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Continuum and all-atom description of the energetics of graphene nanocones

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Abstract

Energies of graphene nanocones with 1–5 pentagonal disclinations are studied on an atomically detailed level. The numerical results are interpreted in terms of three different contributions to the cone energy: the disclination core energy, the bending energy of the cone surface, and the ‘line tension’ energy of the cone edge that originates in reduced coordination of carbon atoms situated at the edge. This continuum description allows for a construction of analytic expressions for the cone energetics and indicates different regimes of cone sizes in which cones with a particular number of disclinations are preferred energywise. An important result of the study is that the energetics of various types of cones profoundly depends upon whether the dangling carbon bonds at the cone basis are saturated by hydrogen atoms or not. This may be of use for explaining the differences in the yields of various cone types in different production processes.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Carbon (C) atoms are famous for their ability to form various hollow structures [1], the best known of them being fullerenes [2] and carbon nanotubes [3]. Soon after the clear experimental detection of carbon nanotubes [3], conical carbon structures were observed in the process of quenching hot carbon vapor on the graphite substrate [4, 5]. These cones all had the same opening angle, the smallest one of the five that can be constructed from the honeycomb graphene structure (see below). It was later demonstrated that structures of the same type can also be obtained by other experimental procedures, such as pyrolysis of hydrocarbons in a plasma torch [6]. In this procedure, five different types of cone geometries were observed. The yield of conical structures in the prepared samples can be quite high (~20%) [6]. This fact alone indicates the importance of such structures. In addition, conical graphene structures are also predicted to have very specific mechanical [7] and electronic [8] properties, and could possibly be used as nanoscopic electron field emitters. Interestingly, graphite cones were found in natural samples [9] which also highlights the need to understand the occurrence of conical shapes made of carbon.

The polyformity that is characteristic of hollow carbon shapes has its parallel in the structures formed by viral proteins. These also form hollow shells (the so called capsids) that protect the viral genetic material (DNA or RNA). Icosahedral viruses have a structure that is the same as the one exhibited by icosahedral fullerenes [10]. The same proteins that form icosahedral shells may, under different conditions, also form tubular structures, similar in structure to carbon nanotubes. There seems to be a parallel for conical structures also—the core capsids of HIV viruses closely resemble (closed) graphene cone structures, as emphasized in [11]. The investigation of graphene cones may thus have an added value due to the parallelism of structures found in graphene shapes and viral capsids.

Unlike the fullerenes and carbon nanotubes, conical carbon structures are relatively poorly explored. Not much is known about the optimal conditions for their production. A complete understanding of the growth of such structures is also lacking, which is not surprising since the details of the growth of the much more investigated fullerenes and carbon nanotubes are still unknown [12]. Although there have been some proposals that the formation of cones is most likely due to their ‘designability’, i.e. the fact that they are a combinatorially

favorable outcome of the growth [13], it is certainly important to first have a good understanding of and reliable estimates for the cone energies. Various contributions to the cone energetics are not completely self-evident, and it is not straightforward, for example, to estimate the importance of the curvature of the cone surface and its contribution to the total energy of the cone.

In this paper I shall examine the energetics of (single-walled) graphene cones. These cones contain multiple pentagonal defects. Cones with defective carbon rings whose number of sides is less than five are not considered in this study as these are shown to be less stable [14]. To understand various factors that influence the energy of the cones, numerical all-atom calculations of the cone energetics are performed. The numerical results are interpreted in terms of different energy contributions that are disentangled from the total energy balance. This enables construction of reliable *analytical* expressions for the cone energetics.

Section 2 discusses the details of the cone geometry and describes a particular construction scheme of the cones that is used in this study.

Section 3 contains the details of the numerical calculations and their results.

In section 4 the numerical data obtained in section 3 is interpreted in a quite general framework that enables construction of analytic expressions for the cone energies. Four contributions to the cone energy, each of them having a different physical origin, are identified.

Section 5 contains a discussion of the results and some propositions that may relate the results of the article with the experimental data on carbon cones.

