} \left( -\frac{A}{\rho^6} + \frac{B}{\rho^{12}} \right) dS_2 dS_1,$$

(2)

where $n_f$, $\rho$, $dS_1$ and $dS_2$ denote the atomic number density, the distance between the centers of two fullerenes, the surface area element of the two fullerenes respectively. Following the same calculation as that derived by Cox et al.\[4, 5\], we obtain

$$V(r) = -Q_6(r) + Q_{12}(r),$$

(3)
where $Q_n$ is defined by

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

where $a$, $C_6$ and $C_{12}$ denote the radius of the C$_{60}$ fullerene, A and B respectively. Given that, the mutual force, $F(r)$ between two fullerenes can be determined by

$$F(r) = -\frac{dV(r)}{dr},$$

where $d/dr$ denotes the derivative in the $r$-direction.

According to Newton’s second law, we can determine the forces acting on a fullerene by the other two fullerenes as

$$m_k \ddot{r}_k = \sum_{j \neq k=1}^3 F(r_{kj}) \frac{r_j - r_k}{r_{kj}},$$

where $m_k$, $r_k$, $r_{kj}$ denote the total mass of the $k$-fullerene, the position vector of the $k$-fullerene and the relative displacement of any two fullerenes $k$ and $j$. We note that Eqs. (5) can not be generally solved analytically. If we make $\vec{r} = \vec{r}_2 - \vec{r}_1$ and we assume that $\vec{R}$ denotes the center of mass of $m_1$ and $m_2$ allocated at the origin of the coordinate system. We further define $\vec{\rho} = \vec{r}_3 - \vec{R} = M\mu^{-1}\vec{r}_3$, where $\mu = m_1 + m_2$. Under these assumptions, we can write these relative displacements as

$$\vec{r}_2 - \vec{r}_1 = \vec{r}, \quad \vec{r}_3 - \vec{r}_1 = \vec{\rho} + m_2\mu^{-1}\vec{r}, \quad \vec{r}_3 - \vec{r}_2 = \vec{\rho} - m_1\mu^{-1}\vec{r}.$$

The equations of motion in terms of the Jacobi coordinates, $\vec{r}$ and $\vec{\rho}$ are then given by

$$\ddot{\vec{r}} = -\frac{\mu}{m_1 m_2} \frac{F(r_{12})}{r_{12}} \vec{r} + \frac{1}{m_2} \frac{F(r_{23})}{r_{23}} (\vec{\rho} - m_1\mu^{-1}\vec{r}) - \frac{1}{m_1} \frac{F(r_{13})}{r_{13}} (\vec{\rho} + m_1\mu^{-1}\vec{r}),$$

$$\ddot{\vec{\rho}} = -\frac{M}{m_3 \mu^{-1}} \left[ \frac{F(r_{13})}{r_{13}} (\vec{\rho} + m_2\mu^{-1}\vec{r}) + \frac{F(r_{23})}{r_{23}} (\vec{\rho} - m_1\mu^{-1}\vec{r}) \right].$$

3 Three identical C$_{60}$ fullerenes

We now make the following three assumptions, referred to as the circular planar restricted problem, to determine the motion analytically:

1. The three fullerenes are moving uniformly in circular orbits
2. They are orbiting collectively in the same plane
3. Their angular velocities are the same

Upon assuming the three fullerenes are moving in plane, we can denote $(x_i, y_i, 0)$ by the coordinates of the $i$-fullerene. Then, the second derivative of $x_i$ and $y_i$ can be written as

$$\ddot{x}_k = m_k^{-1} \sum_{j \neq k} \frac{F(r_{jk})}{r_{jk}} (x_j - x_k), \quad \ddot{y}_k = m_k^{-1} \sum_{j \neq k} \frac{F(r_{jk})}{r_{jk}} (y_j - y_k).$$
We now assume that the three fullerenes have the same (collective) angular velocity \( \omega \), and they are moving uniformly in a circle, such that we can write down the rotating coordinate system

\[
x_k = \xi_k \cos \omega t - \eta_k \sin \omega t.
\]  

(9)

We note that \( y_k \) can be defined in a similar way as \( x_k \). We then substitute Eq. (9) into Eqs. (8) to obtain

\[
\ddot{\xi}_k - 2\omega \dot{\eta}_k - \omega^2 \xi_k = m_k^{-1} \sum_{j \neq k} \frac{F(r_{jk})}{r_{jk}} (\xi_j - \xi_k),
\]

\[
\ddot{\eta}_k + 2\omega \dot{\xi}_k - \omega^2 \eta_k = m_k^{-1} \sum_{j \neq k} \frac{F(r_{jk})}{r_{jk}} (\eta_j - \eta_k).
\]

