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**PUBBLICAZIONI**

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**A NUMERICAL INVESTIGATION ON CARBON-NANOTUBE  
GEOMETRIES**

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# A NUMERICAL INVESTIGATION ON CARBON-NANOTUBE GEOMETRIES

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ABSTRACT. We investigate carbon-nanotubes under the perspective of geometry optimization. Nanotube geometries are assumed to correspond to atomic configurations which locally minimize Tersoff-type interaction energies. In the specific cases of so-called zigzag and armchair topologies, candidate optimal configurations are analytically identified and their local minimality is numerically checked. In particular, these optimal configurations do not correspond neither to the classical Rolled-up model [5] nor to the more recent polyhedral model [3].

## 1. INTRODUCTION

Carbon nanotubes are believed to be promising nanostructures for the development of innovative technologies ranging from next-generations electronics, to optics, mechanics, and pharmacology. Despite the large research activity on these nanostructures, the modeling of their fine geometry is still debated. In fact, different geometric models for carbon nanotubes have been set forth by characterizing indeed the nanostructure by prescribing different atomic positions.

Intuitively, carbon nanotubes can be visualized as atomic configurations showing cylindrical symmetry. One can interpret them as the result of the rolling-up of a graphene strip (sometimes referred to as a *graphene nanoribbon*). More precisely, assume to be given the *hexagonal lattice*  $\{pa+qb+rc : p, q \in \mathbb{Z}, r = 0, 1\}$  with  $a = (\sqrt{3}, 0)$ ,  $b = (\sqrt{3}/2, 3/2)$ , and  $c = (\sqrt{3}, 1)$ . To each vector  $(\ell, m)$  for  $\ell, m \in \mathbb{N}$ ,  $\ell > 2$ , we associate the *nanotube* obtained by identifying the atom  $x$  with  $x + \ell a + m b$  for  $\ell, m \in \mathbb{N}$ . Nanotubes are called *zigzag* for  $m = 0$ , *armchair* for  $\ell = m$ , and *chiral* in all other cases, see Figure 1. We concentrate in the following on zigzag and armchair topologies, leaving the chiral case aside, for it involves additional intricacies.

The purpose of this note is to comment on the possibility of describing nanotube geometries on a purely variational ground. In Section 2 we consider a phenomenological interaction energy of Tersoff type (see (1) and references [16, 17]) and we identify effective nanotube geometries as *stable* configurations, i.e., strict local energy minimizers. In Section 3 we begin by addressing the zigzag geometry and by

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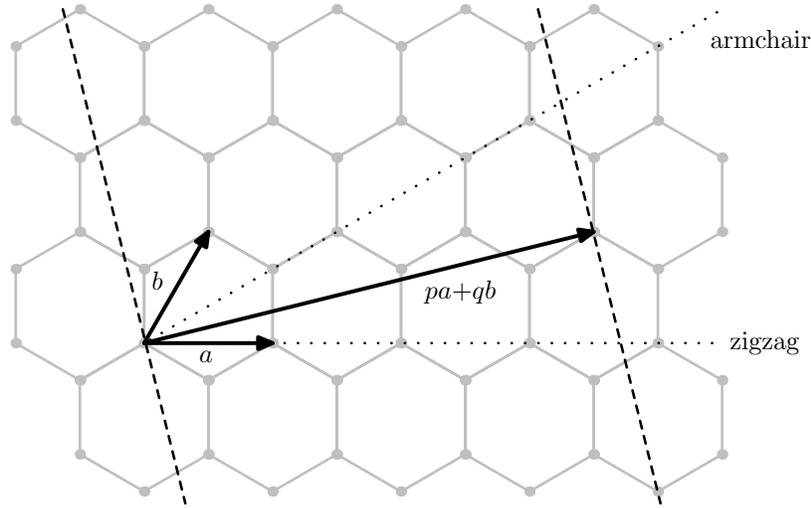


FIGURE 1. Rolling-up of nanotubes from a graphene sheet.

observing that the minimization problem becomes one-dimensional if we reduce to specific classes of *objective structures* (see [7]). In Section 4 we analytically show its well-posedness (see Theorems 4.3). In Section 5 the same program is applied to the armchair geometry (see in particular Theorem 5.2). Finally, in Section 6 we present numerical evidence of the fact that the above-mentioned optimal configurations are indeed strict local minimizers of the energy with respect to general perturbations. An analytical discussion of this point is presented in [15].

As already mentioned, a number of different continuum and atomistic models for zigzag and armchair nanotubes is already available in the literature. Among atomistic models, especially two have drawn the most of the attention. These are the classical *Rolled-up model*, introduced in [4, 5, 10], and the *Cox-Hill model* (also known as *polyhedral model*) advanced in [3]. Both models assume that atoms are arranged on the surface of a cylinder, but differ in the prescription of the bond angles formed at each atom. In the Cox-Hill model all bond angles are assumed to be equal, hence smaller than  $2\pi/3$  in order to allow for the nonplanarity of the structure. On the other hand, in the Rolled-up model some of these angles are set to be equal to  $2\pi/3$  (precisely, one angle for the zigzag and two for the armchair topology, respectively).

In Propositions 4.1 and 4.2 we show that, under generic assumptions on the interaction densities, neither the Rolled-up nor the Cox-Hill model are local minimizers of the energy  $E$ . These results are in accordance with the measurements carried on in [19] reporting indeed on the low accuracy of Rolled-up and Cox-Hill models for extremely thin nanotubes. Furthermore, experimental and computational (molecular dynamics) evidence that different bond angles (and different bond lengths) are needed to properly model these nanotubes is provided in [1, 2, 8, 9, 11, 12].