2. Construction of cones

There are five different classes of cones that can be constructed from the graphene lattice. These differ in the total number of disclinations (i.e. pentagonal carbon rings) that they contain close to the cone apex, which is directly related to the cone opening angle, θ . The cones can be conceptually constructed by cutting out 60° wedges in the graphene plane, thereby creating a cut-and-fold cone ‘origami’ that can be mathematically folded onto a three-dimensional pyramid-like object. Except for the cone with a single pentagonal disclination, this involves creasing along the lines connecting the neighboring pentagons. When the pyramid-like object is relaxed so that its energy is minimal, the shape acquires a cone-like appearance. Additional reconnections between the carbon atoms (e.g. between any two atoms that are on the cone edge and that could possibly form pentagons if they are sufficiently close [15]) are not allowed during the relaxation process.

With the exception of the cone containing a single pentagonal ring close to its apex, all other cones can be constructed in a multitude of ways, depending on the arrangement of the pentagonal disclinations (see e.g. [16]). These details are irrelevant for this study, as its main aim is to rationalize the cone energetics in the terms that belong to the realm of continuum physics. In each of the cone classes considered in the following, a fixed arrangement of the carbon pentagons is assumed. An isolated pentagon rule [17] was respected by all of the constructions so that the carbon pentagons do not share C–C bonds—each of the pentagons

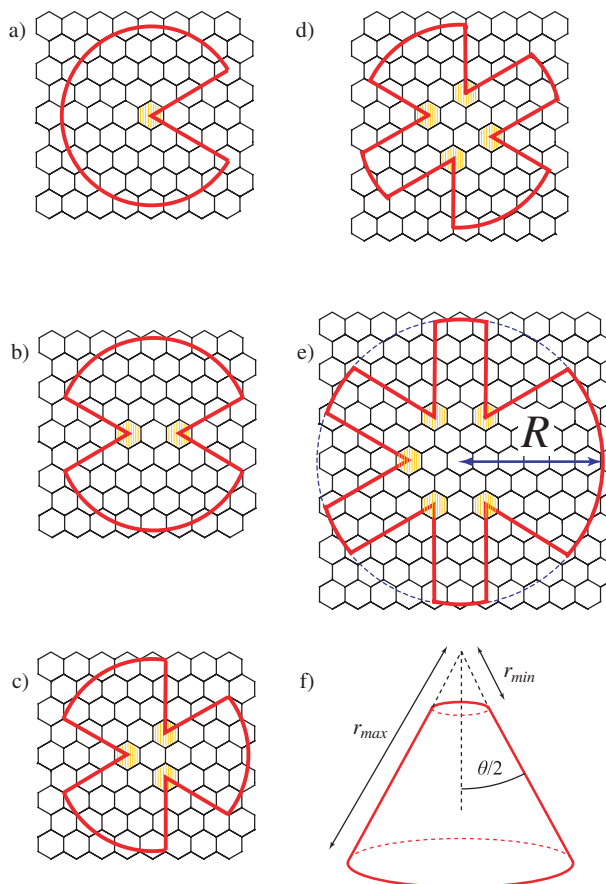


Figure 1. Construction of cones by creation of disclinations (triangular wedges/cuts) in the graphene lattice. The part of the graphene plane bounded by the thick lines is folded into a cone. Panels (a)–(e) display the graphene cut-outs used to construct the cones with one, two, three, four, and five carbon pentagons, respectively. The size of the cones is determined by the radius (R) of the circle denoted by thin dashed line in panel (e). Panel (f) represents the cone and the quantities that define it (see text).

is completely surrounded by hexagons. The parameter that characterizes the cone is its size, i.e. the total number of carbon atoms that it contains. I shall also assume that the distances between the cone apex and its base, measured along the cone surface, are the same irrespective of the point on the base chosen. In other words, this means that the cones considered can be positioned on their base so that the cone apex projects exactly at the center of the base—the cones considered are right cones.

The five different cut-and-fold pieces of graphene plane are illustrated in figure 1. Similar patterns were recently used for the construction of carbon nanotube caps, which necessarily have six pentagonal disclinations [18]. Note that the definition of the cone apex may be somewhat vague. In fact, it may be better to think of these structures as truncated cones or conical frusta. The smaller/top base of the conical frustum is then defined as the region surrounded by the carbon pentagons (for a graphene cone with a single disclination, the top base is the carbon pentagon itself). In the limit of very large cones, the distinction between the truncated cone and the regular cone becomes irrelevant since the radius of the bottom base of the cone is much larger than the radius of the cone top base.