(10)

We can then recast Eq. (10) into a single equation by using \( z_k = \xi_k + i\eta_k \), where \( i \) denotes the usual imaginary unit \( \sqrt{-1} \), so that,

\[
\ddot{z}_k + i2\omega \dot{z}_k - \omega^2 z_k = m_k^{-1} \sum_{j \neq k} \frac{F(r_{jk})}{r_{jk}} (z_j - z_k).
\]

(11)

Since the fullerenes appear to be at rest in the rotating frame, we can simplify Eq. (11) to become

\[
-z_k = \lambda_k \sum_{j \neq i} \frac{F(r_{jk})}{r_{jk}} (z_j - z_k),
\]

(12)

where \( \lambda_k = 1/(m_k\omega^2) \). If we let \( \beta_j = \lambda_k (F(r_{m\ell})/r_{m\ell}) \), where \( m, \ell \neq j \), then Eq. (12) gives the following a system of three linear equations

\[
\begin{align*}
(1 - \beta_3 - \beta_2)z_1 + \beta_3 z_2 + \beta_2 z_3 &= 0, \\
\beta_2 z_1 + \beta_1 z_2 + (1 - \beta_2 - \beta_1)z_3 &= 0, \\
m_1 z_1 + m_2 z_2 + m_3 z_3 &= 0.
\end{align*}
\]

(13)

For the three fullerenes moving in the same plane, geometrically, two possibilities arise, namely; the three fullerenes are not on the same straight line or they lie on the same straight line. For the first scenario, the coefficients of \( z_j \) of Eqs. (13)\_1, (13)\_2 and (13)\_3 must be proportional to each other. Given that the case, we automatically have \( m_1 = m_2 = m_3 = m \), which corresponds to the case of the three identical fullerenes we study in this paper. In addition, we require \( \beta_1 = \beta_2 = \beta_3 = 1/3 \) resulting to the three identical fullerenes allocated at the vertices of an equilateral triangle, i.e., \( r_{kj} = r \). We have

\[
\frac{1}{m_0^2} \frac{F(r)}{r} = \frac{1}{3}, \quad \omega = \sqrt{\frac{3F(r)}{mr}}.
\]

(14)

On the other hand, we can directly obtain the same result by investigating the equation of motion given by Eq. (7)\_1. Upon assuming \( F(r_{12}) = F(r_{12}) = F(r_{13}) = F(r) \) and \( m_1 = m_2 = m_3 = m \), we deduce
\[
\vec{r} = -\frac{2m}{m^2} \frac{F(r)}{r} \vec{r} + \frac{1}{m} \frac{F(r)}{r} \left( r + \frac{m}{2m} - \frac{m}{2m} \right) \vec{r} - \frac{1}{m} \frac{F(r)}{r} \left( r + \frac{m}{2m} + \frac{m}{2m} \right) \vec{r} - \frac{3F(r)}{mr} \vec{r},
\]

which represents a simple harmonic motion with angular velocity \( \omega \), given exactly by Eq. (14).

Radius of \( C_{60} \) \( a = 3.55 \) Å
Carbon-carbon bond length \( \sigma = 1.421 \) Å
Mean surface density of \( C_{60} \) \( n_f = 0.3789 \) Å\(^{-2}\)
Mass of a single carbon atom \( m_c = 1.993 \times 10^{-26} \) kg
Mass of a single \( C_{60} \) fullerene \( m = 1.196 \times 10^{-24} \) kg
Attractive constant \( A = 17.4 \) eV× Å\(^6\)
Repulsive constant \( B = 29 \times 10^3 \) eV× Å\(^{12}\)

| Table 1: Numerical values of constants used in the model |
|--------------------------------------------------------|
| Radius of \( C_{60} \) | \( a = 3.55 \) Å |
| Carbon-carbon bond length | \( \sigma = 1.421 \) Å |
| Mean surface density of \( C_{60} \) | \( n_f = 0.3789 \) Å\(^{-2}\) |
| Mass of a single carbon atom | \( m_c = 1.993 \times 10^{-26} \) kg |
| Mass of a single \( C_{60} \) fullerene | \( m = 1.196 \times 10^{-24} \) kg |
| Attractive constant | \( A = 17.4 \) eV× Å\(^6\) |
| Repulsive constant | \( B = 29 \times 10^3 \) eV× Å\(^{12}\) |