An extension of the classical Cox-Hill model to these situations has been considered in [13] where it is remarked that two bond angles can be expected to be equal in the armchair and in the zigzag geometry (while three different angles seem in general to be needed for modeling chiral nanotubes). This finds confirmation for a specific choice of the interaction energy in [18] where the contribution to the energy of a single carbon atom (plus the three nearest neighbors) is numerically investigated. We follow here a close path, but analyzing numerically the stability of the whole structure and, in addition, by providing analytic results.

## 2. MATHEMATICAL SETTING

Let us introduce the mathematical setting. We identify nanotubes as *configurations* of atoms, i.e. collections of points in  $\mathbb{R}^3$  representing the atomic sites. Since the length of nanotubes may be as long as  $10^7$  times their diameter, we are here not interested in describing the nanotube geometry close to their ends. Therefore, we restrict to *periodic* configurations, i.e., sets  $\{C_n + kTe, k \in \mathbb{Z}\}$  defined for a given vector  $e \in \mathbb{R}^3$  representing the *direction* of the nanotube, for a period  $T > 0$ . Here,  $C_n$  is a periodicity  $n$ -cell, namely a collection of  $n$  points  $\{x_1, \dots, x_n\}$  with  $x_i \cdot e \in [0, T)$ . From here on, we will systematically identify the periodic configuration with its representative  $n$ -cell without explicitly mention it. Note that in case of a cylindrical symmetry the vector  $e$  indicates the direction of the axis.

In the first part of the paper we consider a configurational energy  $E$  defined by

$$E(C_n) := \frac{1}{2} \sum_{i \neq j} v_2(|x_i - x_j|) + \frac{1}{2} \sum_{(i,j,k) \in \mathcal{T}} v_3(\alpha_{ijk}) \quad (1)$$

on every nanotube  $C_n = \{x_1, \dots, x_n\}$ . In (1) we can identify a two-body and a three-body interaction term, respectively modulated by the potentials  $v_2$  and  $v_3$ . We refer to Subsection 2.1 for the detailed descriptions of the hypotheses assumed on  $v_2$  and  $v_3$ . We also notice that by periodicity the distances  $|x_i - x_j|$  to be considered in the first sum in (1) are taken in the nanotube  $C_n$  modulus the period  $T$ . Furthermore,  $\alpha_{ijk}$  stands for the angle formed by the segments  $x_i - x_j$  and  $x_k - x_j$ , see Figure 2. The index set  $\mathcal{T}$  refers to those angles between first-neighboring particles.

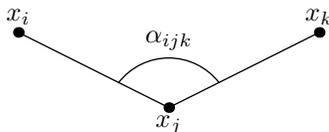


FIGURE 2. Notation for bonds and bond angles.

Since the energy  $E$  is clearly rotation and translation invariant, in the following we will tacitly assume that all statements are to be considered up to isometries. We say that a nanotube  $C_n$  is *stable* if it is a local minimizer of the interaction potential  $E$ .

**2.1. Assumptions on the energy.** In this subsection we detail the hypotheses on the energy  $E$  that we assume throughout the paper. Note that in Section 6 a specific energy that satisfies these hypotheses is considered for the numeric simulations (see (16) and (17)).

The *two-body interaction potential*  $v_2 : \mathbb{R}^+ \rightarrow [-1, \infty)$  is required to assume its minimum value  $-1$  uniquely at 1. Moreover, we ask  $v_2$  to be *short-ranged*, that is to vanish shortly after 1. For the sake of definiteness, let us ask for  $v_2(r) = 0$  for  $r > 1.1$ . We say that two particles  $x_i$  and  $x_j$  are *bonded*, or that the bond between  $x_i$  and  $x_j$  is *active*, namely  $|x_i - x_j| < 1.1$ , and we refer to the graph formed by all the active bonds as the *bond graph*.

The *three-body interaction potential*  $v_3 : [0, 2\pi) \rightarrow [0, \infty)$  is assumed to be symmetric around  $\pi$ , namely  $v_3(\alpha) = v_3(2\pi - \alpha)$ , and to be taking its minimum value 0 only at  $2\pi/3$  and  $4\pi/3$ . Furthermore,  $v_3$  is assumed to be convex, strictly decreasing, and differentiable in a left neighborhood  $I$  of  $2\pi/3$ . Precisely, we define

$$I := (2\pi/3 - \varepsilon, 2\pi/3]$$

for some  $\varepsilon < \pi/6$ . Note that the case of a potential  $v_3$  strictly convex and differentiable in  $I$  is included.

Given three particles  $x_i$ ,  $x_j$ , and  $x_k$ , we denote by  $\alpha_{ijk}$  the angle determined by the two segments  $x_i - x_j$  and  $x_k - x_j$  (clockwise oriented, for the sake of definiteness), and by  $\mathcal{T}$  the set of all triples  $(i, j, k)$  corresponding to *active angles*, that are angles  $\alpha_{ijk}$  separating two active bonds, see Figure 2.

We observe that the above assumptions are generally satisfied by classical interaction potentials for carbon (see [16, 17]). In particular, note that we are not imposing here that the two-body potential  $v_2$  is repulsive at short-range although this is a fairly classical assumption and, currently, the only frame in which crystallization in the hexagonal lattice has been rigorously proved [6, 14].

