Peer-reviewed version available at *Nanomaterials* **2018**, *8*, 624; doi:10.3390/nano8080624

Carbon nanocones with curvature effects close to vertex

Barry J Cox[1] and James M Hill[2]

[1] School of Mathematical Sciences, University of Adelaide, SA 5005, Australia

[2] School of Information Technology and Mathematical Sciences, University of South Australia, SA, Australia

Abstract

The conventional rolled-up model for carbon nanocones assumes that the cone is constructed from a rolled-up graphene sheet joined seamlessly, which predicts five distinct vertex angles. This model completely ignores any effects due to the changing curvature and all bond lengths and bond angles are assumed to be those for the planar graphene sheet. Clearly curvature effects will become more important closest to the cone vertex, and especially so for the cones with the smaller apex angles. Here we construct carbon nanocones which in the assembled cone are assumed to comprise bond lengths and bond angles which are, as far as possible, equal throughout the structure at the same distance from the conical apex. Predicted bond angles and bond lengths are shown to agree well with those obtained by relaxing the conventional rolled-up model using the LAMMPS software. The major objective here is not simply to model physically realisable carbon nanocones for which numerical procedures are far superior, but rather to produce an improved model that takes into account curvature effects close to the vertex, and from which we may determine an analytical formula which represents an improvement on that for the conventional rolled-up model.

1 Introduction

Conventional carbon nanocones are considered to be a sheet of graphene with a section removed which is then rolled and joined seamlessly to form a conical nanostructure [1]. Closed nanocones may have one of five conical angles which are determined by the amount of the graphene sheet that is removed and this in turn determines the number of pentagonal rings required to close the vertex of the cone [2]. The conventional models for both carbon nanotubes and nanocones assume that they comprise rolled-up graphene sheets that are joined seamlessly to form complete structures, and any effects arising from the changing curvature and bond bending and distortion are completely ignored. For

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 16 July 2018 doi:10.20944/preprints201807.0272.v1

Peer-reviewed version available at Nanomaterials 2018, 8, 624; doi:10.3390/nano8080624

carbon nanotubes the present authors have proposed a polyhedral model [3, 4] which properly incorporates a hexagonal framework in which the bond angles and bond lengths are all assumed identical in the cylindrical configuration, and by necessity the sum of the bond angles is less than 360°. In this paper we propose a corresponding model for carbon nanocones, but in this case it is not possible to produce a completely analogous model, since the present structure does not have precise equality of all bond lengths and bond angles since the curvature changes along the length of the nanocone and so too the angle sum of the three bond angles at each carbon atom. Therefore, evidently it is not expected that every point in the graphene lattice can be exactly congruent with all others.

In previous studies on the structure of nanocones there has been considerable interest in the geometry and morphology of the vertex for various cone angles [5, 6, 7, 8], their electronic properties [9, 10, 11] and their mechanical behaviour [12, 13, 14, 15, 16]. However, in the modelling presented here, we concentrate on accounting for the curvature effects relevant along the wall of the nanocone, both close to and further away from the conical vertex. We derive an analytical expression for the cone radius applicable at any distance along the cone wall and we also derive an integral expression for the conical height, which goes some way towards accounting for the varying curvature of the cone wall. An asymptotic expansion of the integral expression gives the conventional rolled-up formula as the leading term, and we may view the higher order terms in the series as higher order corrections to the rolled-up model. The predictions of this model are compared to molecular simulation results performed by the authors using the LAMMPS software package [17].

We comment that the assumptions adopted here for a symmetrical structure involving equal bond lengths and bond angles evidently ignore two important issues. Firstly, such a symmetric structure may not be physically realisable. Secondly, there may be other physical effects close to the vertex that violate the symmetry assumption and the bond length and bond angle equality. However, the major objective of the modelling presented here is to determine a mathematically tractable model that give rise to analytical formulae which represent an improvement on the conventional rolled-up model. We do not claim that this is a universal model applying to all physically realisable carbon nanocones, but rather merely a step-forward towards the determination of an analytical solution of what is after all, a fundamentally difficult problem.

2 Methods

To assess the usefulness of the model proposed here we need careful measurements of cone geometry. As there is at present no known technique to do such measurements from experiment, the approach adopted here is to formulate a geometric model of these structures, and then compare the predictions with those obtained from numerical molecular modelling (LAMMPS) and this is done in §3 and §4. The method employed is to determine a set of atomic positions based

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 16 July 2018 doi:10.20944/preprints201807.0272.v1

Peer-reviewed version available at *Nanomaterials* **2018**, *8*, 624; doi:10.3390/nano8080624

on a bond length of $\sigma = 1.3978$ Å and using the rolled-up model described in §3 to determine initial atomic locations. The simulated cones comprise $n = 2$ panels as described in §3. The panels are extended to 40 rows of carbon atoms and the atoms located closer than $r = 1.667$ Å from the conical axis are excluded from the simulation, which means that the conical cap is excluded from these simulations. Finally, the dangling bonds on both ends of the cone (base and apex) are hydrated to stabilise the overall integrity of the structure for the duration of the simulation.

