Mechanics of spheroidal fullerenes and carbon nanotubes for drug and gene delivery

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Abstract
There is considerable interest in the mechanics of carbon nanostructures, such as carbon nanotubes and fullerenes, and the manner of their interactions at the internuclear level. Medical applications include the use of carbon nanotubes for targeted drug and gene delivery, for which issues relating to immune acceptance and containment of drug or genes are not properly understood. A spheroid is an ellipsoid with two equal axes and the general spheroidal shape includes a wide variety of possible molecular configurations such as spheres, capped cylindrical rubes and ellipsoids of revolution, and therefore the determination of interaction forces for this general shape may have many applications. Phenomena such as the suction of fullerenes into carbon nanotubes due to the van der Waals interatomic interactions and ultra-low friction of a molecule moving inside a carbon nanotube give rise to the possibility of constructing nanoscaled oscillators with frequencies in the gigahertz range. This paper models the mechanics of such a system by employing a six-tweye Lenard-Janes potential taken over two surfaces assumed to be composed of mean distribution of atoms over the two idealized surfaces of an open-ended semi-infinite circular cylinder and a spheroid. Following the methodology of previous work with spherical surfaces, the acceptance energy and suction energy for spheroidal molecules are given and the special case of spherical molecules is also reproduced to validate the method. The results for elliptical molecules are novel and cannot be validated experimentally at this stage, but the results for the special case of spherical molecules are given and shown to be in good agreement with published molecular dynamical simulations. Finally, a general numerical-analytical procedure is proposed to calculate the Lenard-Janes potential for any axially symmetric surface, and the prior results obtained for the spheroid are used to validate the procedure.

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MECHANICS OF SPHEROIDAL FULLERENES AND CARBON NANOTUBES FOR DRUG AND GENE DELIVERY

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Summary

There is considerable interest in the mechanics of carbon nanostructures, such as carbon nanotubes and fullerenes, and the manner of their interactions at the intermolecular level. Medical applications include the use of carbon nanotubes for targeted drug and gene delivery, for which issues relating to the acceptance and containment of drugs or genes are not properly understood. A spheroid is an ellipsoid with two equal axes and the general spheroidal shape includes a wide variety of possible molecular configurations such as spheres, capped cylindrical tubes and ellipsoids of revolution, and therefore the determination of the interaction forces for this general shape may have many applications. Phenomena such as the suction of fullerenes into carbon nanotubes due to the van der Waals interatomic interactions and ultra-low friction of a molecule moving inside a carbon nanotube give rise to the possibility of constructing nanoscaled oscillators with frequencies in the gigahertz range. This paper models the mechanics of such a system by employing a six-twelve Lennard-Jones potential taken over two surfaces assumed to be composed of mean distributions of atoms over the two idealized surfaces of an open-ended semi-infinite circular cylinder and a spheroid. Following the methodology of previous work with spherical surfaces, the acceptance energy and suction energy for spheroidal molecules are given and the special case of spherical molecules is also reproduced to validate the method. The results for elliptical molecules are novel and cannot be validated experimentally at this stage, but the results for the special case of spherical molecules are given and shown to be in good agreement with published molecular dynamical simulations. Finally, a general numerical-analytical procedure is proposed to calculate the Lennard-Jones potential for any axially symmetric surface, and the prior results obtained for the spheroid are used to validate the procedure.

1. Introduction

The discovery of stable families of carbon nanostructures, such as fullerenes (1) and carbon nanotubes (2), has generated considerable interest in the use of these structures in the construction of nanoscaled electromechanical devices. One area of research is that of nanoscaled oscillators, where one molecule moves inside another, and relative oscillatory motion is induced by van der Waals interactions between the two molecules. Cumings and Zettl (3) perform experiments on multiwalled carbon nanotubes and measure an ultra-low-frictional environment which appears not to
suffer from any wear or fatigue on the atomic scale. They also observe that if an inner-tube is extended from the outer-tube and then released, it is pulled back into the outer-tube by attractive van der Waals forces. Zheng and Jiang (4) predict that the period of oscillation could be quite short, leading to frequencies in the gigahertz range. These discoveries have led to the suggestion that nanoscaled devices could be constructed by making use of this phenomenon which would have applications as nano-antennae and optical filters. In addition, carbon nanotubes have attracted much attention for medical applications, especially their use as nancontainers for targeted drug and gene delivery. This is because nanotubes have accessible internal storage capacity via their open ends, which can be filled with chemical or biochemical structures, ranging from small molecules to proteins (5). However, the mechanisms of acceptance and containment of drugs or genes are not properly understood. The present analysis involving a general spheroidal shape might be used to model a wide variety of molecular configurations, which might provide considerable insight into the interaction mechanisms of drugs or genes in nancontainers.

The six-twelve Lennard–Jones potential is an inverse power relationship relating the distance between two atoms and the potential of van der Waals interactions between the two atoms. In terms of modelling the interaction of graphitic molecules, the approach is to smear out the atoms over some idealized surface and then perform surface integrations to calculate the total interaction between the molecules. The method has been employed successfully numerous times and the approach is adopted by Girifalco (6) to compute the interaction potential for pairs of fullerene C\textsubscript{60} molecules for which an analytical result can be obtained. The same approach is employed by Ruoff and Hickman (7) to investigate the van der Waals binding of spherical fullerenes to a flat plane of graphite.

Using the average atom density distributed over an idealized surface, the Lennard–Jones potential function may be evaluated over cylindrical surfaces. Henard et al. (8) use the model to develop an analytical result for the van der Waals interaction in nanotube bundles which they express in terms of hypergeometric functions. We observe that their potential function can also be expressed equivalently in terms of Legendre functions. Girifalco et al. (9) also use the Lennard–Jones potential to investigate the interaction per unit length for carbon nanotubes and determine the ball–tube interaction to predict the entrance potential for a spherical fullerene molecule near the open end of a nanotube and the interaction potential between a fullerene inside a carbon nanotube. Their models are expressed in integral form and their analysis is based on subsequent numerical integration. Hodak and Girifalco (10) examine further interactions, such as coaxial carbon nanotubes, spherical fullerenes and carbon nanotubes, as well as spheroidal fullerenes and carbon nanotubes. In their analysis the cylinders are assumed to be of infinite length and in particular for the spheroids, the integrations are performed numerically and are used to give optimum sizes of such arrangements. In the present paper we perform many of these integrations analytically. Zheng et al. (11) use the same model for multi-walled carbon nanotube configurations which they then use to determine the motion of an extruded inner-core. Their analysis is analytical and expresses the potential in terms of certain elliptical integrals which are not simplified further, in terms of expressing them by other special functions.

Others have modelled non-bonded interactions by pair-wise calculation of the interatomic potentials, using the approach of molecular dynamical simulations and performed for fullerene C\textsubscript{60} and nanotube interactions by Qian et al. (12) and Liu et al. (13). Rivera et al. (14) perform computer simulations of double-walled carbon nanotube oscillators. While at first sight the discrete atom model might seem to be a more realistic model, Girifalco et al. (9) point out that from the actual physical point of view both the discrete and continuum models make assumptions that are
physically inaccurate, and it could perhaps be argued that the continuum model is in fact closer to reality.

In (15) the present authors determine an analytical expression for both the interaction between a single carbon atom and a carbon nanotube, and between a spherical $C_{60}$ fullerene molecule and a carbon nanotube. The analysis also defines and calculates an acceptance condition for the fullerene to be sucked into the carbon nanotube as a function of the dimensions of the configuration and an analytical expression for the suction energy for the fullerene which is converted to kinetic energy of the fullerene. In (16) the present authors determine the equilibrium positions of spherical fullerenes inside carbon nanotubes which can be given in terms of either Jacobian elliptic functions or hypergeometric functions. In the present paper the authors extend this work to spheroidal fullerenes and calculate the acceptance and suction energy as defined in (15). A spheroid is an ellipsoid that has two equal axes and the spheroidal surface complicates the integration somewhat to the extent that the final azimuthal integration must be performed numerically. Alternative expressions for the potential are given at various steps involving Legendre functions, Appell's two variable hypergeometric functions and Jacobian elliptic functions, which is done to demonstrate the various paths that can be taken, and in all cases the different forms given are shown to be numerically equivalent.