### 3. ZIGZAG CARBON NANOTUBE GEOMETRY

We begin by modeling zigzag nanotubes, armchair geometry being described later in Section 5 instead.

By prescribing the position of the atoms on each nanotube section we introduce a one-dimensional family of zigzag configurations  $\mathcal{F}_z$  that will play a crucial role, as already mentioned in the Introduction. These configurations are indeed *objective*, in the sense of [7], as they are obtained as orbits of a finite set of atoms under the

action of a prescribed isometry group. In particular, we fix the integer  $\ell > 3$  (to be taken sufficiently large, see below) and define the family  $\mathcal{F}_z$  as the collection of all configurations that, up to isometries, coincide with

$$\left\{ \left( r \cos \left( \frac{\pi(2i+k)}{\ell} \right), r \sin \left( \frac{\pi(2i+k)}{\ell} \right), k(1+s) + j \right) \mid \right. \\ \left. i = 1, \dots, \ell, j = 0, 1, k \in \mathbb{Z} \right\}$$

where  $r, s > 0$  are chosen in such a way that first-nearest neighbors have distance 1 from each other. This last requirement can be met by imposing

$$s^2 + 4r^2 \sin^2 \left( \frac{\pi}{2\ell} \right) = 1$$

as basic trigonometry ensures. From the latter equality we deduce that,  $\mathcal{F}_z$  is a one-parameter smooth family of configurations as each configuration in  $\mathcal{F}_z$  is uniquely determined by  $r$  or  $s$ .

Let us enlist here some properties of the collection  $\mathcal{F}_z$ .

**Lemma 3.1.** *Let  $F \in \mathcal{F}_z$ . Then, the following properties holds:*

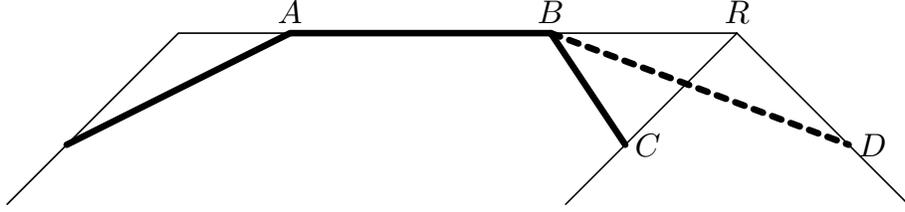
- (a) *Atoms in  $F$  lie on the surface of a cylinder whose axis direction we denote by  $e$ .*
- (b) *All nonempty planar sections of  $F$  perpendicular to  $e$  exactly contain  $\ell$  atoms.*
- (c) *All atoms in  $F$  have exactly 3 (first-nearest) neighbors.*
- (d) *All active bonds have length 1.*
- (e) *The number of bonds parallel to  $e$  is  $1/3$  of the total active bonds.*
- (f) *The configuration  $F$  is invariant under a rotation of  $2\pi/\ell$  around  $e$ , under the translation  $2(1+s)e$ , and under a rototraslation of angle  $\pi/\ell$  along the vector  $(1+s)e$ .*
- (g) *All active angles have either amplitude  $\alpha$  or  $\beta_z$ , with respective proportions  $2/3$  and  $1/3$ .*
- (h) *The angle  $\beta_z$  is given by*

$$\beta_z(\alpha) := 2 \arcsin \left( \sin \alpha \sin \frac{\gamma}{2} \right) \quad (2)$$

where  $\gamma$  is the internal angle of a regular  $2\ell$ -gon, namely,

$$\gamma = \pi \left( 1 - \frac{1}{\ell} \right). \quad (3)$$

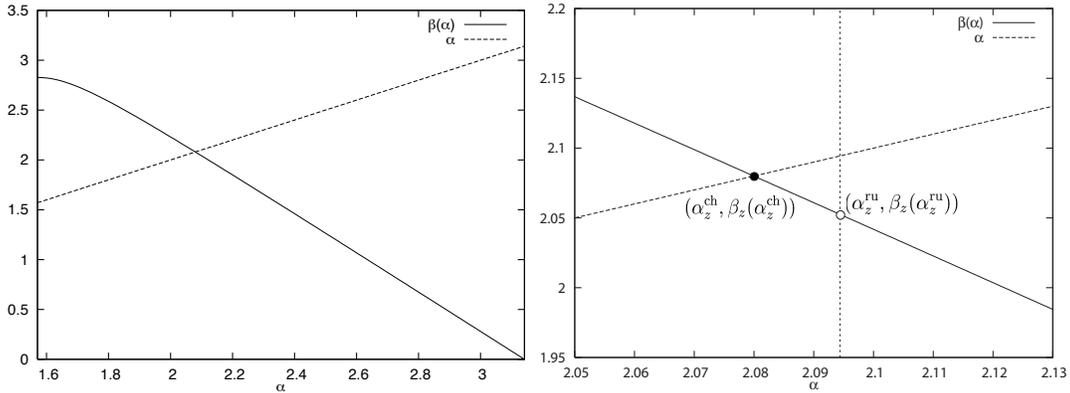
*Proof.* The proof of the first six assertions follow from the very definition of  $\mathcal{F}_z$ . The last two assertions are direct consequences of (f). More precisely, (h) follows from an elementary trigonometry argument. In Figure 3 the two planes that contain each an angle of amplitude  $\alpha$  as well as some bonds are represented. Observe that

FIGURE 3. The construction of the function  $\beta_z$ .