With the cone established using the rolled-up geometry, the atom positions are loaded into LAMMPS and the simulation is run to relax the structure producing a more energetically favourable structure. This is done by starting the simulation at a temperature of 600 K and reducing it as close as possible to 0 K over 10000 time steps using the Adaptive Intermolecular Reactive Empirical Bond Order (AI-REBO) potential of Brenner, *et al.* [18]. After the simulation completes the final atomic locations are extracted and the conical radius for an atom is determined by measuring the distance between an atom on one panel and the matching atom on the second panel. The location of individual carbon atoms in the resulting structure is then analysed and compared with both the initial, rolled-up structure as well as the structural predictions of the new model as described in §4.

3 Theory

3.1 Rolled-up model formulation

In this section we describe the conventional rolled-up model for carbon nanocones which may be used to provide a first approximation for determining the atomic positions, bond lengths and bond angles in such structures. In the rolled-up model we assume that a carbon nanocone comprises from one to five equilateral triangular panels as shown in Fig. 1. In addition, we assume that each triangular panel comprises infinitely many rows of unit equilateral triangles, and we denote each horizontal row of a triangular panel by the parameter t, which is chosen so that each horizontal line corresponds to some $t \in \mathbb{N}$. We also define ϕ to be the angle between the mid-line of the triangle and any lattice point in the triangular panel, and therefore $-\pi/6 \leqslant \phi \leqslant \pi/6$. For the purpose of these calculations we may non-dimensionalise all lengths by the distance between adjacent points in the lattice σ, which corresponds to the covalent bond length. To apply the rolled-up model described here to a physical structure, such as a carbon nanocone, we adopt a linear scaling using the carbon-carbon bond length $\sigma \approx 1.4$ Å, so that all dimensions here need to be multiplied by this value. Likewise for nanocones comprising other hexagonal materials, such as boron nitride nanocones, an appropriate value of σ may be used when applying this model. Thus, to determine atomic locations of every atom, we must be able to locate the vertex of every point in the triangular panel relative to the conical vertex. This may be achieved by using the angle ϕ as defined above and also

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 16 July 2018 doi:10.20944/preprints201807.0272.v1

Peer-reviewed version available at Nanomaterials 2018, 8, 624; doi:10.3390/nano8080624

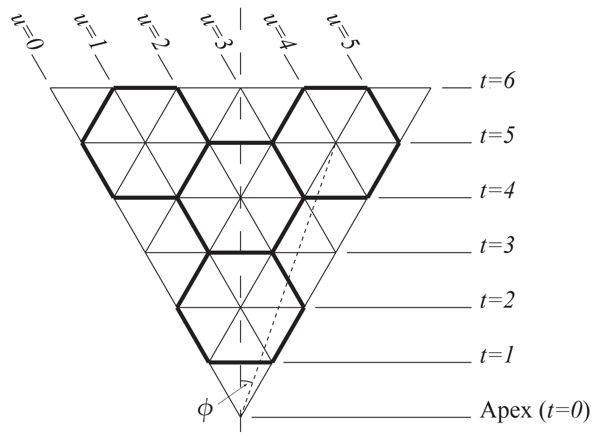

Figure 1: Geometry of single panel (nanocones comprise from one to five such panels mapped onto a right circular cone).

the distance s to any point from the vertex. From the definitions of t and ϕ, given previously, and using basic trigonometry we may derive

$$s = (\sqrt{3}/2)t\sec\phi. \tag{1}$$

The next step in constructing a cone is to map the points from the flat triangular panel(s) onto a right circular cone. An example of such a cone is given in Fig. 2 where the slant length from the vertex s is the same as the distance from the verex to any point in the flat triangular panel defined above, and the parameters r and z denote the radius and height, respectively. Since the surface of the cone comprises an integer number of triangular panels $n \in \{1, 2, 3, 4, 5\}$, then from basic trigonometry we can show that the conical angle $\alpha/2$ is given by $\alpha/2 = \sin^{-1}(n/6)$. From this result we may determine the rolled-up radius r_0 and height z_0 in terms of s and n by the formulae

$$r_0 = ns/6, \quad z_0 = s(1 - n^2/36)^{1/2}. \tag{2}$$

Using these and (1) we are then able to give (2) in terms of t and ϕ as

$$r_0 = \frac{\sqrt{3}}{12}nt\sec\phi, \quad z_0 = \frac{\sqrt{3}}{12}(36 - n^2)^{1/2}t\sec\phi. \tag{3}$$