In section 2 we derive the expression for the potential between a spheroid and a semi-infinite cylinder by analytical integration of the angular variables and the length variable along the length of the cylinder. The potential is first expressed in terms of Legendre polynomials, which when expanded involve elliptic integrals which are then expressed as finite expansions of Jacobian elliptic functions. In Appendix A we give a method for determining the suction energy by considering an infinite cylinder is given and expressed in terms of hypergeometric functions and alternatively Legendre functions. In Appendix B we give an alternative expression for the semi-infinite integrals in terms of Appell's $F_1$ hypergeometric functions and in Appendix C the elliptic integral is expressed as a different set of Appell's $F_1$ functions which can be transformed into a series of standard hypergeometric functions which can be further transformed into a series of incomplete beta functions. In all cases it is only the azimuthal integration over the spheroid for which an analytical expression does not appear possible. In section 3 we propose a semi-analytical procedure, involving dividing any axially symmetric surface into infinitesimal right circular conical frusta, so as to calculate the Lennard–Jones potential for the arbitrary surface to interact with a carbon nanotube. In section 4 we take the expressions derived in sections 2 and 3 and evaluate them using numerical integration of the azimuthal variable where necessary to calculate the acceptance and suction energy for spheroidal and spheroidal fullerenes, and an arbitrary surface of revolution interacting with various configurations of carbon nanotubes. The procedures are validated by comparison with the previously derived result for the sphere and spheroid. Finally, in section 5 the results are discussed and conclusions are stated.

2. Derivation of the expression for the potential

2.1 Problem definition

We consider the Lennard–Jones interaction between an ellipsoidal fullerene and a carbon nanotube. The fullerene is modelled as a spheroidal shell and the carbon nanotube is modelled as a right circular cylinder with open ends. We define two coordinate systems, one for each of the surfaces and the parametric equations for the surfaces are as follows.
First, we define a rectangular coordinate system \((x, y, z)\) which is used as a reference system. Next we introduce a cylindrical polar coordinate system \((r, \psi, z)\) with the same origin, such that \(x = r \cos \psi\) and \(y = r \sin \psi\). We consider the carbon nanotube as a semi-infinite cylinder of radius \(a\) and centred on the \(z\)-axis, extending from the origin in the positive \(z\)-direction. The parametric form of the surface of the cylinder in terms of the rectangular coordinates \((x_c, y_c, z_c)\) is \(x_c = a \cos \psi, \ y_c = a \sin \psi, \ z_c = z, \) where \(\psi \in [0, 2\pi]\) and \(z \in [0, \infty)\).

Now we introduce a spheroid with the axis of rotation collinear with the \(z\)-axis and centred at the point \((0, 0, Z)\). The equatorial semi-axes have length \(b\) and the polar semi-axis (along the \(z\)-axis) has length \(c\). We introduce a system of spheroidal coordinates \((\xi, \phi, \theta)\) with an origin located at the centre of the spheroid. The relation between the spheroidal and rectangular coordinates is given by

\[
x = a \sinh \xi \sin \phi \cos \theta, \quad y = a \sinh \xi \sin \phi \sin \theta, \quad z = a \cosh \xi \cos \phi + Z,
\]

where \(a\) is the parameter of the coordinate system, \(\xi \in [0, \infty), \ \phi \in [0, \pi]\) and \(\theta \in [0, 2\pi]\). We now fix \(a\) and \(\xi\) such that \(b = a \sinh \xi\) and \(c = a \cosh \xi\). Then we can express the parametric form of the surface of the spheroid in rectangular coordinates \((x_s, y_s, z_s)\) by

\[
x_s = b \sin \phi \cos \theta, \quad y_s = b \sin \phi \sin \theta, \quad z_s = c \cos \phi + Z,
\]
as shown in Fig 1.

The derivation of the Lennard–Jones potential is performed by integrating the potential function \(\Phi(\rho)\) over the surfaces of both molecules. The form of the potential is

\[
\Phi(\rho) = -A\rho^{-6} + B\rho^{-12}, \tag{2.1}
\]

where \(\rho\) is the distance between typical surface elements. That is, the total potential between both surfaces \(V\) is given by

\[
V = \eta_c \eta_f \iiint_{S_c} \iiint_{S_f} \Phi(\rho) \, dS_c \, dS_f,
\]

where \(S_c\) and \(S_f\) are the surfaces of the spheroid and cylinder respectively, \(\eta_c\) and \(\eta_f\) are their atomic densities per unit area and \(dS_c\) and \(dS_f\) are their surface elements. From the parametric forms of the surfaces we know that

\[
\rho^2 = (b \sin \phi \cos \theta - a \cos \psi)^2 + (b \sin \phi \sin \theta - a \sin \psi)^2 + (c \cos \phi + Z - z)^2. \tag{2.2}
\]
Furthermore, the surface elements are
\[ dS_1 = a \, d\phi \, dz, \quad dS_2 = b \sin \phi \sqrt{b^2 \cos^2 \phi + c^2 \sin^2 \phi} \, d\phi \, d\theta. \]

Thus, the problem of determining the total potential \( V \) consists in evaluating the following integral:
\[
V = ab \eta_1 \eta_2 \int_0^\pi \int_0^{\infty} \int_0^{2\pi} \left( -\frac{A}{\rho^6} + \frac{B}{\rho^{12}} \right) \sin \phi \sqrt{b^2 \cos^2 \phi + c^2 \sin^2 \phi} \, d\psi \, dz \, d\phi \, d\theta.
\]

We emphasize that generally these integrations are highly non-trivial. For example, even for the electrostatic or Newtonian gravitational potential \( \Phi(\rho) = -A\rho^{-1} \), Jeans (17, p.33) states, 'An attempt to perform the integration, in even a few simple cases, will speedily convince the student that the form is not one which lends itself to rapid progress.'

2.2 Rotational symmetry: \( \theta \) or \( \psi \) integration

As the problem possesses rotational symmetry around the \( z \)-axis it is possible, without loss of generality, to remove the dependence on either \( \theta \) or \( \psi \) by choosing a particular value and then performing the trivial integration of that variable immediately. Mathematically, this is because the integrand depends explicitly on \( \cos(\theta - \psi) \), an even function of \( \theta - \psi \). If we choose to perform this by adopting the value \( \psi = 0 \) and then evaluate that integration, there remains
\[
V = 2\pi ab \eta_1 \eta_2 \int_0^{\pi} \int_0^{\infty} \int_0^{2\pi} \left( -\frac{A}{\rho^6} + \frac{B}{\rho^{12}} \right) \sin \phi \sqrt{b^2 \cos^2 \phi + c^2 \sin^2 \phi} \, d\phi \, dz \, d\theta,
\]

where \( \rho_\alpha^2 = (b \sin \phi \cos \theta - a)^2 + (b \sin \phi \sin \theta)^2 + (c \cos \phi + Z - z)^2 \). Alternatively, we may choose \( \theta = 0 \) and likewise obtain
\[
V = 2\pi ab \eta_1 \eta_2 \int_0^{\pi} \int_0^{\infty} \int_0^{2\pi} \left( -\frac{A}{\rho_0^6} + \frac{B}{\rho_0^{12}} \right) \sin \phi \sqrt{b^2 \cos^2 \phi + c^2 \sin^2 \phi} \, d\phi \, dz \, d\phi,
\]

where
\[
\rho_0^2 = (b \sin \phi - a \cos \psi)^2 + (a \sin \psi)^2 + (c \cos \phi + Z - z)^2.
\]

2.3 Integration with respect to the angular variable

The two forms of \( V \) from (2.4) and (2.5) are equivalent and if we substitute \( \theta \) for \( \psi \) then it can be shown that \( \rho_\alpha = \rho_0 \). So either form may be used as the starting point for the integration of the second axial variable. From (2.6) we may rearrange to obtain
\[
\rho_0^2 = (b \sin \phi - a)^2 + (c \cos \phi + Z - z)^2 + 4ab \sin \phi \sin^2 (\psi/2),
\]
and therefore on defining \( \beta_1 = a - b \sin \phi, \beta_2 = a + b \sin \phi, \gamma = z - c \cos \phi - Z, \)
\[
\lambda_1 = \sqrt{\beta_1^2 + \gamma^2}, \quad \lambda_2 = \sqrt{\beta_2^2 + \gamma^2},
\]
we are left to evaluate integrals in \( \psi \) of the general form
\[
I_n = \int_0^{2\pi} \left[ \lambda_1^2 - (\beta_1^2 - \beta_2^2) \sin^2 (\psi/2) \right]^{-3n} d\psi = 2 \int_0^{\pi} \left[ \lambda_1^2 - (\beta_1^2 - \beta_2^2) \sin^2 u \right]^{-3n} du,
\]
where \( n \in \{1, 2\} \). Split the range of integration in two, giving an integral from \( u = 0 \) to \( u = \pi/2 \) plus an integral from \( u = \pi/2 \) to \( u = \pi \). In the second integral, substitute \( u - \pi \) for \( u \). Then, taking out a factor of \( \lambda_1^{-6n} \) gives

\[
I_n = 4\lambda_1^{-6n} \int_0^{\pi/2} \left[ 1 - \left( 1 - \lambda_2^2/\lambda_1^2 \right) \sin^2 u \right]^{-3n} \, du \\
= 2\lambda_1^{-6n} \int_0^1 t^{-\frac{1}{2}} (1 - t)^{-\frac{1}{2}} \left[ 1 - \left( 1 - \lambda_2^2/\lambda_1^2 \right) t \right]^{-3n} \, dt,
\]

with the substitution \( t = \sin^2 u \). The integral is of standard hypergeometric form, and therefore we obtain

\[
I_n = 2\pi \lambda_1^{-6n} F \left( 3n, 1/2; 1; 1 - \lambda_2^2/\lambda_1^2 \right) \\
= 2\pi \lambda_1^{-1} \lambda_2^{-6n} F \left( 3n, 1/2; 1; 1 - \lambda_2^2/\lambda_1^2 \right), \tag{2.7}
\]

using (18, §2.9(2)); since \( n \in \{1, 2\} \) we obtain two terminating series.