$\alpha = \widehat{ABC} = \widehat{ABD}$  and that  $\overline{CR} = \overline{BC} \sin \alpha$  since  $\widehat{BRC} = \pi/2$ . Hence, we compute that

$$\overline{CD} = 2\overline{CR} \sin(\gamma/2) = 2\overline{BC} \sin \alpha \sin \frac{\gamma}{2} \quad (4)$$

where  $\gamma = \widehat{CRD}$  is the internal angle the regular  $2\ell$ -gon, see (3). Now, relation (2) follows from (4) since  $\overline{BC} = \overline{BD} = 1$  and  $\beta_z(\alpha) = \widehat{CBD}$ .  $\square$

FIGURE 4. The angle  $\beta_z$  as a function of the angle  $\alpha$  (left) and a zoom (right) with the points  $(\alpha_z^{\text{ru}}, \beta_z(\alpha_z^{\text{ru}}))$  and  $(\alpha_z^{\text{ch}}, \beta_z(\alpha_z^{\text{ch}}))$ .

As already mentioned, the crucial feature of the collection  $\mathcal{F}_z$  is that all its configurations are smoothly and uniquely determined by the specification of a single scalar parameter. Among the few equivalent choices for such a parameter, we concentrate here on the angle  $\alpha$  (see point (g) of Proposition 3.1). From the definition of  $\mathcal{F}_z$  (in particular, from  $s > 0$ ) it follows that for all  $\alpha \in (\pi/2, \pi)$  we have exactly one configuration  $F_\alpha \in \mathcal{F}_z$  featuring  $2/3$  of bond angles of value  $\alpha$ . Moreover, the configuration  $F_\alpha$  depends smoothly on  $\alpha$ . Since the three angles at each atom of  $F_\alpha$  necessarily fulfill the elementary constraint

$$\beta_z + 2\alpha < 2\pi, \quad (5)$$

we have that the function  $\beta_z$  (introduced in (2) and defined in  $(\pi/2, \pi)$ ) satisfies  $\beta_z(\alpha) \in (0, 2(\pi-\alpha))$ , see Figure 4. One explicitly computes that

$$\beta'_z(\alpha) = \frac{2 \sin \frac{\gamma}{2} \cos \alpha}{\sqrt{1 - \sin^2 \alpha \sin^2 \frac{\gamma}{2}}} < 0, \quad \beta''_z(\alpha) = -\frac{2 \sin \alpha \sin \frac{\gamma}{2} \cos^2 \frac{\gamma}{2}}{\left(1 - \sin^2 \alpha \sin^2 \frac{\gamma}{2}\right)^{3/2}} < 0 \quad (6)$$

for every  $\alpha \in (\pi/2, \pi)$ . Thus,  $\beta_z$  is strictly decreasing and strictly concave on  $(\pi/2, \pi)$ .

Moreover, we observe that

$$\beta_z\left(\frac{2\pi}{3}\right) > \beta_z\left(\frac{2\pi}{3} + \frac{\varepsilon}{2} - \sigma\right) \geq \frac{2\pi}{3} - \varepsilon \quad (7)$$

for  $\sigma \in (0, \varepsilon/2)$  and  $\ell$  large enough, since

$$\sin\left(\frac{\gamma}{2}\right) \geq \frac{\sin\left(\frac{\pi}{3} - \frac{\varepsilon}{2}\right)}{\sin\left(\frac{2\pi}{3} + \frac{\varepsilon}{2} - \sigma\right)}. \quad (8)$$

In particular, we have

$$\beta_z(\alpha) \geq \frac{2\pi}{3} - \varepsilon$$

for every

$$\alpha \in A := \left(\frac{2\pi}{3} - \varepsilon, \frac{2\pi}{3} + \frac{\varepsilon}{2} - \sigma\right).$$

**3.1. Rolled-up and Cox-Hill zigzag models.** The configurations corresponding with the Rolled-up and the Cox-Hill models (henceforth indicated as Rolled-up and Cox-Hill configurations) are included in the collection  $\mathcal{F}_z$  along with the choices  $\alpha = \alpha_z^{\text{ru}} := 2\pi/3$  and  $\alpha = \alpha_z^{\text{ch}}$ , respectively. The latter  $\alpha_z^{\text{ch}}$  is the unique solution of the equation

$$\beta_z(\alpha_z^{\text{ch}}) = \alpha_z^{\text{ch}}$$

which exists as  $\beta_z$  is smooth and strictly decreasing in  $(\pi/2, \pi)$  from (6),  $\beta_z(3\pi/5) > 3\pi/5$ , and  $\beta_z(2\pi/3) < 2\pi/3$ , see Figure 4. By recalling the constraint (5) we also have that  $\alpha_z^{\text{ch}} < 2\pi/3$ .

Note that by assuming (8) the fact that  $\alpha_z^{\text{ch}} \in I$  follows from

$$2\pi/3 \geq \alpha_z^{\text{ch}} = \beta_z(\alpha_z^{\text{ch}}) \geq \beta_z(2\pi/3) > 2\pi/3 - \varepsilon.$$

We have hence checked that  $\alpha_z^{\text{ru}} > \alpha_z^{\text{ch}}$ . As both  $\alpha_z^{\text{ch}}$  and  $\alpha_z^{\text{ru}}$  are in  $A$ , it makes sense to tacitly assume from here on that the parameter  $\alpha$  belongs to  $A$  as well.