We now introduce a variable u which denotes the individual points on a single horizontal line. With reference to Fig. 1 we see that every point on a single panel may then be determined from a unique pair of numbers (t, u) where t denotes the line and u the point on that line such that $u \in \{0, 1, 2, \ldots, t\}$. The angle ϕ is given by

$$\phi = \tan^{-1}\left(\frac{2u - t}{\sqrt{3}t}\right). \tag{4}$$

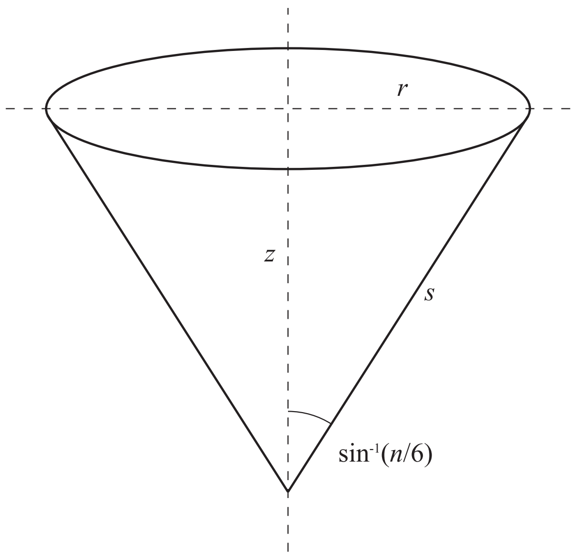

Figure 2: Geometry of right circular cone showing radius r, height z and slant length from vertex s (cone angle is determined from number of panels n).

The numbers (t, u) may also be used to determine the points in the panel which correspond to atomic locations and those which do not. To transform the triangular lattice into an hexagonal lattice (for the case of a carbon nanocone) one third of the points represent the holes at the centre of hexagons and therefore do not correspond to atoms, and the remaining two thirds of lattice points then denote the locations of carbon atoms in the panel. With reference to Fig. 1 we see that when $t + u = 3k$, where k is any integer, so that the lattice point denoted by (t, u) corresponds to a hole. Furthermore, from (4) it follows that

$$\sec\phi = \frac{2}{\sqrt{3}t}(t^2 - tu + u^2)^{1/2},$$

and thus from (3) we may derive

$$r_0 = \frac{n}{6}(t^2 - tu + u^2)^{1/2}, \quad z_0 = \frac{(36 - n^2)^{1/2}}{6}(t^2 - tu + u^2)^{1/2}. \tag{5}$$

With all the points on a single panel determined by the variables (t, u) and the radius r_0 and height z_0 determined in terms of these variables, all that remains is to map these points to a system of three dimensional Cartesian coordinates (x, y, z). With reference to Fig. 3, it is clear that n copies of the panel are needed to complete the cone and we align each panel such that its centre lies on the angle $\theta = 2\pi k/n$, where $k \in \{0, 1, \ldots, n-1\}$, and thus the coordinates of a lattice point mapped onto the three dimensional surface are

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 16 July 2018 doi:10.20944/preprints201807.0272.v1

Peer-reviewed version available at *Nanomaterials* **2018**, *8*, 624; doi:10.3390/nano8080624

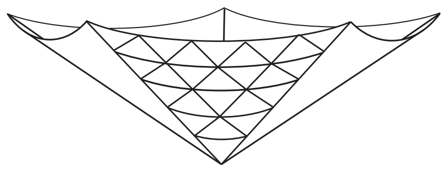

Figure 3: Example of cone comprising five panels (triangular tessellation is shown on only one panel).

given by

$$x = r_0 \cos\left(6\phi/n + \theta\right), \quad y = r_0 \sin\left(6\phi/n + \theta\right), \quad z = z_0, \tag{6}$$

where r_0 is given by $(5)_1$, ϕ is given by (4), and the z-coordinate is precisely as given in $(5)_2$.

Therefore, by mapping points from triangular shaped panels onto a right circular cone, we are able to uniquely determine the coordinates of any point in the rolled-up model. An example of a cone constructed from the rolled-up model with $n = 5$ is shown in Fig. 4. However, in so doing we compromise the assumption that all bond lengths are equal since the bonds lying in planes including the on axis (for example, using the (t, u) notation, those between the points $(t, 0)$ and $(t + 1, 0)$) have no shortening due to curvature, yet all other bonds do have some curvature induced shortening. The bonds most affected are those lying in planes perpendicular to the conical axis, and furthermore those bonds lying nearer to the conical vertex are affected more than those further from the axis where the conical radius is larger. In the following section we will describe a new geometric model which makes some correction for this curvature induced shortening.