Now from (18, §3.2(28)) we may derive

\[
F (-\nu, 1/2; 1; z) = (1 - z)^{\frac{1}{2}\nu} P_\nu \left( (2 - z) / 2\sqrt{1 - z} \right), \tag{2.8}
\]

where \( P_\nu(z) \) for \( \nu \in \{1, 2, 3, \ldots\} \) denotes the Legendre polynomial. Using (2.8) to substitute for \( F(a, b; c; z) \) in (2.7) we obtain

\[
I_n = 2\pi (\lambda_1 \lambda_2)^{-3n} P_{3n-1} (\delta), \tag{2.9}
\]

where \( \delta = \cosh (\ln \lambda_1 - \ln \lambda_2) = (\lambda_1^2 + \lambda_2^2)/(2\lambda_1 \lambda_2) \), and substituting back into (2.5) gives

\[
V = 4\pi^2 abc \eta \int_0^\pi \int_0^{\infty} \left[ -\frac{A P_2(\delta)}{\lambda_1 \lambda_2^3} + \frac{B P_3(\delta)}{\lambda_1 \lambda_2^6} \right] \sin \phi \sqrt{b^2 \cos^2 \phi + c^2 \sin^2 \phi} \, dz \, d\phi, \tag{2.10}
\]

remembering that \( \lambda_1, \lambda_2 \) and \( \delta \) all depend on \( z \) as well as \( \phi \).

### 2.4 Possibility of integrating \( \phi \) analytically

By making the substitution \( s = \cos \phi \) it is possible to express (2.10) as an algebraic expression in the variable \( s \) instead of trigonometric functions of \( \phi \). First, we define

\[
\chi = (\lambda_1^2 + \lambda_2^2) / 2 = a^2 + b^2 - b^2 s^2 + (z - Z - cs)^2,
\]

and

\[
\omega^2 = \lambda_1^2 \lambda_2^2 = (a^2 - b^2 + b^2 s^2)^2 + \chi (z - Z - cs)^2.
\]

Now the infinitesimal relation is \( d\phi = -ds / \sin \phi \) and therefore the integral becomes

\[
V = 4\pi^2 ab \eta c \int_{-1}^1 \int_{0}^{\infty} \left[ -A \omega^{-3} P_2 (\chi / \omega) + B \omega^{-6} P_3 (\chi / \omega) \right] \sqrt{c^2 - (c^2 - b^2 s^2)} \, dz \, ds.
\]

However, this does not appear to be readily integrable with respect to \( s \). Therefore, the integration of the spheroid's azimuthal angle is done numerically later.
2.5 Integration along the length of the cylinder

Here we consider the $z$ integration and in this case integration is possible via either Jacobian elliptic functions or by Appell hypergeometric functions. In this section we develop the former approach and for completeness the latter approach is outlined in Appendix C.

Firstly we observe that we have two specific Legendre polynomials of order $3m - 1$, argument $\delta = (\lambda_1/\lambda_2 + \lambda_2/\lambda_1)/2$, and the polynomial is then divided by an expression of the form $(\lambda_1/\lambda_2)^{3m}$, where $m \in (1, 2)$. This leads to a finite sum of integrals of the form

$$J_{m,n} = \int_{\gamma_0}^{\infty} (\beta_2^2 + \gamma^2)^{-n}(\beta_1^2 + \gamma^2)^{1-3m+n} \left((\beta_2^2 + \gamma^2)(\beta_1^2 + \gamma^2)^{-1}\right) dy,$$

where $\gamma_0 = -c \cos \phi - Z$ and $n \in [0, 1, \ldots, 3m - 1]$. Specifically

$$\int_0^{\infty} (\lambda_1/\lambda_2)^{-3} P_2 (\delta) \, dz = [3 \left(J_{1,0} + J_{1,2}\right) + 2J_{1,1}] / 8,$$

$$\int_0^{\infty} (\lambda_1/\lambda_2)^{-6} P_5 (\delta) \, dz = [63 \left(J_{2,0} + J_{2,5}\right) + 35 \left(J_{2,1} + J_{2,4}\right) + 30 \left(J_{2,2} + J_{2,3}\right)] / 256.$$

We comment that for the region $\phi \in (0, \pi)$, $\beta_2 > \beta_1$ and we assume for the moment that $\beta_1 > 0$ and $\gamma_0 > 0$ then following Byrd and Friedman (19, eqn (222)) we make the following substitutions:

$$t = \beta_2 / \gamma, \quad u = t^{n-1} (\beta_2/\gamma_0) = \sin^{-1} \left(\frac{\beta_2}{\sqrt{\beta_2^2 + \gamma^2}}\right), \quad k^2 = 1 - \beta_2^2 / \beta_1^2,$$

so that the integral takes the form

$$J_{m,n} = \beta_2^{-6m} \int_0^{\infty} \sin^2 u \, du \int_0^{\infty} \sin^2(3m-1-n) \, du \, du.$$

Applying the recurrence formula of (19, eqn (351.51)) with $n = 0$ gives

$$\int \sin^2 u \, du \, du = k^{-2p} \sum_{i=0}^{p} (-1)^i \binom{p}{i} \int \sin^{2(p-i)} u \, du,$$

which on substitution produces the following expression for the general integral:

$$J_{m,n} = \beta_2^{-1}(\beta_2^2 - \beta_1^2)^{1-3m} \sum_{i=0}^{3m-1} (-1)^i \binom{3m-1}{i} \int_0^{\infty} \sin^{2(3m-1-n-i)} u \, du.$$

We have reduced the problem to calculating integrals of the function $\text{nd}^r u$, where $r \in \{-5, -4, \ldots, 4, 5\}$. This task can be achieved by again following (19, eqns (314), (315)) and recalling that $\text{nd} = 1/\text{nd}u$, we have in the case that $r < 0$,

$$G_m = \int \text{nd}^m \, du, \quad G_0 = u, \quad G_2 = \text{E}(u),$$

$$G_{2m+2} = \left[k^2 \text{nd}^{2m-1} u \, \text{sn} \, \text{nu} + (1 - 2m) k^2 G_{2m-2} + 2m(2 - k^2) G_{2m} \right] / (2m + 1),$$

and when $r \geq 0$,

$$H_m = \int \text{nd}^m \, du, \quad H_0 = u, \quad H_2 = \left[\text{E}(u) - k^2 \text{sn} \, \text{nu} \, du \right] / k^2,$$

$$H_{2m+2} = \left[2m(2 - k^2)H_{2m} + (1 - 2m)H_{2m-2} - k^2 \text{sn} \, \text{nu} \, nd^{2m+1} \right] / (2m + 1)k^2.$$
where $E(u)$ is Legendre’s incomplete integral of the second kind and $k'$ is the complementary modulus, $k' = \sqrt{1 - k^2}$. Now we turn to the case of $\gamma_0 < 0$. Here we comment that the form of the integrand under consideration (which we denote by $j(\gamma^2)$) is an even function of $\gamma$ and therefore when $\gamma_0 < 0$, we have
\[
\int_{-\gamma_0}^{\gamma_0} j(\gamma^2) d\gamma = \int_{-\gamma_0}^{0} j(\gamma^2) d\gamma + \int_{0}^{\gamma_0} j(\gamma^2) d\gamma = 2 \int_{0}^{\infty} j(\gamma^2) d\gamma - \int_{-\gamma_0}^{0} j(\gamma^2) d\gamma,
\]
and both of these integrals are in the form already considered (that is, with the lower limit at least 0). Now using the recurrence relationships (2.13) and (2.14) we can express $J_{m,n}$ as a finite series of elliptic integrals and functions and therefore calculate the value using these well-studied special functions.