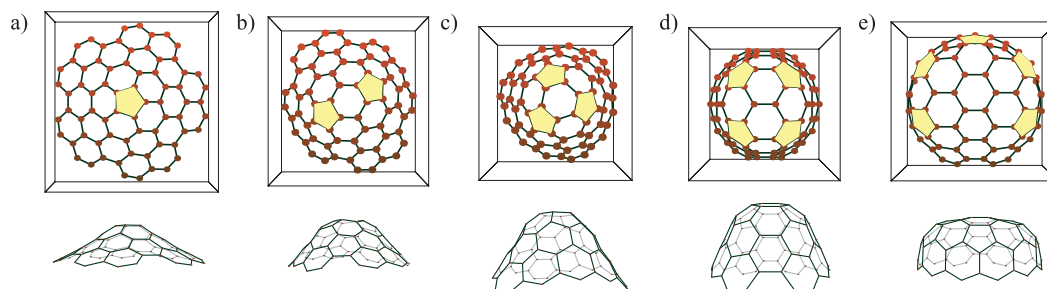


Figure 2. Five different types of cones viewed from above (top row of images) and the side (bottom row of images). Panels (a)–(e) represent the $n = 1$, $n = 2$, $n = 3$, $n = 4$, and $n = 5$ cones, respectively. The cones contain 70, 70, 69, 72, and 74 C atoms for $n = 1, 2, 3, 4$, and 5, respectively.

It is easy to show that the opening angle of the idealized cone (θ , see figure 1(f)) can be related to the total number of disclinations (n) as

$$\theta_n = 2 \arcsin \left(1 - \frac{n}{6} \right). \quad (1)$$

This produces a discrete sequence of possible opening angles, $\theta_n = 112.89^\circ, 83.62^\circ, 60^\circ, 38.94^\circ$, and 19.19° , for $n = 1, \dots, 5$. It shall prove to be of use to consider a (planar) graphene disk as a special case of this construction. In this case, $n = 0$, and $\theta_0 = 180^\circ$.

3. Numerical results for the cone energies

The energetics of carbon–carbon bonding is simulated by using a second-generation reactive empirical bond-order potential by Brenner *et al* [19] which belongs to the Abell– Tersoff class of bond-order potentials. This potential is known to properly account for the anisotropy of C–C bonding. It also approximately includes the many-body effects. After the mathematical folding of the piece of graphene plane was performed and the broken C–C bonds re-established along the edges of the shape (this part of the procedure also forms the carbon pentagons), the resulting structure is used as an initial guess for the conjugate gradient procedure that optimizes its shape so as to minimize the total energy. The numerical procedure used for this purpose is described in detail in [20]. A similar computational procedure (the construction of initial mathematically folded shapes and subsequent relaxation using the conjugate gradient method in combination with Brenner’s potential) has also been used in [21].

Figure 2 displays the top and side views of the five types of cones that have been relaxed to their minimum energy configuration. The cones chosen for display are relatively small so that the details of the shape, including the pentagons around the cone apex, can be easily discerned.

Figure 3 displays the energies of the cones depending on the number of C atoms they contain. In these simulations, the radius of the cut-out shape (denoted by R in figure 1(f)) was varied. The energies displayed are in fact the *excess* energies (ΔE), i.e. the extra energy that the cones have with respect to the energy that the same number of carbon atoms would have in the infinite graphene plane. Brenner’s potential [19] predicts that the binding energy per carbon atom in graphene is $\epsilon_b = -7.39494$ eV [21], so that the energy of $I = N\epsilon_b$ was