4 Calculation

4.1 New geometric model formulation

The starting point for the new geometric model is to reconsider equations $(2)_1$ and $(2)_2$ in an effort to prescribe relationships for r and z which take into account the curvature issues mentioned in the previous section. We remark that in the construction of this new model we will continue to use the parameter s, even though it no longer denotes the slant length from the vertex in the new model. Strictly speaking the new model admits some freedom and does not describe a geometrically precise cone. Therefore, whenever s is used, it should be thought of as a parameter which only corresponds to the slant length in the case of the cone in the corresponding rolled-up model. As we shall show, the scale of s is preserved in the new model so that it represents distance along the profile of the cone.

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 16 July 2018 doi:10.20944/preprints201807.0272.v1

Peer-reviewed version available at *Nanomaterials* **2018**, *8*, 624; doi:10.3390/nano8080624

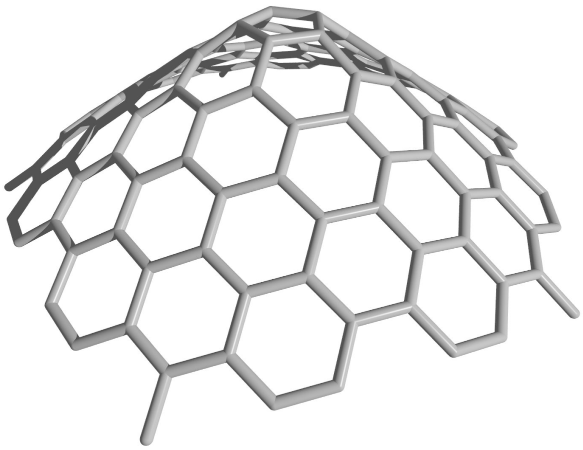

Figure 4: Cone constructed from rolled-up model with $n = 5$.

As previously mentioned, the bonds lying in the planes perpendicular to the cone axis suffer the greatest curvature distortion in terms of the shortening of the Euclidean distance between lattice points. Therefore, a first step in formulating a corrected curvature model is to adjust the radius r so that these bonds are identically equal to the bond length. With reference to Fig. 1 we see that the bonds in question are those that are bisected by the mid-line of the triangle and occur for every odd value for t. We denote the angle ϕ for these bonds as ϕ_r and from geometric considerations we can show that

$$\phi_r = \sin^{-1}(1/2s). \tag{7}$$

Now if we consider a triangle lying in the plane perpendicular to the cone axis and containing one of these bonds, and we construct an isosceles triangle comprising the bond in questions as its base and the point where the cone axis passes through the plane as the third vertex. From this it is clear that the two equal sides of this triangle are of length r and the third side is unity. Furthermore the angle between the equal sides is $2\phi_r$ which has been scaled by a factor $6/n$. Therefore, from the cosine rule we may write

$$1 = 2r^2 \left[1 - \cos\left(\frac{12\phi_r}{n}\right)\right],$$

which can be rearranged to give

$$r = \frac{1}{2}\mathrm{cosec}\left(\frac{6}{n}\phi_r\right),$$

and substituting (7) finally yields

$$r = \frac{1}{2}\mathrm{cosec}\left(\frac{6}{n}\sin^{-1}\left(\frac{1}{2s}\right)\right). \tag{8}$$

Peer-reviewed version available at Nanomaterials 2018, 8, 624; doi:10.3390/nano8080624

Thus, we have derived an equation which approximates $(2)_1$ for large values of s. This large s behaviour can be quickly established by considering the limit of s becoming large so that in that limit $\sin^{-1}(1/2s)$ approaches $1/2s$ and likewise $\operatorname{cosec}(3/sn)$ approaches $sn/3$. We also comment that while the derivation of (8) proceeds from discrete considerations, it can be applied for arbitrary real values of s and n, provided that care is taken to avoid the nonanalytic points. In particular, we note that the vertex itself corresponds to the value $s = 0$ in the rolled-up model, but in the new model the radius is not defined for $s = 0$. Further, we comment that the expression in (8) can be expanded as a series in terms of $1/s$ and in doing so yields

$$r = \frac{sn}{6}\left(1 + \frac{36 - n^2}{24n^2s^2} + \frac{(36 - n^2)(17n^2 + 252)}{5760n^4s^4}\right) + \mathcal{O}\left(\frac{1}{s^5}\right),$$

which shows that the leading order term is precisely the expression for r_0 and subsequent terms can be thought of as correction terms to the rolled-up conical radius.