2.6 Degenerate case: $\beta_1 = 0$, and nearly degenerate case: $\beta_1 \ll \beta_2$

When $\beta_1 = 0$ then $J_{m,n}$, as shown in (2.11), degenerates into a non-elliptic integral which can be evaluated by use of a change of variable using a hyperbolic function. However, during the numerical evaluation of $J_{m,n}$ for the region $\beta_1 \ll \beta_2$ we find that an approximation expressed as a series expansion in powers of $\beta_1/\beta_2$ leads to more sensible results. For both cases we use the $k \sim 1$ approximations for $sn u$ and $dn u$ given in (19, eqn (127.02)) which are exact for $k = 1$. Using these it can be shown that
\[
\begin{align*}
\text{sn}^{2(3m-1)} u &= \tanh^{2(3m-1)} u [1 + (3m - 1)(1 - \text{sech} u \ \text{csch} u)k^2/2] + O(k^4), \\
\text{dn}^{2(3m-1-n)} u &= \text{sech}^{2(3m-1-n)} u [1 + (3m - 1 - n)(\sinh^2 u + \tanh u)k^2/2] + O(k^4),
\end{align*}
\]
and by substitution of these expressions into (2.12) we derive the following expression which is exact for $\beta_1 = 0$ and useful numerically when $\beta_1 \ll \beta_2$:
\[
J_{m,n} = \beta_2^{-1+2m} \int_{0}^{1} \text{sinh}^{2(3m-1)} u \ \text{sech}^{2m} u \left\{\beta_2^2 + \beta_0^2 (3m - 1)(1 - \text{sech} u \ \text{csch} u)\right\}
- (3m - 1 - n) \left(\sinh^2 u + \tanh u\right) \left/O \left(\beta_1^4/\beta_2^4\right), \right.)
\]

(2.15)
where the resulting integrals in (2.15) for specific values of $m \in \{1, 2\}$ and $n \in \{0, 1, \ldots, 3m - 1\}$ are rational functions of the standard hyperbolic functions that can be easily calculated.

3. Interaction of an arbitrary surface of revolution with a cylinder

In this section we propose a numerical method for calculating the interaction potential between a cylinder and a body consisting of a surface of revolution of arbitrary shape. In the following section this method is applied to a spheroid and compared with the results from section 2 to verify its validity and it is also applied to more complicated surfaces of revolution such as may be useful for other carbon nanostructures, drugs and genes.

The proposed method is to discretize the surface of revolution into a series of right circular conical frustums, where it is assumed that the interaction over the whole surface of each frustum is proportional to both the surface area and the exact interaction potential for the two circles which define each frustum. The next step is to estimate the interaction for each section using the previously determined exact expression for the two circular ends of each section. Finally, the total interaction is calculated
by summing the interaction potential for each frustum. This has the effect of constructing a
Riemann sum for the exact integral under investigation and by taking a finer mesh size it is possible
to calculate an interaction to any required accuracy. The limit as the number of frusta approaches
infinity, and therefore the mesh size approaches zero, is the exact value of the integral.

The value for the interaction of a ring centred on the z-axis at a position \( z_k \) and radius \( r_k \)
with a semi-infinite cylinder centred on the z-axis with radius \( a \) and extending from the origin in the
positive direction of \( z \), is given by the equation (2.10) by fixing the value of \( \phi = \pi /2 \) and replacing
the surface element \( dS \) by the radius of the ring, \( r_k \), and replacing the spheroid’s position \( Z \)
with the ring position \( z_k \). With these changes the expression (2.11) for \( J_{m,n} \) can be used directly with the
following redefinitions: \( \beta_1 = a - r_k, \beta_2 = a + r_k, \gamma = z - z_k \) and \( \eta_0 = -z_k \). Then the interaction
\( V_k \) is given by

\[
V_k = 4\pi^2a r_k \eta_k \left\{ -A \left[ 3 (J_{1,0} + J_{1,2}) + 2J_{1,1} \right] /8 \\
+ B \left[ 63 (J_{2,0} + J_{2,3}) + 35 (J_{2,1} + J_{2,4}) + 30 (J_{2,2} + J_{2,3}) \right] /256 \right\}.
\]  

(3.1)

Now if we consider the surface area \( S \) of the frustum of a right circular cone defined by two circles
of radius \( r_k \) and \( r_{k+1} \) located at \( z_k \) and \( z_{k+1} \) respectively, we have the usual expression

\[
S = \pi (r_k + r_{k+1}) \sqrt{(r_k - r_{k+1})^2 + (z_k - z_{k+1})^2}.
\]

and if we rearrange terms and introduce variables for the circumference of the circles \( C_k \) and \( C_{k+1} \)
respectively, we can express this surface area as

\[
S = (C_k + C_{k+1}) \sqrt{(r_k - r_{k+1})^2 + (z_k - z_{k+1})^2}/2.
\]  

(3.2)

Therefore, we apply this formula to the problem of determining the potential by arguing that the
relationship between the circumference of the circles at each end of the frustum and the frustum’s
surface area is the same as the relationship between the interaction energy of the two rings and the
total interaction of the conical surface. However, this method relies on the mesh size being sufficiently fine so that the interaction across each surface section does not appreciably vary. Accepting
this argument allows the following expression for the interaction for a frustum:

\[
V_k^* = \eta_k (V_k + V_{k+1}) \sqrt{(r_k - r_{k+1})^2 + (z_k - z_{k+1})^2}/2,
\]  

(3.3)

where \( \eta_k \) is the atomic density for the frustum, and with this method \( \eta_k \) may vary for each discrete
section of the mesh. So the method then is to discretize the surface into a mesh of \( N + 1 \) circles
of radii \( \{r_0, r_1, \ldots, r_N\} \) located at positions \( \{z_0, z_1, \ldots, z_N\} \), and we then form the sum using (3.1)
and (3.3) which gives

\[
V^* = \frac{1}{2} \sum_{k=0}^{N-1} \eta_k (V_k + V_{k+1}) \sqrt{(r_k - r_{k+1})^2 + (z_k - z_{k+1})^2}.
\]  

(3.4)

By taking larger values of \( N \) it is possible to construct finer mesh sizes and in the limit as \( N \)
approaches infinity, \( V^* \) approaches the exact value \( V \) for the surface in question.

Another way of considering this proposal is that a circumference can be expressed as the problem
of calculating the value of a line integral of the unit function and a surface area can be thought of
as the integral of the unit function over the surface in question. In the case of a conical frustum,
(3.2) provides the relationship between the value of a surface integral \( S \) and those of the two line
integrals $C_k$ and $C_{k+1}$ that define the surface. Therefore, by adopting this equation and replacing the unit function with the Lennard–Jones potential function (2.1) we can justify equation (3.3) for a single frustum and by extrapolation also the sum (3.4) for the entire surface. We demonstrate in the following section that application of (3.4), using a reasonably small value for the number of partitions $N$, leads to results which are in excellent agreement with existing analytical results for spheres. We also show excellent agreement when comparing the results of this method with those of section 2 for the case of spheroids.

4. Interaction of various molecules located on the axis of a single-walled carbon nanotube

Following the analysis in (15) we calculate the acceptance and suction energies for various molecules interacting with carbon nanotubes of various configurations. The acceptance energy calculation addresses the issue of whether van der Waals forces alone are sufficient for the molecule to be accepted into the interior of the carbon nanotube. The suction energy is the magnitude of the total energy imparted to the molecule upon entering the carbon nanotube. Cox et al. (15) demonstrate that for certain configurations of spherical fullerene and carbon nanotubes the suction energy is positive, indicating the inside of the nanotube is energetically favourable, however, the acceptance energy is negative. This situation indicates that the energetically favourable position in the interior of the nanotube is unreachable due to an energetically unfavourable barrier at the nanotube opening. It is quite likely that analogous configurations also exist with spheroidal fullerenes and more general surfaces of revolution and therefore the analysis here includes a calculation for both the acceptance and the suction energies. In the analysis below we assume all the Lennard–Jones constants $A$ and $B$ are those that apply for graphitic carbon interactions (here we use the values from (9)). These and the other constants used in the calculations are shown in Table 1.

4.1 Interaction of a spherical C_{60} fullerene molecule

In this section we use the energy expressions derived in sections 2 and 3 to calculate the acceptance and suction energies for a spherical C_{60} fullerene and carbon nanotubes of various radii.

| Table 1 | Constants used in the model |
|--------------------------------|
| Radius of (8, 8) | $a = 5.428 \text{ Å}$ |
| Radius of (10, 10) | $a = 6.784 \text{ Å}$ |
| Radius of C_{60} | $b = 3.55 \text{ Å}$ |
| Carbon–carbon bond length | $\sigma = 1.421 \text{ Å}$ |
| Mean surface density for fullerene $[60/(4\pi b^2)]$ | $\eta_0 = 0.3789 \text{ Å}^{-2}$ |
| Mean surface density for graphene $[4\sqrt{3}/(9\sigma^2)]$ | $\eta_g = 0.3812 \text{ Å}^{-2}$ |
| Mass of a single carbon atom | $m_o = 1.993 \times 10^{-26} \text{ kg}$ |
| Mass of a single C_{60} fullerene $[60m_o]$ | $m_f = 1.196 \times 10^{-24} \text{ kg}$ |
| Attractive constant | $A = 17.4 \text{ eV} \times \text{ Å}^6$ |
| Repulsive constant | $B = 20 \times 10^3 \text{ eV} \times \text{ Å}^{12}$ |
The purpose of this exercise is to validate the expressions derived in the present paper for the special case of spherical particle interactions.