4. MINIMIZING THE ENERGY ON  $\mathcal{F}_z$ 

The minimization of  $E$  over ( $n$ -cell configurations in) the family  $\mathcal{F}_z$  is straightforward. Indeed, given  $F_\alpha \in \mathcal{F}_z$  we have that

$$E(F_\alpha) = -\frac{3n}{2} + n\widehat{E}_z(\alpha).$$

The first term in the above right-hand side is nothing but the two-body energy contribution and it is independent of  $\alpha$ . On the other hand, the *zigzag angle energy*  $\widehat{E}_z$  is defined by

$$\widehat{E}_z(\alpha) := v_3(\beta_z(\alpha)) + 2v_3(\alpha) \quad (9)$$

and represents the three-body energy contribution given by each atom of  $F_\alpha$ . Hence, we have that

$$F \text{ minimizes } E \text{ on } \{F_\alpha \in \mathcal{F}_z \mid \alpha \in A\} \iff \alpha \text{ minimizes } \widehat{E}_z \text{ on } A.$$

We start by providing two negative results.

**Proposition 4.1.** *The Cox-Hill zigzag configuration is not a critical point for the energy.*

*Proof.* Let us start by proving that  $\beta'_z > -2$ . Indeed, we easily check the chain of elementary equivalences

$$\begin{aligned} -2 < \beta'_z(\alpha) &\iff -\cos \alpha \sin \frac{\gamma}{2} < \sqrt{1 - \sin^2 \alpha \sin^2 \frac{\gamma}{2}} \\ &\iff \cos^2 \alpha \sin^2 \frac{\gamma}{2} < 1 - \sin^2 \alpha \sin^2 \frac{\gamma}{2} \\ &\iff \sin^2 \frac{\gamma}{2} < 1 \end{aligned}$$

which holds since  $\gamma \in [2\pi/3, \pi)$  for every  $\ell$ . By (9) we obtain that

$$\widehat{E}'_z(\alpha_z^{\text{ch}}) = 2v'_3(\alpha_z^{\text{ch}}) + v'_3(\alpha_z^{\text{ch}})\beta'_z(\alpha_z^{\text{ch}}) = v'_3(\alpha_z^{\text{ch}})(2 + \beta'_z(\alpha_z^{\text{ch}})) < 0$$

since  $\beta_z(\alpha_z^{\text{ch}}) = \alpha_z^{\text{ch}}$  and  $v'_3(\alpha_z^{\text{ch}}) < 0$ . Hence,  $\alpha_z^{\text{ch}}$  is not a critical point of  $\widehat{E}$  and the Cox-Hill configuration  $F_{\alpha_z^{\text{ch}}}$  is not a critical point for the energy  $E$  on  $\{F_\alpha \in \mathcal{F}_z \mid \alpha \in A\}$ . A fortiori,  $F_{\alpha_z^{\text{ch}}}$  is not a critical point of the energy  $E$ .  $\square$

**Proposition 4.2.** *The Rolled-up zigzag configuration is not a critical point for the energy.*

*Proof.* Upon noting that  $\beta_z(2\pi/3) \in A$ , it suffices to compute

$$\widehat{E}'_z(2\pi/3) = 2v'_3(2\pi/3) + v'_3(\beta_z(2\pi/3))\beta'_z(2\pi/3) = v'_3(\beta_z(2\pi/3))\beta'_z(2\pi/3) > 0.$$

Thus,  $2\pi/3$  is not a critical point of  $\widehat{E}$ . Hence, the Rolled-up configuration  $F_{\alpha_z^{\text{ru}}}$  is not a minimizer of the energy  $E$  on  $\{F_\alpha \in \mathcal{F}_z \mid \alpha \in A\}$ . A fortiori,  $F_{\alpha_z^{\text{ru}}}$  is not a critical point for the energy  $E$ .  $\square$

We now prove that  $\widehat{E}_z$  admits a unique minimizer in an open neighborhood of the interval  $(\alpha_z^{\text{ch}}, \alpha_z^{\text{ru}})$ .

**Theorem 4.3.** *There exists an open set  $U_z$  with  $A^* := (\alpha_z^{\text{ch}}, 2\pi/3) \subsetneq U_z$  in which  $\widehat{E}_z$  admits a unique global minimizer  $\alpha_z^* \in A^*$ . Correspondingly,  $F_z^* := F_{\alpha_z^*}$  is the unique minimizer of  $E$  on  $\{F_\alpha \in \mathcal{F}_z \mid \alpha \in U_z\}$ .*

*Proof.* We begin by observing that there is no local minimizer of  $\widehat{E}_z$  in a left neighborhood of  $\alpha_z^{\text{ch}}$ . In fact,  $\widehat{E}_z$  is convex in  $(2\pi/3 - \varepsilon_z, \alpha_z^{\text{ch}}]$  where  $\varepsilon_z \leq \varepsilon$  is defined by

$$\beta_z \left( \frac{2\pi}{3} - \varepsilon_z \right) = \frac{2\pi}{3},$$

and hence, we have that

$$\widehat{E}'_z(\alpha) \leq \widehat{E}'_z(\alpha_z^{\text{ch}}) < 0$$

for every  $\alpha \in (2\pi/3 - \varepsilon_z, \alpha_z^{\text{ch}}]$ .