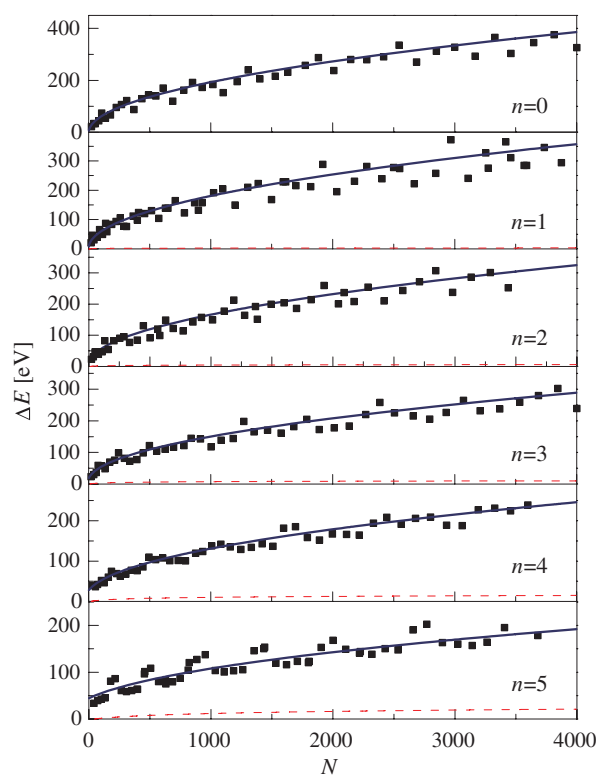


Figure 3. Energies of carbon cones as a function of the total number of carbon atoms. In addition to results for $n = 1, n = 2, n = 3, n = 4$, and $n = 5$ cones, the data for ‘ $n = 0$ cones’ i.e. graphene disks is also shown. The numerical results in these plots are denoted by full squares. Full thick lines are a result of the analytical expression for the cone energy, equation (7). The thin dashed lines denote the bending (curvature) contribution to the cone energy, equation (2).

subtracted from the total energy of the cones in order to obtain the excess energy. The results for excess energies of graphene disks are also included in figure 3. Note the scatter of the data. It is not due to some numerical instability as shall be explained in section 4.

4. General considerations of the cone energetics and interpretation of numerical data

To understand the numerical results obtained in the previous section, it helps to isolate four different contributions to the

energy of a cone. First, there is a part of the energy that is directly related to the number of disclinations in the cone. Each of the pentagonal disclinations (defects) carries the so-called disclination core energy (D) [21, 22] that is related to the change (reduction) of the local coordination of entities in the disclination. Second, the cones have a curved surface, so that there is a contribution to the total energy that is of the bending type (B) and directly related to nonvanishing curvature of the cone surface. For $n \neq 0$ this energy can be expressed as [21]

$$B = \pi c_0 \frac{\cos^2(\frac{\theta_n}{2})}{\sin(\frac{\theta_n}{2})} \ln\left(\frac{r_{\max}}{r_{\min}}\right), \quad (2)$$

where c_0 is the graphene bending rigidity [21], and r_{\min} and r_{\max} are the distances from the cone apex to the approximate top and bottom bases of the cone, respectively (see figure 1(f)). Equation (2) does not include the contribution related to bending of the shape surface in the top base, i.e. in the region where the disclinations accumulate. Assuming that the top base is nearly flat, or that the number of atoms that make it is much smaller than the total number of atoms in a whole conical shape, this part of the energy can be neglected. Third, there is an energy resulting from the coordination of the entities in a shape. This energy can be approximated as a sum of the energy that the same number of carbon atoms would have in the infinite graphene sheet (negative, binding contribution, I) and the cone-edge energy related to reduced coordination of atoms located along the line that defines the bottom cone base (positive contribution, L). The effect of the reduced number of neighbors for the atom at the cone edge could also be called the edge-tension energy and is obviously proportional to the length of the cone base. The total cone energy, E is thus $E = nD + B + I + L$. Note that B , I , and L depend on the size of the cone, i.e. on the total number of atoms, N , that make it, but in a very different functional manner. The excess energy of the cones is obviously given by

$$\Delta E = nD + B + L. \quad (3)$$

The total area, A , of the conical shape can be approximately written as

$$A = \pi \sin\left(\frac{\theta_n}{2}\right) \left\{ r_{\max}^2 - r_{\min}^2 \left[1 - \sin\left(\frac{\theta_n}{2}\right) \right] \right\}, \quad (4)$$

so that the total number of atoms in the shape is

$$N = A/A_c, \quad (5)$$

where the area per atom in the infinite planar sheet of graphene is given by $A_c = r_0^2 \sqrt{3}/2$. For the equilibrium nearest neighbor C–C distance in graphene, r_0 , Brenner's potential predicts a value of [21] $r_0 = 1.4204 \text{ \AA}$. The cone-edge energy depends on the total number of entities along the bottom basis of the cone. The total length of the bottom base edge is $2r_{\max} \sin(\theta_n/2)\pi$, so that