While (8) is a compact expression, it does involve trigonometric functions. However, it is worth noting that for $n \in \{1, 2, 3, 4\}$, (8) can be expressed explicitly as algebraic functions of s. For some particular values of n (most notably $n = 2$) these relations are strikingly simple and given by

$$\begin{aligned}
\mathrm{n} = 1, \quad r &= \frac{s^6}{(4s^2-1)^{1/2}\,(3s^4 - 4s^2 + 1)},\\
\mathrm{n} = 2, \quad r &= \frac{s^3}{3s^2 - 1},\\
\mathrm{n} = 3, \quad r &= \frac{s^2}{(4s^2-1)^{1/2}},\\
\mathrm{n} = 4, \quad r &= \frac{s^{3/2}}{\left[2s^3 - (s^2-1)(4s^2-1)^{1/2}\right]^{1/2}},
\end{aligned}$$

and the derivations of these relations are given in the Appendix. We note that the case for $n = 2$, the relationship for r reduces to a very simple rational function of s.

The next step in the development of the new model is to derive a new relationship for z. If we consider the expressions from the rolled-up model given in $(2)_1$ and $(2)_2$, we notice that they satisfy the identity

$$\left(\frac{dr_0}{ds}\right)^2 + \left(\frac{dz_0}{ds}\right)^2 = 1, \tag{9}$$

and this relationship is independent of the value of n. This result has an obvious geometric interpretation, which says the infinitesimals dr_0 and dz_0 are the perpendicular sides of a right-angle triangle with hypotenuse ds, which is to say that ds is the infinitesimal distance along the slanted profile of the cone. In this new model we determine z by imposing that s continues to represent the slant length in the new model and therefore the relationship (9) continues to hold for r and z. In other words, we define z by the indefinite integral

$$z = \int_0^s \left\{ 1 - \left[\frac{d}{d\xi} \left(\frac{1}{2\sin\left(\frac{6}{n}\sin^{-1}\frac{1}{2\xi}\right)} \right) \right]^2 \right\}^{1/2} d\xi, \tag{10}$$

which satisfies the constraint that for $s = 0$ then $z = 0$. By evaluating the derivative in (10) and simplifying yields

$$z = \int_0^s \left(1 - \frac{9\cos^2\left(\frac{6}{n}\sin^{-1}\frac{1}{2\xi}\right)}{n^2\xi^2(4\xi^2-1)\sin^4\left(\frac{6}{n}\sin^{-1}\frac{1}{2\xi}\right)} \right)^{1/2} d\xi. \tag{11}$$

However, the integrals (10) or (11) are not trivial to perform analytically and so for the purposes of calculation it is useful to calculate a series for z in terms of $1/s$. Taking the asymptotic series for the integrand in (11) and integrating term by term we find that

$$z = \frac{s\sqrt{36-n^2}}{6} \left(1 - \frac{1}{24s^2} - \frac{17n^2+192}{5760n^2s^4} \right) + \mathcal{O}\left(\frac{1}{s^5}\right), \tag{12}$$

where we comment that the leading order term is precisely the expression for z_0 and subsequent terms can be considered curvature related corrections to the z coordinate. By this we mean that the higher order terms in (12) arise directly from the attempt to accommodate changes in curvature close to the vertex. We also comment that the series or the integrand converges absolutely for $s > 1$ and thus for all physically interesting values of s, the changing the order of the sum and integral is valid.

5 Results and discussion

In Fig. 5 we show on the (r, z)-plane the locations for atoms close to the conical vertex. Here we see the main difference in the predictions between the rolled-up and new geometric models is that r tends to be slightly larger in the new geometric model, meaning the cones would tend to have a slightly puckered shape. The results of the simulation confirm that the new geometric model is closer to to the resulting structure after relaxation than the conventional rolled-up model. In fact, it would appear that the new geometric model slightly underestimates the degree of puckering that results from the numerical relaxation process.

In Fig. 6 we plot the carbon-carbon bond length as a function of conical height z. In this figure we see that the rolled-up model predicts that as we approach the vertex, certain bond lengths are substantially less than the bond length in the flat graphene. This is not an intentional prediction of the model but rather an artifact of the rolled-up process. In the case of the new geometric

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 16 July 2018 doi:10.20944/preprints201807.0272.v1

Peer-reviewed version available at *Nanomaterials* **2018**, *8*, 624; doi:10.3390/nano8080624

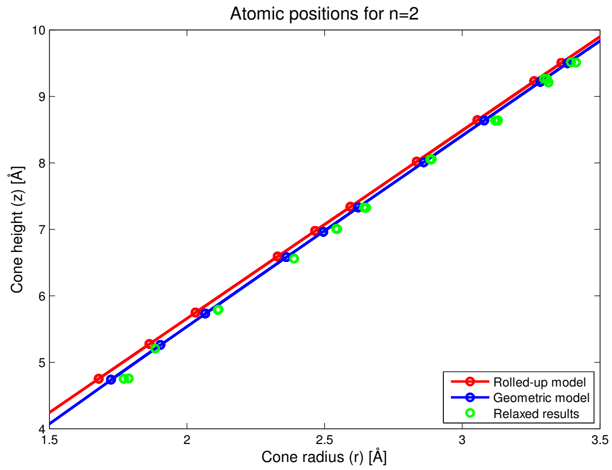

Figure 5: Atomic positions as predicted by rolled-up, new geometric and simulation models.