On the other hand, by Proposition 4.2 there exists no global minimizer of  $\widehat{E}_z$  in  $[2\pi/3, 2\pi/3 + \varepsilon/2 - \sigma)$ . In fact, by (7) and the fact that  $\beta_z$  is strictly decreasing we obtain that

$$\beta_z \left( \frac{2\pi}{3} \right) \geq \beta_z(\alpha) > \beta_z \left( \frac{2\pi}{3} + \frac{\varepsilon}{2} - \sigma \right) \geq \frac{2\pi}{3} - \varepsilon \quad (10)$$

for every  $\alpha \in [2\pi/3, 2\pi/3 + \varepsilon/2 - \sigma)$ , and so

$$\begin{aligned} E(\alpha) &= 2v_3(\alpha) + v_3(\beta_z(\alpha)) > 2v_3(2\pi/3) + v_3(\beta_z(\alpha)) \\ &\geq 2v_3(2\pi/3) + v_3(\beta_z(2\pi/3)) = E(2\pi/3) \end{aligned}$$

where in the first inequality we used that  $2\pi/3$  is a global minimizer of  $v_3$ , while in the second we used (10).

Finally, since  $\widehat{E}_z$  is continuous it admits a global minimizer  $\alpha_z^*$  in  $\overline{A^*}$ . As we have already shown that neither  $\alpha_z^{\text{ch}}$  nor  $\alpha_z^{\text{ru}}$  are critical points of  $\widehat{E}_z$ , the minimizer  $\alpha_z^*$  necessarily belongs to  $A^*$ . Let us now observe that  $\beta_z(A^*) \subset I$  by (7), and so, since the composition of  $v_3$  (convex and strictly decreasing) and  $\beta_z$  (strictly concave) is strictly convex, it follows from (9) that  $\widehat{E}_z$  is strictly convex in  $A^*$ . Therefore,  $\alpha^*$  is the unique minimizer of  $\widehat{E}_z$  in  $A^*$ , hence in

$$U_z := \left( \frac{2\pi}{3} - \varepsilon_z, \frac{2\pi}{3} + \frac{\varepsilon}{2} - \sigma \right). \quad \square$$

The optimal configuration  $F_z^*$  does not coincide neither with the Cox-Hill nor with the Rolled-up configuration and it is rather some intermediate configuration (intermediate in the sense of the parametrization via  $\alpha$ ). As such it qualifies as a new, variationally-based, geometric model for zigzag nanotubes. The configuration  $F_z^*$  is uniquely defined in  $\mathcal{F}_z$ . Its most striking feature is that it is locally stable with respect to perturbations, not necessarily restricted to the family  $\mathcal{F}_z$  (see Section 6). This fact is particularly remarkable as it allows to rigorously justify the geometry the  $3n$ -dimensional nanotube configuration moving from variational considerations in one dimension.

## 5. ARMCHAIR GEOMETRY

We now address the armchair nanotube geometry and observe that the program outlined in the previous two sections for the zigzag nanotube can be carried out analogously.

First of all we introduce a family  $\mathcal{F}_a$  of specific armchair configurations whose  $n$ -cell is the union of sections consisting of an even integer  $\ell > 2$  of atoms. In each section the  $\ell$  atoms are arranged by dividing them in two groups of  $\ell/2$  atoms, and then placing the atoms of each group at the vertices of a regular  $(\ell/2)$ -gon.

More precisely, let  $\ell > 2$  be an even integer and define the family  $\mathcal{F}_a$  as the collection of all configurations that, up to isometries, coincide with

$$\left\{ \left( r \cos \left( \frac{2\pi}{\ell}(2i+k) + qj \right), r \sin \left( \frac{2\pi}{\ell}(2i+k) + qj \right), pk \right) \mid \right. \\ \left. i = 1, \dots, \ell/2, j = 0, 1, k \in \mathbb{Z} \right\}$$

where  $p$ ,  $r$ , and  $q > 0$  are chosen in such a way that first-nearest neighbors have distance 1 from each other. We may take

$$p^2 + 4r^2 \sin^2 \left( \frac{\pi}{\ell} - \frac{q}{2} \right) = 1$$

and  $q := 2 \arcsin(1/2r)$ . Therefore,  $\mathcal{F}_a$  is a one-parameter smooth family of configurations. Let us collect in the following Lemma some geometric properties which hold for all the elements of  $\mathcal{F}_a$ .

**Lemma 5.1.** *Let  $F \in \mathcal{F}_a$ . Then,  $F$  satisfies properties (a)-(d) of Lemma 3.1 and the following assertions:*

- (e') *The number of bonds whose projection onto the nanotube axis reduces to a point is  $1/3$  of the total active bonds.*

- (f') *The configuration  $F$  is invariant under a rotation of  $4\pi/\ell$  around the axis  $e$ , under the translation  $2pe$ , and under a rototraslation of an angle  $2\pi/\ell$  and the vector  $pe$ .*
- (g') *All active angles have either amplitude  $\alpha$  or  $\beta_a$ , with respective proportions  $2/3$  and  $1/3$ .*
- (h') *The angle  $\beta_a$  is given by*

$$\beta_a(\alpha) := 2 \arccos \left( \frac{\cos \alpha}{\cos \gamma} \right) \quad (11)$$

where  $\gamma$  is defined by (3).