Here, we carry out the theoretical results derived above. All the necessary constants used in this paper can be found in Table. We note that while the molecular interactions are attractive at long range due to the van der Waals forces, they are repulsive at short range as the result of overlapping electron orbitals. The total pairwise molecular interactions between two \( C_{60} \) fullerenes, which is approximated by the continuous approach, termed the total molecular energy, is shown in Eq. (2) and is plotted in Fig. 2. We find that the most stable configuration for two \( C_{60} \) fullerenes are at 9.8 Å with a much higher energy well depth in comparison to that of the two carbon atoms that is 0.28 eV. Given the total molecular energy, we can determine the total molecular forces between two fullerenes by differentiating, and the force \( F(r) \) given in Eq. (4). Here, we define positive forces to be attractive forces and vice versa. Since the centripetal forces between three fullerenes are provided by the attractive van der Waals forces between molecules only, upon using Eq. (14), we can predict the collective angular velocity \( \omega \), which is plotted in Fig. 4. Since only attractive van der Waals forces contribute to the orbiting behavior, no orbiting phenomenon can be observed for \( r < 10 \) Å, where the van der Waals forces become repulsive. Given the orbiting regimes, the maximum angular velocity is found to occur at 0.12 THz, which is substantially higher than all gigahertz nanoscillators proposed in the existing literature. As such the three \( C_{60} \) fullerenes might be used as a possible ultra high frequency nano-device.

### 4 Capture of a carbon atom by two fullerenes

In this section, we investigate the motion of a carbon atom under the influence of the potential energy from two \( C_{60} \) fullerenes. We assume that the molecular interactions of the carbon atom is so small that it cannot influence the dynamics of the two \( C_{60} \) fullerenes. From which, the Jacob coordinates, i.e. Eq. (7) reduce to
Figure 2: Total molecular energy $V(r)$ of two C$_{60}$ fullerenes

Figure 3: Total molecular force $F(r)$ acting on one fullerene
Maximum angular velocity 0.12 THz at approximately $r = 10.5$ Å.

$$\ddot{r} = -\frac{2}{m} \frac{F(r_{12})}{r_{12}} \dot{r},$$
$$\ddot{\rho} = -\frac{1}{m_c} \left[ \frac{F(\rho_1)}{\rho_1} (\dot{\rho} + \frac{1}{2} \dot{r}) + \frac{F(\rho_2)}{\rho_2} (\dot{\rho} - \frac{1}{2} \dot{r}) \right],$$
\begin{equation}
(16)
\end{equation}

where $m$, $m_c$, $\rho_1$ and $\rho_2$ denote the mass of the C$_{60}$ molecule, the mass of the carbon atom, the distance between the atom and the first fullerene and the distance between the atom and the second fullerene respectively. Eq. (16) constitutes the usual two body problem, which has the usual physical interpretation. If we assume the same scenario as in Section 2 but for the two fullerenes, that is the two fullerenes move collectively in a circular orbit of radius $R$ in a plane and with the same angular velocity $\omega$, Eq. (16) becomes simple harmonic motion with angular velocity equal to $\sqrt{2F(r)/mr}$ for a fixed $r$ and this is plotted in Fig. 5. In the later part of this section, we denote $R = 10.5$ Å to be the circular radii, where the collective angular velocity of the two body systems attains maximum value.

Similarly, we assume that the center of mass of the two fullerenes are located at the center of a cartesian coordinate system and we introduce a rotating frame $(\xi, \eta)$ with the same angular rate as the collective angular velocity $\omega$ so that the two fullerenes remain stationary with respect to the rotating frame. The position of the two fullerenes can then be determined by solving $\xi_1 + \xi_2 = 0$ and $\xi_2 - \xi_1 = R$ simultaneously and the situation is shown schematically in Fig. 5. Since the dynamics of the two body systems is determined, the only problem now left is the motion of the carbon atom about the center of mass, which has to be solved from Eq. (16)$_2$.

Now making the same circular planar assumptions as above, the third component, i.e. the equations of motion of the carbon atom, i.e. Eqs. (10) becomes
Figure 5: Collective angular velocity $\omega$ versus $r$, where the maximum angular velocity occurs at 0.1 THz around $r = 10.5$ Å

Figure 6: Capture of carbon atom by two identical C$_{60}$ fullerene
\[\ddot{\xi} - 2\omega \dot{\eta} - \omega^2 \xi = \frac{1}{m_c} \left\{ \frac{F(\rho_1)}{\rho_1} (\xi_1 - \xi_3) + \frac{F(\rho_2)}{\rho_2} (\xi_2 - \xi_3) \right\},\]

\[\ddot{\eta} + 2\omega \dot{\xi} - \omega^2 \eta = \frac{1}{m_c} \left\{ \frac{F(\rho_1)}{\rho_1} (\eta_1 - \eta_3) + \frac{F(\rho_2)}{\rho_1} (\eta_2 - \eta_3) \right\},\]  