model we try as much as is possible to make all the bond lengths the same but this is not completely satisfied and we observe that some bonds closer to the vertex are larger than the bond length in the flat graphene. Although it should be noted that this is an artifact of the assumptions of the geometric model and not an intentional prediction of the model. However, the magnitude of the lengthening is generally less than the degree of shortening in the rolled-up case. The results of the simulation show a definite trend of bond lengthening closer to the conical vertex, which is probably due to repulsive interactions between atoms on opposite sides of the cone. We comment that the primary effect in approaching the cone vertex is an increased localisation of the double bonding and a reduction in the aromaticity, approaching fullerene behaviour. This means that bonds become increasingly single or double in character. It is revealed in the relaxed numerical results in Figure 6, and it is an effect that is not taken into account in the new geometric model proposed here.

In Fig. 7 we plot the bond angles as a function of conical height z. In this figure we see that the two models are in approximate agreement, although the variance in the bond angle for a particular value of z is lower than that in the geometric prediction. The results of the simulation show the trend of decreasing bond angle is also matched in the simulation. For small values of z (less than 10 Å) the variance in the simulation data is even lower than that predicted by the new geometric model which means that once again the geometric model is capturing the right trend but slightly under estimating the numerical picture.

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 16 July 2018 doi:10.20944/preprints201807.0272.v1

Peer-reviewed version available at Nanomaterials 2018, 8, 624; doi:10.3390/nano8080624

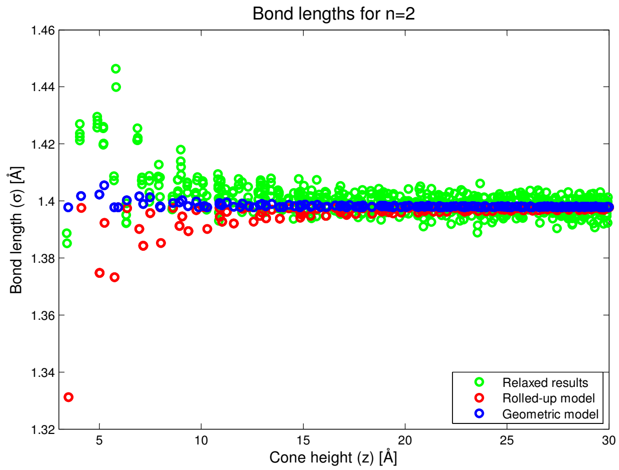

Figure 6: Bond lengths as predicted by rolled-up, new geometric and simulation.

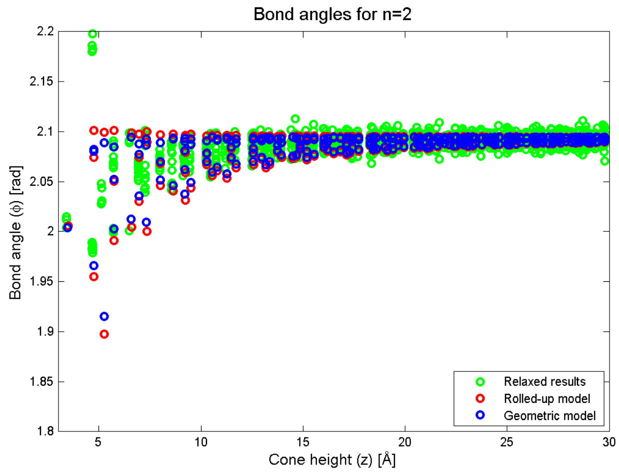

Figure 7: Bond angles as predicted by rolled-up, new geometric and simulation.

6 Conclusions

In this paper we have proposed a new geometric model for carbon nanocones and we have examined the fine geometric structure using molecular simulation as a way of assessing the two models for nanocone geometric structure: the classical rolled-up model and a new geometric model proposed here by the authors. The

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 16 July 2018 doi:10.20944/preprints201807.0272.v1

Peer-reviewed version available at *Nanomaterials* **2018**, *8*, 624; doi:10.3390/nano8080624

results indicate that key features of the geometric structure such as conical radius r as a function of distance from the vertex z, and variation in bond angle exhibit trends which are predicted by the geometric model. However, the new geometric model slightly underestimates both of these effects. The simulation also shows a marked increase in bond length which is also an artefact of the geometric model. Again the magnitude of this effect is underestimated by the geometric model. A future direction of research will be to modify the geometric model to accurately capture the bond lengthening effect which will yield even better predictions for atomic locations and bond angle variability. An additionally future direction may be the introduction of a Burgers vector which may enable the model to be applied to nanocones with a screw dislocation stacking fault.