Analogously to the zigzag family, also the elements of  $\mathcal{F}_a$  are smoothly and uniquely determined by the angle  $\alpha \in (\pi/2, \pi)$ . The function  $\beta_a$ , that is defined by (11) on  $(\pi/2, \pi)$ , is such that  $\beta_a(\alpha) \in (0, 2(\pi - \alpha))$  since the elementary constraint needs to be satisfied

$$\beta_a + 2\alpha < 2\pi. \quad (12)$$

Furthermore,  $\beta_a$  is strictly decreasing and strictly concave since

$$\beta'_a(\alpha) = -\frac{\sin \alpha}{\sqrt{\cos^2 \gamma - \cos^2 \alpha}} < 0 \quad \text{and} \quad \beta''_a(\alpha) = \frac{\cos \alpha \sin^2 \gamma}{(\cos^2 \gamma - \cos^2 \alpha)^{3/2}} < 0 \quad (13)$$

for every  $\alpha \in (\pi/2, \pi)$ , see Figure 5. Moreover, by a similar reasoning to the one used for the zigzag geometry we have that

$$\beta_a(\alpha) \geq \frac{2\pi}{3} - \varepsilon$$

for  $\ell$  large enough and every  $\alpha \in A$ . In addition, it follows that for  $\ell$  large enough  $\alpha_a^{\text{ch}} \in I$  since

$$\frac{2\pi}{3} \geq \alpha_a^{\text{ch}} = \beta_a(\alpha_a^{\text{ch}}) \geq \beta_a \left( \frac{2\pi}{3} \right) > \frac{2\pi}{3} - \varepsilon.$$

Moreover, the configurations corresponding to the Rolled-up and Cox-Hill armchair models belongs to  $\mathcal{F}_a$ . In fact, we can identify the Rolled-up configuration with  $F_{\alpha_a^{\text{ru}}}$  where the angle  $\alpha_a^{\text{ru}}$  is uniquely defined by

$$\beta_a(\alpha_a^{\text{ru}}) = \frac{2\pi}{3}.$$

Furthermore, the Cox-Hill configuration is identified by  $F_{\alpha_a^{\text{ch}}}$  where the angle  $\alpha_a^{\text{ch}}$  is uniquely defined as the solution of the equation:

$$\beta_a(\alpha_a^{\text{ch}}) = \alpha_a^{\text{ch}}.$$

Let us observe that from the monotonicity of  $\beta_a$  it follows that

$$\alpha_a^{\text{ru}} < \alpha_a^{\text{ch}} < \frac{2\pi}{3},$$

since by (12) we have that

$$\beta_a(\alpha_a^{\text{ru}}) = \frac{2\pi}{3} > \alpha_a^{\text{ch}} = \beta_a(\alpha_a^{\text{ch}}). \quad (14)$$

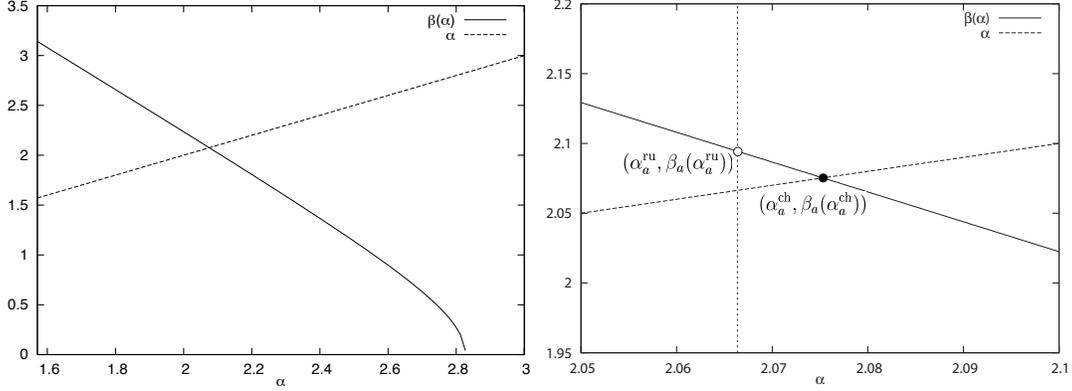


FIGURE 5. The angle  $\beta_a$  as a function of the angle  $\alpha$  (left) and a zoom (right) with the points  $(\alpha_a^{\text{ru}}, \beta_a(\alpha_a^{\text{ru}}))$  and  $(\alpha_a^{\text{ch}}, \beta_a(\alpha_a^{\text{ch}}))$ .

In analogy to Section 4, we now introduce the variationally-based geometric model for the armchair nanotube by minimizing  $E$  over the family  $\mathcal{F}_a$ , and we verify that it differs from the Cox-Hill and the Rolled-up configurations.

To this aim, let us denote by  $\widehat{E}_a$  the *armchair-angle energy* that is the three-body energy contribution provided by each of the atoms of a configuration  $F_\alpha \in \mathcal{F}_a$  to its overall energy. Since every atom of a configuration  $F_\alpha \in \mathcal{F}_a$  has exactly three bonds of length 1, and

$$\widehat{E}_a(\alpha) = v_3(\beta_a(\alpha)) + 2v_3(\alpha), \quad (15)$$

we deduce that

$$E(F_\alpha) = -\frac{3n}{2} + n\widehat{E}_a(\alpha).$$

Therefore,

$$F \text{ minimizes } E \text{ on } \{F_\alpha \in \mathcal{F}_a \mid \alpha \in A\} \iff \alpha \text{ minimizes } \widehat{E}_a \text{ on } A.$$

**Theorem 5.2.** *The Rolled-up and Cox-Hill armchair configurations are not critical points of  $E$ . Moreover, there exists an open set  $U_a$  with  $A^* := (\alpha_a^{\text{ch}}, 2\pi/3) \subsetneq U_a$  in which  $\widehat{E}_a$  admits a unique global minimizer  $\alpha_a^* \in A^*$ . Thus,  $F_a^* := F_{\alpha_a^*}$  is the unique minimizer of  $E$  on  $\{F_\alpha \in \mathcal{F}_a \mid \alpha \in U_a\}$ .*