The Lennard–Jones potential $V$ as calculated using the elliptic integral method described in section 2 for a spherical $C_{60}$ fullerene and various sized carbon nanotubes of radius $a$ is shown in Fig. 2, where the final $\phi$ integration is performed using Simpson's rule with 20 intervals. Following the analysis for the mechanics of fullerenes and carbon nanotube interactions in (15) the graph shows that for carbon nanotubes where the radius is less than some critical value, the energy has a local maximum in the neighbourhood of the tube extremity, the difference between the potential energy well outside the nanotube and this local maximum is termed the acceptance energy in (15). Figure 2 shows that the critical value of nanotube radius where the acceptance energy is zero is $a \approx 6.338$ Å. Furthermore, the value of nanotube radius where the force experienced by the fullerene is not negative at any stage, and therefore the local maximum ceases to be a feature of the energy graph for $a$ in excess of 6.509 Å. Both these calculations show excellent agreement with (15). It can be seen from the plot that a nanotube with radius 6.3 Å would not accept a $C_{60}$ fullerene from rest since there exists an energy barrier at the tube opening, the magnitude of which is approximately 0.548 eV which again is in excellent agreement with the findings of (15).

The difference between the potential energy well outside the nanotube and that well inside the nanotube is termed the suction energy in (15). In Fig. 2 this is shown as the asymptotic limit which the potential energy is rapidly approaching as $Z$ increases. The values derived using the approach of section 2 of the present paper show excellent agreement with (15) with the values shown for the
Table 2  Constants used for spheroidal fullerenes

\[
\begin{array}{ll}
C_{70} \text{ equatorial semi-axis length} & b = 3.59 \text{ Å} \\
C_{70} \text{ polar semi-axis length} & c = 4.17 \text{ Å} \\
\text{Mean surface density for fullerene } C_{70} & \eta_{70} = 0.3896 \text{ Å}^{-2} \\
C_{80} \text{ equatorial semi-axis length} & b = 3.58 \text{ Å} \\
C_{80} \text{ polar semi-axis length} & c = 4.73 \text{ Å} \\
\text{Mean surface density for fullerene } C_{80} & \eta_{80} = 0.4072 \text{ Å}^{-2}
\end{array}
\]

four nanotube radii plotted at \( Z = 15 \text{ Å} \) corresponding to the absolute suction energy calculated in (15) and there is a relative error of less than 0.01. Using an arbitrarily large value of \( Z \) leads to even closer agreement. The calculation repeated for a value of \( Z = 100 \text{ Å} \) gives a relative error less than 0.0001 for the four nanotube radii shown.

Next the calculations for a \( C_{60} \) fullerene and nanotube interaction are repeated using the conical frustum technique described in section 3. In this case no Simpson’s rule numerical integration is necessary but the number of conical frusta is set to 20, which is approximately the same computational effort as required for the first method. Again excellent agreement is found with the values from the previous section. In general the relative error between the results using the methods from sections 2 and 3 is shown to be less than 0.01. However, in the region where the potential energy has a value near zero much higher relative errors are found, but in all cases the absolute error is always less than 0.01 eV.

4.2 Interaction of spheroidal fullerene molecules

With the two methods validated by the analysis in the previous section we now proceed to analyse the interaction between carbon nanotubes and spheroidal fullerenes. We investigate the fullerene \( C_{70} \) and fullerene \( C_{80} \) molecules which we model as spheroidal surfaces of uniform atomic density. The dimensions \((b \text{ and } c)\) are taken from (20) and the atomic density is calculated by dividing the number of atoms by the surface area of the idealized spheroid and these values are shown in Table 2. The method used is that detailed in section 2 and as in the previous section the \( \phi \) integration is performed numerically using Simpson’s rule with 20 partitions.

The results for the calculation for a \( C_{70} \) fullerene and carbon nanotubes of various radii are shown in Fig. 3. This shows that an increase in the radius of the nanotube is necessary to accommodate the \( C_{70} \) molecule as compared to the case of the \( C_{60} \) fullerene. The radius of the nanotube which leads to a zero acceptance energy is \( a \approx 6.383 \text{ Å} \) which is a small increase on that of a \( C_{60} \) fullerene. Figure 4 shows the potential energy for a \( C_{80} \) fullerene and carbon nanotubes of various radii. It shows that \( C_{80} \) fullerenes are accepted into slightly smaller tubes and this demonstrates that \( b \) (the equatorial semi-axes lengths) is the major determining factor in prescribing the nanotube size. In other words, the polar semi-axis length (or longitudinal dimension) \( c \) which is 0-56 Å longer for a \( C_{80} \) than for a \( C_{70} \) did not increase the size of tube necessary to accept the fullerene. However, the 0.01 Å decrease in \( b \) did reduce the required nanotube radius \( a \). The nanotube radius which leads to a zero acceptance energy is \( a \approx 6.376 \text{ Å} \) which is a decrease of approximately the same magnitude as the decrease in \( b \) compared to the \( C_{70} \) fullerene.

To conclude this section we compare the suction energies \( W \) for fullerenes \( C_{60}, C_{70} \) and \( C_{80} \) which are shown in Fig. 5. The nanotube radius which maximizes the suction energy for a \( C_{70} \)
fullerene is $a \approx 6.83 \text{ Å}$, which is just a small increase in the radius when compared to the findings for the $C_{60}$ molecule. The maximum value of the suction energy $W$ is increased when compared to that of the $C_{60}$ case but there is no practical increase in the energy per atom, and so this leads to the same final velocity for a molecule being sucked into the nanotube. Therefore we conclude there is not a configuration for $C_{70}$ and a single-walled carbon nanotube which leads to higher frequencies of oscillation as compared to a similar configuration with a $C_{60}$ molecule. The nanotube radius which has a maximum suction energy $W$ for a $C_{80}$ fullerene is $a \approx 6.82 \text{ Å}$, which is again very similar to the value for a $C_{70}$ fullerene and, as before, the maximum potential energy per atom in the fullerene is very similar and therefore in terms of producing a maximal oscillator, the $C_{80}$ would not appear to offer any advantages in terms of van der Waals suction energy per unit mass.

4.3 Interaction of an arbitrary surface of revolution

Here we investigate those surfaces of revolution which do not lend themselves to an analytical analysis and we adopt the numerical approach outlined in section 3. When considering the interaction of drugs and genes with carbon nanotubes, one scenario is that of a long thin molecule which is aligned on the $z$-axis and is being accepted into the carbon nanotube which is situated on the same $z$-axis. Unlike the case of fullerenes, these molecules may be an irregular shape, but one feature is that the molecule thickness varies along its length. Therefore for the purposes of this exercise we model the interacting molecule as a displaced sinusoidal curve which is then revolved around the
z-axis. That is, the molecule is assumed to have the parametric form \((r_m, \theta_m, z_m)\) such that

\[
r_m = \sigma_1 \left[ 1 - \sigma_2 \left[ 1 + \cos(\pi \sigma_3 t) \right] \right], \quad z_m = \sigma_4 t,
\]

where \(\sigma_1\) is the maximum radius of the surface in the \(r\)-direction, \(\sigma_2\) is a measure of the relative magnitude of the surface undulations for which we assume here that \(\sigma_2 \in [0, 1/2]\), \(\sigma_3\) is the number of undulations along the length of the molecule, \(\sigma_4\) is the half-length of the surface in the \(z\)-direction, \(t\) is the parametric variable for which we consider \(t \in [-1, 1]\), and \(\theta_m \in [0, 2\pi]\). We comment that this system can be applied to any surface of revolution and in particular, even one for which the curve is multi-valued or totally irregular and cannot be prescribed with a function at all. However, for the purposes of this analysis here, we use a surface as described above with the values as shown in Table 3, and a wire-frame diagram of this surface is shown in Fig. 6.