$$L = 2\delta r_{\max} \pi \sin\left(\frac{\theta_n}{2}\right), \quad (6)$$

where δ is the average line tension energy per unit length of the cone base. Combining equations (3), (2), and (6) yields the

analytical expression for the dependence of the excess energy on the r_{\max} parameter of the cone:

$$\Delta E = nD + \pi c_0 \frac{\cos^2(\frac{\theta_n}{2})}{\sin(\frac{\theta_n}{2})} \ln\left(\frac{r_{\max}}{r_{\min}}\right) + 2\delta r_{\max} \pi \sin\left(\frac{\theta_n}{2}\right). \quad (7)$$

The dependence of r_{\max} on N can be obtained from equations (4) and (5) which yields

$$r_{\max} = \sqrt{\frac{NA_c}{\pi \sin(\frac{\theta_n}{2})} + r_{\min}^2 \left[1 - \sin\left(\frac{\theta_n}{2}\right) \right]}. \quad (8)$$

As mentioned earlier, the r_{\min} parameter is somewhat difficult to fix, but it can be estimated on the basis of constructions shown in figure 1. Values of $r_{\min} = \{r_0/\sin(\theta_1/2), r_0\sqrt{3}/\sin(\theta_2/2), r_0\sqrt{3}/\sin(\theta_3/2), r_0\sqrt{21}/[2\sin(\theta_4/2)], 2r_0\sqrt{3}/\sin(\theta_5/2)\}$ were used for $n = \{1, 2, 3, 4, 5\}$ constructions from figure 1, respectively. For $r_{\max} \gg r_{\min}$, the precise value of r_{\min} becomes irrelevant. It can be seen in figure 3 that equation (7) (full thick lines) nicely accounts for numerical data on cone energetics for all n values. In these calculations, the core disclination energy and the graphene bending rigidity were set to $D = 1.83 \text{ eV}$ and $c_0 = 0.83 \text{ eV}$, respectively, in agreement with the values found in [21], and the best-fit value for δ was found to be $\delta = 1.30 \text{ eV \AA}^{-1}$ (the same value was used for all n values of the cones). This should be the edge energy lost per unit length of the edge due to the reduced coordination of the carbon atoms situated on the cone edge. The atoms at the edge can have one, two, but also three nearest neighbors (see cones in figure 2). The energy that is lost due to a missing neighbor should be about $2.46 \text{ eV} (|\epsilon_b|/3)$. The exact value of δ depends on the edge of a particular cone considered, i.e. the number of singly, doubly, and triply coordinated carbon atoms and their distances. These characteristics depend both on the construction of the cone and on its total size (r_{\max}). This explains the reason for the scatter of the data in figure 3—cones of different sizes generally have differently coordinated edges, so it may happen that in a cone of a particular size all of the edge atoms are doubly or triply coordinated, which is an energetically favorable case (this is the case for all cones shown in figure 3). Cones of some other sizes may have edges that contain many singly coordinated edge atoms. Since all of the structures are constructed from a periodic lattice, cones with many singly coordinated edge atoms repeatedly appear (as a function of the cone size) as do those that have a minimal number of poorly coordinated edge atoms. This effect can be seen in figure 3, especially for $n = 4$ and $n = 5$ cones, as a kind of modulation of the energy curve. This is an interesting combinatorial problem that I shall not dwell too much upon, as the details of the shape that depend on the precise arrangement of atoms are not of interest in this article. Nevertheless, it should be noted that the value of δ obtained from the fits can be nicely explained on the basis of the energetics of C–C bonding. An important objection that could be made here is that the effective Brenner's potential cannot be reliably used in situations when there are dangling bonds. In [23] it was suggested that Tersoff's version of carbon–carbon bonding overestimates the excess dangling bond energy. Complex non-pairwise-additive effects may be also expected in cases when there are dangling bonds and