We further comment that the model proposed here has certain limitations in its applicability. Firstly, the curvature effect addressed is a secondary one, since as the distance from the cone tip increases, the effect rapidly decays. Hence, it is only a relatively small correction as the tip is approached, and as the above numerical results indicate, can be accommodated by numerical modelling with a relatively few number of molecular dynamics iterations, or via the first few steps in geometric optimisation using a quantum chemical code. Nevertheless, the new model proposed here has the potential to save computing time in such alternatives. Secondly, the new model only applies to a very limited range of cone geometries, namely symmetrical cones and in particular those with a symmetrical vertex. We have avoided this difficulty by simply removing the cone vertex from the analysis, to avoid addressing this question. For example, the new model does not apply when a pentagon associated with the nanocone vertex does not lie exactly on the cone axis. Of course, this significantly reduces the utility of the model, and for example in the case of four panel cones with a square at the cone vertex, the model does not address the necessary structural rearrangements in order to convert such a vertex into one containing only pentagons. Such structural rearrangements have significant effects on the bond lengths out to at least 1nm, and this is the range over which the current model shows the most deviation from the conventional model. However, our results do apply for all five vales of n, and in particular for $n = 2$ as shown in Fig. 6 and Fig. 7 where the cone vertex has been replaced by hydrogen atoms, and we emphasise that the model presented here focusses on the structure leading up to the vertex, rather than the vertex structure itself.

A Algebraic formulae for r

In this appendix we outline the derivation of algebraic expressions for r for $n \in \{1, 2, 3, 4\}$. The method of removing the trigonometric functions from (8) is to use the part angle and multiple angle formulae for the sine function to produce an expression with terms of the form $\sin\left(\sin^{-1} x\right)$ and $\cos\left(\sin^{-1} x\right)$, and then replace these expressions with x and $\sqrt{1-x^2}$, respectively. We comment that in this process we are dealing with essentially multivalued functions. However,

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 16 July 2018 doi:10.20944/preprints201807.0272.v1

Peer-reviewed version available at *Nanomaterials* **2018**, *8*, 624; doi:10.3390/nano8080624

for our purposes, we require only the value which is usually the positive root and which includes zero in the range of possible values.

For $n = 1$ we make use of the trigonometric identity

$$\sin 6\theta = 6\cos^5\theta\sin\theta - 20\cos^3\theta\sin^3\theta + 6\cos\theta\sin^5\theta, \tag{13}$$

so that

$$\begin{aligned} r &= \left[2\sin\left(6\sin^{-1}\frac{1}{2s}\right)\right]^{-1} \\ &= \left[2\left(6\frac{(4s^2-1)^{5/2}}{(2s)^6} - 20\frac{(4s^2-1)^{3/2}}{(2s)^6} + 6\frac{(4s^2-1)^{1/2}}{(2s)^6}\right)\right]^{-1} \\ &= \frac{16s^6}{(4s^2-1)^{1/2}\left[3(4s^2-1)^2 - 10(4s^2-1) + 3\right]} \\ &= \frac{s^6}{(4s^2-1)^{1/2}(3s^4-4s^2+1)}. \end{aligned}$$

On utilising the trigonometric identity

$$\sin 3\theta = 3\cos^2\theta\sin\theta - \sin^3\theta, \tag{14}$$

and substituting into (8), for $n = 2$ we obtain

$$\begin{aligned} r &= \left[2\sin\left(3\sin^{-1}\frac{1}{2s}\right)\right]^{-1} \\ &= \left[2\left(3\frac{4s^2-1}{(2s)^3} - \frac{1}{(2s)^3}\right)\right]^{-1} \\ &= \frac{4s^3}{12s^2-3-1} \\ &= \frac{s^3}{3s^2-1}. \end{aligned}$$

The only other case which can be evaluated analytically using just the multiple angle formulae is $n = 3$. Here we employ the simple trigonometric identity

$$\sin 2\theta = 2\cos\theta\sin\theta,$$

which gives

$$r = \left[2\sin\left(2\sin^{-1}\frac{1}{2s}\right)\right]^{-1} = \left[4\frac{(4s^2-1)^{2/3}}{(2s)^2}\right]^{-1} = \frac{s^2}{(4s^2-1)^{1/2}}.$$

In the case $n = 4$, we must use a combination of the trigonometric identity (14) and the half-angle formula

$$\sin\frac{\theta}{2} = \left(\frac{1-\cos\theta}{2}\right)^{1/2},$$

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 16 July 2018 doi:10.20944/preprints201807.0272.v1