The Lennard–Jones potential \(V\) as calculated using the method described in section 3 for the surface of revolution and various sized carbon nanotubes of radius \(a\) is shown in Fig. 7. Since this is a typical example of the method, emphasis is not placed on a physical interpretation of the results other than to comment that for shapes of this type it is clear that the acceptance energy \(W_a\) is lower than the suction energy \(W\) and hence there exist configurations that are energetically favourable to the molecule to position itself inside the nanotube, but due to a barrier at the tube end, spontaneous suction into the nanotube does not occur. We also note that in this case there are a number of local maxima and minima matching the number of undulations of the surface. However, once the first undulation has entered the nanotube, subsequent undulations enter more freely.
Fig. 5 Suction energy $W$ for fullerenes $C_{60}$, $C_{70}$ and $C_{80}$ for carbon nanotubes of varying radius $a$

Table 3  Constants used for the surface of revolution

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum radius in the $r$-direction</td>
<td>$\sigma_1 = 3.55 , \text{Å}$</td>
</tr>
<tr>
<td>Relative magnitude of undulation</td>
<td>$\sigma_2 = 0.25$</td>
</tr>
<tr>
<td>Number of undulations</td>
<td>$\sigma_3 = 4$</td>
</tr>
<tr>
<td>Half-length of the surface in the $z$-direction</td>
<td>$\sigma_4 = 15 , \text{Å}$</td>
</tr>
<tr>
<td>Mean atomic density for the surface</td>
<td>$\eta_m = 0.3812 , \text{Å}^{-2}$</td>
</tr>
<tr>
<td>Number of conical frusta</td>
<td>$N = 64$</td>
</tr>
</tbody>
</table>

5. Conclusions
In this paper we consider various analytical approaches for determining van der Waals interaction potential for graphic systems involving spherical and spheroidal fullerenes and carbon nanotubes. We also detail a semi-analytical method to determine the van der Waals potential for arbitrary surfaces of revolution and carbon nanotubes. By comparing the results of these methods with previously published studies for systems of spherical fullerenes and carbon nanotubes (15) we are able to validate both methods. Once the validity is established we then apply the methods to various physically interesting configurations.
For spheroidal C_{70} and C_{80} systems we find that the overall nature of the van der Waals interaction energy is similar to that found for spherical fullerene C_{60} systems. There exists a critical nanotube radius below which a local maximum occurs in the potential energy, the magnitude of which is the acceptance energy $W_\alpha$ as defined in (15). At some value of the nanotube radius $\alpha$ the acceptance energy $W_\alpha$ becomes negative and for all smaller nanotubes the fullerene is not sucked into the nanotube from rest due to the energy barrier at the tube entrance.
The final potential energy level attained by a fullerene moving into a nanotube to some distance away from the tube end corresponds to the increase in kinetic energy experienced by the fullerene and termed the suction energy \( W \) in (15). For the spheroidal fullerenes considered here, there exists a nanotube radius \( a_{\text{max}} \) which leads to a maximum value of \( W \) and therefore represents the ideal single-walled carbon nanotube with which to construct a gigahertz oscillator for the spheroidal molecule in question. In the case of the fullerenes \( C_{70} \) and \( C_{80} \) the values are provided in section 4 and are very similar to those previously found for the \( C_{60} \)-nanotube oscillator. It is also found that the magnitude of the maximum suction energy per atom is almost exactly the same for all three fullerenes under consideration and therefore there does not appear to be one which would make a higher frequency oscillator than any other.

In this paper, we also propose a semi-analytical method based on approximating any surface of revolution by a finite sum of conical frusta. The results presented here show that this method is in good agreement with those of the fully analytical solution of section 3 and also an example is given for an arbitrary shape of revolution which provides some insight into the mechanics of long molecules of various intermediate radii interacting with carbon nanotubes as might occur with drug and gene capture in nanocontainers. However, the method is sufficiently general to extend to other configurations of interest in drug and gene capture, and also in the construction of nanoscale devices which interact with nanostructures such as tubes, cones, discs, tori, unduloids and other engineered devices made from combinations of these shapes and others. The present authors plan to publish further work on specific cases of interest in a future paper.

Finally, the present work also demonstrates the non-trivial nature of the analytical evaluation of integrals arising from the Lennard–Jones potential function in various physically interesting contexts. Furthermore, the method of the evaluation and the order in which the surface integrals are considered lead to various different representations. In this paper we have utilized certain special functions such as hypergeometric functions, Appell’s hypergeometric function of two variables, Legendre functions and Jacobian elliptic functions in a variety of different combinations. Those analytical details are presented in Appendices A, B and C and demonstrate the close connections between such special functions, noting that the distinct representations obtained may be shown to be numerically equivalent.

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References


**APPENDIX A**

In this Appendix we consider the case of a spheroidal fullerene centred on and rotationally symmetric around the z-axis, and enclosed in a cylinder of infinite extent and centred around the z-axis. Hodak and Girifalco (10) examine the case of an ellipsoid inside a cylinder of infinite length but in this Appendix we extend the analysis of the integrations further than was done in (10). In this case, the form of the integral is equivalent to (2.3) except that the lower z limit is changed to $-\infty$ and the parameter defining the location of the spheroid, $Z = 0$. 


That is,
\[
V = ab\eta c n_s \int_{0}^{2\pi} \int_{0}^{\pi} \int_{-\infty}^{\infty} \int_{0}^{2\pi} \left( -\frac{A}{p^6} + \frac{B}{p^{12}} \right) \sin \phi \sqrt{b^2 \cos^2 \phi + c^2 \sin^2 \phi} \, dz \, d\phi \, d\theta, \quad (A.1)
\]
where \( p \) is defined in (2.2). In this derivation of the expression, the infinite extent of \( x \) in both directions makes it possible to consider this integration first. To this end we make the substitution
\[
\kappa^2 = (b \sin \phi \cos \theta - a \cos \psi)^2 + (b \sin \phi \sin \theta - a \sin \psi)^2 = \beta_1^2 - (\beta_1^2 - \beta_2^2) \sin^2((\theta - \psi)/2), \quad (A.2)
\]
where \( \beta_{1,2} \) are as defined previously, and then consider
\[
I_2 = \int_{-\infty}^{\infty} \left\{-A(\kappa^2 + (z - c \cos \phi - Z)^2)^{-3} + B(\kappa^2 + (z - c \cos \phi - Z)^2)^{-6}\right\} \, dz
\]
\[
= \int_{-\infty}^{\infty} \left\{-A(\kappa^2 + \gamma^2)^{-3} + B(\kappa^2 + \gamma^2)^{-6}\right\} \, d\gamma,
\]
using the substitution \( \gamma = z - c \cos \phi - Z, \) as before. Then \( \gamma = \kappa \tan \tau \) gives
\[
I_2 = \int_{-\pi/2}^{\pi/2} \left(-A\kappa^{-5} \cos^4 \tau + B\kappa^{-11} \cos^{10} \tau \right) \, d\tau = \frac{3\pi}{8} \left[-A\kappa^{-5} + (2B/32)\kappa^{-11} \right].
\]
Next we perform the integral of \( I_2 \) over the angles \( \theta \) and \( \psi, \) namely
\[
I_{\theta,\psi} = \frac{3\pi}{8} \int_{0}^{2\pi} \int_{0}^{\pi} \left[-A\kappa^{-5} + (2B/32)\kappa^{-11} \right] \, d\phi \, d\theta, \quad (A.3)
\]
with \( \kappa \) defined by (A.2). Appealing to the same arguments of rotational symmetry presented in section 2.2, the double integral in (A.3) can be reduced to a single integral with respect to \( \theta. \) Then by bisecting the interval of integration and making the substitution \( t = \sin^2(\theta/2), \) we obtain
\[
I_{\theta,\psi} = \frac{3\pi^2}{2} \int_{0}^{1} \left\{-A \left(1 - \frac{\beta_2^2}{\beta_1^2} \right) \right\} \left[1 - \left(1 - \frac{\beta_2^2}{\beta_1^2} \right) t\right]^{-1/2} \frac{21B}{32\beta_1^{11}} \left[1 - \left(1 - \frac{\beta_2^2}{\beta_1^2} \right) t\right]^{-1/2} t^{-1/2} (1 - t)^{-1/2} \, dt.
\]
This involves the fundamental integral representation for the hypergeometric function \( F(a, b; c; z), \) as given in (18, §2.1.3), so that
\[
I_{\theta,\psi} = (3\pi^2/2) \left[-A\beta_1^{-5} F(5/2, 1/2; 1; 1 - \beta_2^2/\beta_1^2) + (2B/32)\beta_1^{-11} F(11/2, 1/2; 1; 1 - \beta_2^2/\beta_1^2) \right].
\]
We note that from (18, §2.9(4), §3.2(28)) we can show
\[
F \left(a, 1/2; 1; 1 - \beta_2^2/\beta_1^2 \right) = (\beta_1/\beta_2)^{a} P_{a-1} (\epsilon), \quad (A.4)
\]
where \( \epsilon = (\beta_1/\beta_2 + \beta_2/\beta_1)/2. \) With the use of (A.4) the integral \( I_{\theta,\psi} \) becomes
\[
I_{\theta,\psi} = (3\pi^2/2) \left[-A(\beta_1\beta_2)^{-5/2} P_{3/2} (\epsilon) + (2B/32)(\beta_1\beta_2)^{-11/2} P_{9/2} (\epsilon) \right].
\]
Thus, the potential \( V \) for an ellipsoidal fullerene inside an infinite carbon nanotube can now be written in the form
\[
V = 3\pi^3 ab \eta c n_s \left[-A I_{5/2} + (2B/32) I_{11/2} \right],
\]
where the integral \( I_n \) is defined by
\[
I_n = \int_{0}^{\pi/2} P_{n-1} \left(\frac{a^2 + b^2 \sin^2 \phi}{a^2 - b^2 \sin^2 \phi} \right) \frac{\sin \phi \sqrt{c^2 \sin^2 \phi + b^2 \cos^2 \phi}}{(a^2 - b^2 \sin^2 \phi)^n} \, d\phi.
\]
Fig. A Variation of the interaction potential of ellipsoidal fullerenes with respect to the radius of carbon nanotubes