(17)

where \(m_c, \xi, \eta, \rho_1 = \sqrt{(\xi + R/2)^2 + \eta^2}\) and \(\rho_2 = \sqrt{(\xi - R/2)^2 + \eta^2}\) denote the mass of the carbon atom, \(\xi_3, \eta_3, r_{13}\) and \(r_{23}\) respectively. For simplicity, we only work on Eq. (17)\textsubscript{1} and Eq. (17)\textsubscript{2} can be determined in a very similar way. Starting from Eq. (17)\textsubscript{1} we may deduce

\[\ddot{\xi} - 2\omega \dot{\eta} - \omega^2 \xi = \frac{1}{2m_c} \left\{ \frac{F(\rho_1)}{\rho_1} \left(\frac{R}{2} - \xi\right) + \frac{F(\rho_2)}{\rho_2} \left(\frac{R}{2} - \xi\right) \right\} = \frac{1}{2m_c} \left\{ \frac{F(\rho_1)}{\rho_1} \partial \rho_1 \frac{\partial \Phi}{\partial \xi} + \frac{F(\rho_2)}{\rho_2} \partial \rho_2 \frac{\partial \Phi}{\partial \xi} \right\} = \frac{1}{2m_c} \left\{ \frac{\partial V(\rho)}{\partial \xi} \right\};\]  

(18)

where \(V(\rho) = V(\rho_1) + V(\rho_2)\). We can further simplify Eq. (18) to become

\[\ddot{\xi} - 2\omega \dot{\eta} = \frac{1}{2m_c} \frac{\partial \Phi}{\partial \xi},\]  

(19)

where \(\Phi = \Phi_1 + \Phi_2\), and \(\Phi_1 = V(\rho) + m_c \omega^2 \xi^2\) and \(\Phi_2 = V(\rho) + m_c \omega^2 \eta^2\). We therefore conclude that

\[\ddot{\xi} - 2\omega \dot{\eta} = \frac{1}{2m_c} \frac{\partial \Phi}{\partial \xi}, \quad \ddot{\eta} + 2\omega \dot{\xi} = \frac{1}{2m_c} \frac{\partial \Phi}{\partial \eta},\]  

(20)

and Eq. (20) can then be recast in the form

\[\frac{d}{dt} \left[ \frac{1}{2} m_c \left( \dot{\xi}^2 + \dot{\eta}^2 \right) \right] = \frac{\partial \Phi}{\partial t},\]  

(21)

and on integrating both sides, we obtain the energy integral

\[\frac{1}{2} m_c \left( \dot{\xi}^2 + \dot{\eta}^2 \right) = \Phi + C \geq 0,\]  

(22)

where \(C\) denotes the Jacobi constant. As in the classical three body problems, we are interested in determining where the carbon atom is stationary with respect to the rotating frame under the influence of the two fullerenes. In other words, we require the velocity in both the \(\xi\)-direction and the \(\eta\)-direction to be zero, i.e. \(\dot{\xi} = \dot{\eta} = 0\) and hence from Eq. (20), we have \(\partial \Phi / \partial \xi = \partial \Phi / \partial \eta = 0\).

The positions, for which \(\dot{\xi} = \dot{\eta} = 0\) is satisfied, are numerically obtained and shown in Fig. 7. We note that two minima are located inside the two fullerenes, which indicate
the encapsulation of the carbon atom inside the fullerenes and due to the symmetry of the system, all minimum occur at either $\xi = 0$ or $\eta = 0$. Since $C$ is an integral constant throughout the conservative system, we can obtain the value of $C$ from a particular case, the simplest one is $(\dot{\xi}, \dot{\eta}) = (0, 0)$ when $(\xi, \eta) = (0, 0)$. $C = -\Phi(\xi = 0, \eta = 0)$ is found to be $9 \times 10^{-18}$ J. Upon substituting $C$ back into Eq. (22), we can determine the velocity profile of the carbon atom and hence the maximum velocity of the carbon atom, which is also shown in Fig. 7.

5 Conclusion

We adopt the continuous approximation together with the Lennard-Jones potential to model the van der Waals between fullerenes. The total pairwise molecular interactions of the atoms between two fullerenes, using molecular dynamics simulations usually takes a substantial computational effort to implement. Here, such a total molecular energy is computed analytically and the corresponding total molecular force can be determined by differentiating. For the restricted three body problems derived in section 2, we can estimate the collective angular velocity of the two and three fullerenes systems. In particular, the maximum angular velocity reaches the terahertz range. In addition, we determine the stationary points and the points with maximum velocity of the carbon atom captured by two oscillating fullerenes.
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