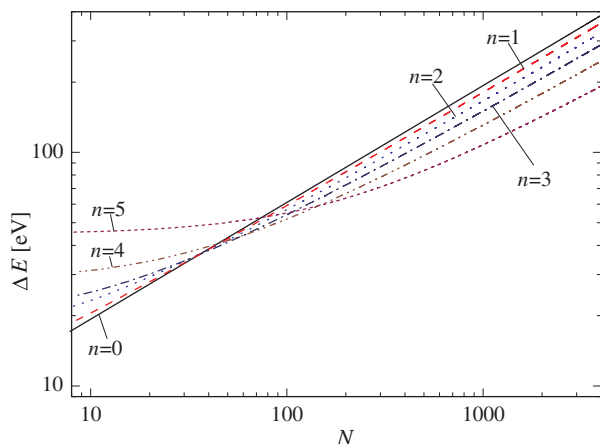


Figure 4. Analytic (continuum) expressions for the cone energetics as a function of the total number of atoms in the cones for the case when the dangling carbon bonds at the cone edge are not saturated ($\delta = 1.30 \text{ eV } \text{\AA}^{-1}$).

these could be beyond the reach of the potential model used in this study. Nevertheless, these effects can be expected only to renormalize the value of δ , while the effective ‘line-tension’ energy should still remain a useful concept even in that case. Even if the dangling bonds of C atoms at the cone edge were saturated by adsorption of hydrogen atoms [24–26], the reasoning in terms of the edge (line) tension energy would still be useful, only the value of δ would differ (see below). It is also appropriate to note here that the calculations that treated the dangling bonds in the same fashion as described above have been used in a molecular dynamics scheme to simulate the dynamics of carbon ‘ribbons’ that may form cylinders (nanotubes) by saturating some of their dangling bonds [15].

Looking at the data in figure 3 it may seem that the edge-tension energy dominates the cone energetics. This is evident both from the scatter of the data and from the apparent \sqrt{N} behavior of the excess energy. It is indeed the case except perhaps for $n = 5$ cones, for which the bending contribution to the cone energy becomes important. This can be seen from the dashed lines in figure 3 that indicate the bending contribution to the cone energy (equation (2)). This is in fact one of the important results of this study: the bending/curvature contribution to the cone energetics is secondary when compared to the dangling bond/edge energy, so the considerations that concentrate exclusively on this part of the cone energy in order to explain the occurrence of the cones with a particular opening angle in fact deal with a rather small contribution to the total cone energy [4] (at least in cases when the bonds are not saturated by hydrogen atoms, see below).

It is instructive to compare the analytic expressions for the cone energetics in a single plot, as is done in figure 4 (note the log scales on both axes and that the curve corresponding to graphene disks is a straight line). It can be seen that the graphene disks have the smallest excess energies for a small number of C atoms ($N < 50$). When the number of atoms in the structures reaches about $N = 50$, the excess energies of all of the cones except the $n = 5$ cone become smaller than the excess energy of the disk. At this point the radius

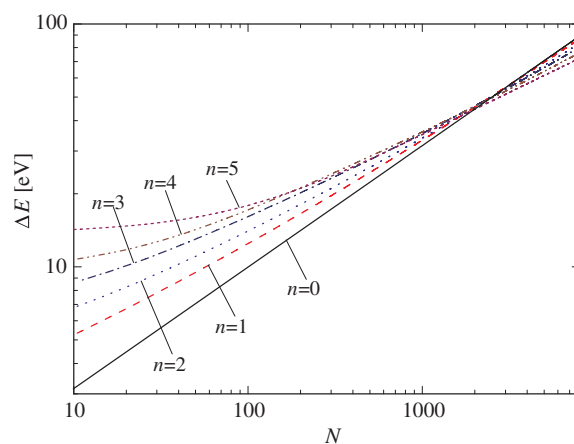


Figure 5. Analytic (continuum) expressions for the cone energetics as a function of the total number of atoms in the cones for the case when the dangling carbon bonds at the cone edge are saturated with hydrogen atoms ($\delta = 0.213 \text{ eV } \text{\AA}^{-1}$).

of the disk is about 0.7 nm. When N reaches about 150 atoms, the excess energy of $n = 5$ cones becomes the smallest and remains so as N increases. The transition region in the cone sizes that is observed in the energetics of the cones smaller than about 150 atoms is a consequence of the interplay of different contributions to the excess energy of the cone. After a critical size of the graphene disk ($N \approx 50$) the cone structures become energetically preferable, since the energy that is lost due to the creation of disclinations is compensated by the reduced length of the cone edges in comparison with the circumference of the graphene disk. For large enough cones ($N > 150$), this effect dominates the energetics of the structures considered, and $n = 5$ cones thus have the lowest excess energies, although they contain five pentagonal disclinations and their surface has the largest curvature.