In Fig. A we plot $V$ as given by (A.5) with respect to $a$, for different values of $b$ and $c$. It is evident from this graph that the value of $b$ is the dominant factor for determining the nanotube radius $a$, suitable for accepting the fullerene in question, as was also mentioned in section 4.2.

APPENDIX B

Here we consider the case of a semi-infinite carbon nanotube ($0 \leq z < \infty$). The potential $V$ for an ellipsoidal fullerene interacting with the carbon nanotube is given by (2.3). As in Appendix A, we first consider the integral along the cylinder, that is,

$$I_z = \int_0^\infty \left\{ -A[k^2 + (z - c \cos \phi - Z)^2]^{-3} + B[k^2 + (z - c \cos \phi - Z)^2]^{-6} \right\} dz,$$

where $\kappa$ is defined in (A.2). We make the substitution $z - c \cos \phi - Z = \kappa \tan \tau$ giving

$$I_z = \int_{\tan^{-1}(\gamma_0/\kappa)}^{\kappa/2} \left( -A \kappa^{-5} \cos^4 \tau + B \kappa^{-11} \cos^{10} \tau \right) d\tau,$$

where $\gamma_0 = -c \cos \phi - Z$. Integrating, we obtain

$$I_z = -A[3\pi/2 - \tan^{-1}(\gamma_0/\kappa) - \kappa \gamma_0(k^2 + \gamma_0^2)^{-1}] - 2\kappa^3 \gamma_0(k^2 + \gamma_0^2)^{-2}/8\kappa^5$$

$$+ B[315\pi/2 - \tan^{-1}(\gamma_0/\kappa) - \kappa \gamma_0(k^2 + \gamma_0^2)^{-1}] - 210\kappa^3 \gamma_0(k^2 + \gamma_0^2)^{-2}$$

$$- 168\kappa^5 \gamma_0(k^2 + \gamma_0^2)^{-3} - 144\kappa^7 \gamma_0(k^2 + \gamma_0^2)^{-4} - 128\kappa^9 \gamma_0(k^2 + \gamma_0^2)^{-5}]/1280\kappa^{11},$$
noting as in (A.2), \( x^2 \) can be written as \( x^2 = \beta_1^2 - (\beta_1^2 - \beta_2^2) \sin^2 ((\theta - \psi)/2) \). Next we evaluate the integral of \( I_\theta \) over the angles \( \theta \) and \( \psi \), namely

\[
I_{\theta, \psi} = \int_0^{2\pi} \int_0^{2\pi} I_\theta \, d\theta \, d\psi = 2\pi \int_0^{2\pi} I_{\theta|\psi=0} \, d\theta,
\]

using the same arguments of rotational symmetry presented in section 2.2. Substituting \( x = \theta/2 \), and then bisecting the interval, (B.1) becomes

\[
I_{\theta, \psi} = \pi \int_0^{\pi/2} \left[ -A[3(\pi/2 - \tan^{-1}(\gamma_0 p^{-1/2}))p^{-5/2} - \gamma_0 (3p^{-2}q^{-1} + 2p^{-1}q^{-2})] 
\right.

\[
+ \beta(315(\pi/2 - \tan^{-1}(\gamma_0 p^{-1/2}))p^{-11/2})p^{-3/2} - \gamma_0 (315p^{-5}q^{-1} + 210p^{-4}q^{-2} + 168p^{-3}q^{-3} + 144p^{-2}q^{-4} + 125p^{-1}q^{-5})]/160) \, dx,
\]

where \( p = \beta_1^2 - (\beta_1^2 - \beta_2^2) \sin^2 x \) and \( q = p + \gamma_0^2 \). We note that the integrals is (B.2) involving \( q \) are all of the form

\[
J_{m,n} = \int_0^{\pi/2} p^{-m}q^{-n} \, dx,
\]

where \( m + n = 3 \) or 6. Making the substitution \( u = \sin^2 x \) gives

\[
J_{m,n} = \frac{1}{2\beta_1^{2m}(\beta_1^2 + \gamma_0^2)^n} \int_0^{1} u^{-\frac{1}{2}} (1-u)^{-\frac{1}{2}} \left[ 1 + u \left( 1 - \frac{\beta_2^2}{\beta_1^2} \right)^{-m} \left[ 1 + u \left( \frac{\beta_1^2 - \beta_2^2}{\beta_1^2 + \gamma_0^2} \right) \right]^{-n} \right] \, du,
\]

which, from (18, §5.8.2(5)), can be written as

\[
J_{m,n} = (\pi/2)\beta_1^{-2m}(\beta_1^2 + \gamma_0^2)^{-n} F_1 \left( \frac{1}{2}, m, n, 1; \zeta_1, \zeta_2 \right),
\]

where \( \zeta_1 = 1 - \beta_2^2/\beta_1^2, \zeta_2 = (\beta_1^2 - \beta_2^2)/(\beta_1^2 + \gamma_0^2) \) and \( F_1(a, b', c; z, x') \) is the Appell hypergeometric function.

Further to this, we need to evaluate the integrals in (B.2) which do not involve \( q \) terms, namely

\[
K_m = \int_0^{\pi/2} p^{-m-\frac{1}{2}} \, dx,
\]

for \( m = 2 \) and \( 5 \). Again using the substitution of \( u = \sin^2 x \) produces

\[
K_m = \frac{1}{2\beta_1^{2m+1}} \int_0^{1} u^{-\frac{1}{2}} (1-u)^{-\frac{1}{2}} (1 - \zeta_1 u)^{-m-\frac{1}{2}} \, du
\]

\[
= \frac{\pi}{2\beta_1^{2m+1}} F\left(m + \frac{1}{2}, \frac{1}{2}; 1; \zeta_1 \right) = \frac{\pi}{2(\beta_1^2)^{m+\frac{1}{2}}} P_{m-\frac{1}{2}}(\epsilon),
\]

using (A.4), where \( P_m(\epsilon) \) is the Legendre function of the first kind.

Finally, we consider the only term of (B.2) which has not been integrated, namely

\[
L_m = \int_0^{\pi/2} p^{-m-\frac{1}{2}} \tan^{-1}(\gamma_0 p^{-\frac{1}{2}}) \, dx,
\]

where \( m = 2 \) or \( 5 \). Here we use two different series representations of the arctangent depending on the value of the argument. One is given in (21, §1.644(1)) and is

\[
\tan^{-1}(x) = \frac{x}{\sqrt{1+x^2}} \sum_{k=0}^{\infty} \frac{(2k)!}{2^k(k!)^2(2k+1)} \left( \frac{x^2}{1+x^2} \right)^k,
\]
for any real $x$. The other series representation is also from (21, §1.644(2)) and is

$$
\tan^{-1}(x) = \text{sgn}(x) \frac{\pi}{2} - \sum_{k=0}^{\infty} \frac{(-1)^k}{(2k+1)(2k+1)^{x}}.
$$