Peer-reviewed version available at *Nanomaterials* **2018**, *8*, 624; doi:10.3390/nano8080624

and we are interested in the positive square root. Thus substituting into (8) we may derive

$$r = \left[2\sin\left(\frac{3}{2}\sin^{-1}\frac{1}{2s}\right)\right]^{-1} = \left\{2\left[\frac{1}{2} - \frac{(4s^2-1)^{3/2}}{2(2s)^3} + 3\frac{(4s^2-1)^{1/2}}{2(2s)^3}\right]^{1/2}\right\}^{-1}$$
$$= \frac{2s^2}{\left[8s^4 - s(4s^2-1)^{3/2} + 3s(4s^2-1)^{1/2}\right]^{1/2}} = \frac{s^2}{\left[2s^4 + s(1-s^2)(4s^2-1)^{1/2}\right]^{1/2}}.$$

Finally, for $n = 5$, we comment that an algebraic expression with real coefficients is possible but cumbersome and we note that a general n algebraic expression for r is given by

$$r = \frac{i(2s)^{6/n}}{\left(\sqrt{4s^2-1}+i\right)^{6/n} - \left(\sqrt{4s^2-1}-i\right)^{6/n}},$$

which holds for all $n \in \{1, 2, 3, 4, 5\}$, and from which the simple expressions for $n = 1$, 2 and 3 can be seen to originate immediately.

References

[1] T. W. Ebbesen, Cones and tubes: Geometry in the chemistry of carbon, Acc. Chem. Res. 31 (1998) 558–566.

[2] I. Ihara, S. Itoh, K. Akagi, R. Tamura, M. Tsukada, Structure of polygonal defects in graphitic carbon sheets, Phys. Rev. B 54 (1996) 14713–14719.

[3] B. J. Cox, J. M. Hill, Exact and approximate geometric parameters for carbon nanotubes incorporating curvature, Carbon 45 (2007) 1453–1462.

[4] B. J. Cox, J. M. Hill, Geometric structure of ultra-small carbon nanotubes, Carbon 46 (2008) 711–713.

[5] J. Han, R. Jaffe, Energetics and geometries of carbon nanoconic tips, J. Chem. Phys. 108 (1998) 475672 (7 pages).

[6] H. Heiberg-Anderen, A. Skjeltorp, Stability of conjugated carbon nanocones, J. Math. Chem. 38 (2005) 589–604.

[7] A. Balaban, D. J. Klein, X. Liu, Graphitic cones, Carbon 32 (1994) 357–359.

[8] D. J. Klein, A. T. Balaban, The eight classes of positive-curvature graphitic nanocones, J. Chem. Inf. Model. 46 (2006) 307–320.

[9] J.-C. Charlier, G.-M. Rignanese, Electronic structure of carbon nanocones, Phys. Rev. Lett. 86 (2001) 5970–5973.

[10] R. Mota, M. Machado, P. Piquini, Structural and electronic properties of 240^o nanocones, Phys. Stat. Sol. (c) 0 (2003) 799–802.

[11] R.Pineak, V. A. Osipov, Localized electron states near pentagons in variously shaped carbon nanoparticles, Phys. Lett. A 314 (2003) 315–321.

[12] K. M. Liew, J. X. Wei, X. Q. He, Carbon nanocones under compression: Buckling and post-buckling behaviors, Phys. Rev. B 75 (2007) 195435 (6pp).

[13] P.-C. Tsai, T.-H. Fang, A molecular dynamics study of the nucleation, thermal stability and nanomechanics of carbon nanocones, Nanotech. 18 (2007) 105702 (7pp).

[14] J. X. Wei, K. M. Liew, X. Q. He, Mechanical properties of carbon nanocones, Appl. Phys. Lett. 91 (2007) 261906 (3pp).

[15] S. Zhang, Z. Yao, S. Zhao, E. Zhang, Buckling and competition of energy and entropy lead conformation of single-walled carbon nanocones, Appl. Phys. Lett. 89 (2006) 131923 (3pp).

[16] S. P. Jordan, V. H. Crespi, Theory of carbon nanocones: Mechanical chiral inversion of a micron-scale three-dimensional object, Phys.Rev.Lett. 93 (2004) 255504 (4pp).

[17] S. J. Plimpton, Fast parallel algorithms for short-range molecular dynamics, J. Comp. Phys. 117 (1995) 1–19.

[18] D. W. Brenner, O. A. Shenderova, J. A. Harrison, S. J. Stuart, B. Ni, S. B. Sinnott, A second-generation reactive empirical bond order (REBO) potential energy expression for hydrocarbons, J. Phys.: Condens. Matter 14 (2002) 783–802.