It should be instructive to see how all of these conclusions change if the dangling bonds were saturated by hydrogen atoms. This may be the case for carbon cones obtained by pyrolysis of hydrocarbons [6]. The energy of the C–C bond in graphene is [19] 4.93 eV, while the energy of the C–H bond is [19] 4.526 eV. Thus the energy that is lost when replacing the C–C with a C–H bond is 0.404 eV. This is also the energy that is lost *per carbon atom* at the cone edge when one of its bonds has been saturated by a H atom. This is significantly smaller than the 2.46 eV lost per carbon atom with a missing carbon neighbor. The line tension energy in this case is thus $\delta = 0.404/2.46 \times 1.30 \text{ eV } \text{\AA}^{-1} = 0.213 \text{ eV } \text{\AA}^{-1}$, more than six times smaller than in the case of unsaturated bonds. Figure 5 shows how the energetics of cones and disks whose edges are saturated by hydrogen atoms changes with the total number of carbon atoms in the structures. It can be seen that the graphene disks are the structures with the lowest excess energies up to a total number of about $N = 2000$ carbon atoms (compare this with $N = 50$ in the unsaturated bond case). When $N > 2000$, the cones have lower excess energies than graphene disks. Again, the $n = 5$ cones are the most favorable in this respect. There is also an interesting crossover in cone energetics when $N < 2000$ —note how the curve for $n = 5$ crosses the $n = 4$ and 3 curves for $N \approx 170$ and

700, respectively. In this case, the bending contribution to the cone energy becomes important even for large cones. For example, for the $n = 5$ cone containing ≈ 9000 carbon atoms, the bending contribution to its energy is $B = 27.1$ eV, while the edge energy is $L = 39.1$ eV.

Intriguingly, for the case of carbon cones whose edge atoms are saturated by hydrogen atoms, the flat disk structures have the lowest excess energies up to a much larger number of atoms than in the case of unsaturated, dangling carbon bonds at the cone edges. The crossover region at which the cones become preferred energywise is in this case positioned at a significantly larger number of carbon atoms (2000 versus 150 for the dangling bonds case).

5. Discussion

This study has demonstrated that graphene cones are superior to graphene disks with respect to their excess energy for structures made of a relatively small number of atoms ($N > 50$ for the dangling bond case and $N > 2000$ for the hydrogen saturated bonds at the cone edge). For structures containing a very large number of atoms, $n = 5$ cones always have the smallest excess energy. For the dangling bond case, of all the shapes considered in this study that contain more than $N = 150$ atoms, the $n = 5$ cones have the smallest excess energy. One could speculate that this may be one of the reasons for the initial experimental observation of only $n = 5$ structures [4, 5]. Later experiments have detected all possible cones [6] and yields of cones of different n -type show a non-monotonic dependence on the number of disclinations, n . It would be tempting to assign this effect to the details of the energetics of carbon cones in the crossover region of sizes ($50 < N < 150$). This explanation would require that the stable seeds for the cone growth are nucleated in this interesting region of sizes. Of course, one should keep in mind that the growth of these structures is most likely governed by kinetics and entropy in addition to energetics.

Intriguingly, it has been shown that the energetics importantly changes when one considers the cones whose edges are saturated by hydrogen atoms. In that case, the crossover region is positioned at a much larger number of atoms, and the flat graphene disks are the lowest excess energy structures up to about 2000 carbon atoms. It is thus plausible that the yields of different cone structures will be different depending on whether the hydrogen atoms are present in the production process, assuming of course that they have an active role in stabilizing the carbon edges.

In summary, it has been demonstrated that the cone-edge energy is the most important contribution to the total energy for cones that have more than about 150 (2000) carbon atoms. The bending energy is significantly smaller from the dangling bond energy and becomes progressively less important for

larger cones, since it scales with the total number of atoms, N , as $\log(N)$, while the dangling bond energy scales as \sqrt{N} . For cones whose edges are saturated by the hydrogen atoms, consideration of the bending contribution to the total energy is essential for structures containing up to about 2000 carbon atoms.

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