(B.7)

for real $|x| > 1$. An investigation of convergence indicates that ten terms are sufficient for five significant digits of accuracy, provided that (B.6) is used when $|x| < 1 - 3$ and which we term $L_m^\ast$; and (B.7) is used with $|x| > 1 - 3$ and which we term $L_m^\dagger$. First considering (B.6) it follows that

$$
p^{-m-\frac{1}{2}} \tan^{-1}(\gamma_0 p^{-\frac{1}{2}}) = \frac{\gamma_0}{p^m + \frac{1}{2}} \sum_{k=0}^{\infty} \frac{(2k)!}{2^{2k}(k!)^2(2k+1)} \left( \frac{\gamma_0^2}{q} \right)^k,
$$

and finally by substitution in (B.5)

$$
L_m^\ast = \sum_{k=0}^{\infty} \frac{(2k)!}{2^{2k}(k!)^2(2k+1)} \int_0^{\pi/2} p^{-m-\frac{1}{2}} q^{-k+1} \sin x \, dx,
$$

upon which we observe that the integral is of the form previously defined as $J_{m+\frac{1}{2},k+1}$ and therefore

$$
L_m^\ast = \frac{\pi}{2\gamma_0^2} \sum_{k=0}^{\infty} \frac{(2k)!}{2^{2k}(k!)^2(2k+1)} \left( \frac{\gamma_0^2}{\beta_1^2 + \beta_2^2} \right)^{k+1} \text{F}_1\left(\frac{1}{2}, m + \frac{1}{2}, k + 1, 1; \beta_1, \beta_2\right). \quad \text{(B.8)}
$$

Now considering the second series expansion for $\tan^{-1} x$, (B.7), we have

$$
p^{-m-\frac{1}{2}} \tan^{-1}(\gamma_0 p^{-\frac{1}{2}}) = \frac{\gamma_0}{p^m + \frac{1}{2}} \left( \text{sgn}(\gamma_0 p^{-\frac{1}{2}}) \frac{\pi}{2} - \sum_{k=0}^{\infty} \frac{(-1)^k}{(2k+1)(2k+1)^{x}} \right),
$$

and since $p > 0$ and the remaining integrals only involve $p$, which have been considered previously, we have

$$
L_m^\circ = \gamma_0 \frac{\pi}{2} K_m - \sum_{k=0}^{\infty} \frac{(-1)^k}{(2k+1)(2k+1)} \text{K}_{m+k-1/2},
$$

and therefore

$$
L_m^\circ = \frac{\pi}{2\beta_1 \beta_2 (m+1)^{1/2}} \left[ -\text{A} \left( 3 (K_2 \pi/2 - L_2) - \gamma_0 (3 J_{2,1} + 2 A_1,2) \right) + \text{B} \left( 315 (K_5 \pi/2 - L_5) - \gamma_0 (315 J_{5,1} + 210 J_{2,1} + 168 J_{3,1} + 144 J_{4,1} + 128 J_{1,5}) \right) / 160 \right]. \quad \text{(B.9)}
$$

So by using either (B.8) or (B.9) we are able to calculate a quickly convergent value of $L_m$, and therefore additionally using (B.3) and (B.4) we can determine a value for $L_{\theta,\psi}$ as shown in (B.2) as

$$
L_{\theta,\psi} = \gamma_0 \left[ \frac{\pi}{2} (K_2 \pi/2 - L_2) - \gamma_0 (3 J_{2,1} + 2 A_1,2) \right] + \gamma_0 \left[ 315 (K_5 \pi/2 - L_5) - \gamma_0 (315 J_{5,1} + 210 J_{2,1} + 168 J_{3,1} + 144 J_{4,1} + 128 J_{1,5}) \right] / 160.
$$

We note from (22) that the Appell function $F_1(1/2, m, n, 1; \beta_1, \beta_2)$ contained in $J_{m,n}$ and $L_m^\ast$ can be written in terms of hypergeometric functions as

$$
F_1\left(\frac{1}{2}, m, n, 1; \beta_1, \beta_2\right) = \sum_{i=0}^{\infty} \frac{\left(\frac{1}{2}\right)_i (m)_i}{(i+1)!} \frac{\left(\frac{1}{2}\right)_i (n)_i}{(i)!} \frac{1}{2} F\left(\frac{1}{2}, i, n; 1 + i; \beta_1, \beta_2\right),
$$

where $(a)_i$ is the Pochhammer symbol. This representation turns out to be useful for computational purposes in mathematical packages (such as MAPLE) which have implemented the usual hypergeometric function but not Appell's hypergeometric function. Finally, the potential energy $V$ can then be obtained from

$$
V = ab \eta c \eta s \int_0^{\pi} L_{\theta,\psi} \sin \phi \sqrt{c^2 \sin^2 \phi + b^2 \cos^2 \phi} \, d\phi.
$$
APPENDIX C

We consider the integral (2.11) and incorporate the separate terms raised to the negative one-half power into the terms of integer powers giving

\[ J_{m,n} = \int_{r_0}^{r \to \infty} (\beta_1^2 + y_1^2)^{1/2 - 3m + n} (\beta_2^2 + y_2^2)^{-n - 1} \, dy, \]  

(C.1)

and rather than calculating this using elliptic integral functions as explained in the text, we express this integral as an Appell's \( F_1 \) hypergeometric function which in turn can be re-expressed as a series of incomplete beta functions and the derivation of this form is presented here.

First of all we make the substitution \( \gamma = \beta_1 \tan \tau \), so that \( d\gamma = \beta_1 \sec^2 \tau \, d\tau \). We also define an angle \( r_0 = \tan^{-1} (y_0/\beta_1) \). So then our equation becomes

\[ J_{m,n} = \beta_1^{1-6m+2n} \int_{r_0}^{r/2} \cos^{6m-2n-3} \tau (\beta_1^2 + \beta_1^2 \tan^2 \tau)^{n-1/2} \, d\tau \]

\[ = \beta_1^{1-6m+2n} \int_{r_0}^{r/2} \cos^{6m-2} \tau (\beta_1^2 - (\beta_2^2 - \beta_2^2) \cos^2 \tau)^{-n-1/2} \, d\tau. \]

Now we make the substitution \( r = \cos^2 \tau \) and define \( t_0 = \cos^2 \tau_0 = \beta_1^2/(\beta_1^2 + \gamma_0^2) \), and then we have

\[ J_{m,n} = \frac{1}{2} \beta_1^{1-6m} \int_{t_0}^{t_0} \tau^{3m-1/2} (1-t)^{-1/2} \left[ 1 - t \left( \frac{\beta_1^2 - \beta_2^2}{\beta_1^2} \right) \right]^{n-1/2} \, dt. \]

This is almost the standard hypergeometric form except that the upper limit of the integral is not unity. By making the substitution \( u = t/t_0 \) we derive the equation

\[ J_{m,n} = \frac{1}{2} \beta_1^{1-6m} \int_{u_0}^{1} u^{3m-3/2} \left[ 1 - u \left( \frac{\beta_1^2}{\beta_1^2 + \gamma_0^2} \right) \right]^{-1/2} (1-uc_2)^{-n-1/2} \, du, \]

where as before \( c_2 = (\beta_2^2 - \beta_2^2)/(\beta_1^2 + \gamma_0^2) \) and which is of the Appell form such that

\[ J_{m,n} = \frac{\beta_1^2 + \gamma_0^2}{6m - 1} F_1 \left( 3m - \frac{1}{2}, \frac{1}{2}, n + \frac{1}{2}; 3m + \frac{1}{2}; -\frac{\beta_1^2}{\beta_1^2 + \gamma_0^2}, c_2 \right), \]

which in turn can be written as a series of standard hypergeometric functions using (22, p. 79),

\[ F_1(a, \beta, \beta'; \gamma; x, y) = \sum_{k=0}^{\infty} \frac{(a)_k (\beta)_k}{k!(\beta')_k} F(a + k, \beta'; \gamma + k; y)x^k, \]

where \((a)_k\) is the Pochhammer symbol. This allows us to write

\[ J_{m,n} = \sum_{k=0}^{\infty} \frac{(2k - 1)!! \beta_1^{2k}}{2^k k!(2k + 6m - 1) (\beta_1^2 + \gamma_0^2)^{k + 3m - 1/2}} F(k + 3m - \frac{1}{2}, n + \frac{1}{2}; k + 3m + \frac{1}{2}; c_2), \]

and noting that this hypergeometric function is of a form where \( c - a = 1 \) we can then apply the relationship between hypergeometric and incomplete beta functions as outlined in (18, §25.5.3),

\[ B_{\gamma}(p, q) = p^{-1} x^{p} F(p, 1 - q; p + 1; x), \]

and therefore we can express \( J_{m,n} \) as

\[ J_{m,n} = \sum_{k=0}^{\infty} \frac{(2k - 1)!! \beta_1^{2k}}{2^k k!(\beta_1^2 - \beta_2^2)^{k + 3m - 1/2}} B_{c_1}(k + 3m - \frac{1}{2}, \frac{1}{2} - n), \]

and by using the previously defined \( c_1 = 1 - \beta_2^2/\beta_1^2 \) we can also express in the compact form

\[ J_{m,n} = (\beta_1^2 - \beta_2^2)^{1/2 - 3m} \sum_{k=0}^{\infty} \frac{(2k - 1)!!}{2^k k!} c_1^{-k} B_{c_1}(k + 3m - \frac{1}{2}, \frac{1}{2} - n). \]