*Proof.* We begin by observing that the fact that the Rolled-up armchair configuration is not a critical point for the energy easily follows from the first inequality in (13)

and (14), since they imply that

$$\widehat{E}'_a(\alpha_a^{\text{ru}}) = 2v'_3(\alpha_a^{\text{ru}}) + v'_3(2\pi/3)\beta'_a(\alpha_a^{\text{ru}}) = 2v'_3(\alpha_a^{\text{ru}}) < 0.$$

Furthermore, by the same argument used in Proposition 4.1 we have that also the Cox-Hill armchair configuration is not a critical point for the energy and that, in particular,  $\widehat{E}'_a(\alpha_a^{\text{ch}}) < 0$ . In fact, we have that

$$-2 < \beta'_a(\alpha) \iff 4 \cos^2 \gamma > 3 \cos^2 \alpha + 1$$

and hence,  $\beta'_a(\alpha_a^{\text{ch}}) > -2$  is satisfied for large  $\ell$  since  $\alpha_a^{\text{ch}} < 2\pi/3$ . Furthermore, since  $\widehat{E}_a$  is convex in a left neighborhood of  $\alpha_a^{\text{ch}}$ , it attains no local minimum in such neighborhood.

In addition, since

$$\widehat{E}'_a(2\pi/3) = 2v'_3(2\pi/3) + v'_3(\beta_a(2\pi/3))\beta'_a(2\pi/3) = v'_3(\beta_a(2\pi/3))\beta'_a(2\pi/3) > 0,$$

by the same reasoning used in the Theorem 4.3 there exists also no global minimizer of  $\widehat{E}_a$  in  $[2\pi/3, 2\pi/3 + \varepsilon/2 - \sigma)$ . Therefore, the assertion follows from the fact that  $\widehat{E}_a$  is continuous and strictly convex in  $A^*$ .  $\square$

## 6. NUMERICAL INVESTIGATION ON STABILITY

The optimal geometries obtained above have been checked to be local energy minimizers within the restricted class of highly-symmetric configurations  $\mathcal{F}_a$  and  $\mathcal{F}_z$ , respectively. The aim of this section is to provide numerical evidence of the fact that they are optimal with respect to generic small perturbations, possibly not restricted to  $\mathcal{F}_a$  and  $\mathcal{F}_z$ . This entails that these optimal configurations are indeed strict local energy minimizers. We shall detail elsewhere the analytical discussion of this problem and limit ourselves here in presenting the corresponding simulations.

**6.1. Minimization of the energy in  $\mathcal{F}_a$  and  $\mathcal{F}_z$ .** We provide here an illustration to the analysis of the previous sections. Let us start by clarifying the simulation setting. The energy of the configuration  $E = E_2 + E_3$  will be defined as in (1).

In all computations we prescribe the interaction energy densities as

$$v_2(r) = \begin{cases} f(r) - f(R) & \text{if } 0 < r < R, \\ 0 & \text{otherwise} \end{cases} \quad (16)$$

$$f(r) = \frac{1}{2r^{12}} - \frac{1}{r^6},$$

$$v_3(\theta) = 10(\cos \theta + 1/2)^2. \quad (17)$$

In particular, note that  $v_2$  is short-ranged and it is minimized uniquely at  $r = 1$ . Along with this provisions, we can immediately compute the energy  $\widehat{E}_i$  along the corresponding family  $\mathcal{F}_i$  for  $i = a, z$ , see Figure 6.

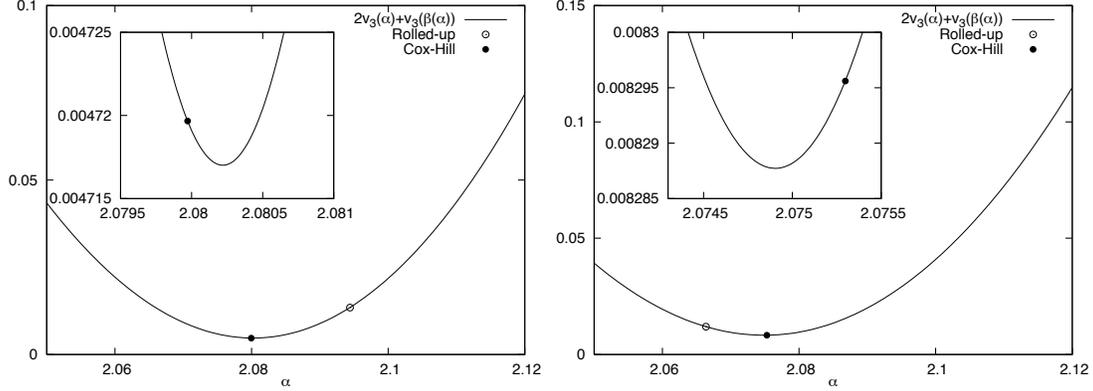


FIGURE 6. The energy-per-particle  $\widehat{E}_i$  in the zigzag (left) and in the armchair (right) family, as a function of the angle  $\alpha$ , together with a zoom about the minimum.

Notice that the above computation illustrates the already analytically proven fact that neither the *Rolled-up* angle  $\alpha_i^{\text{ru}}$  nor the *Cox-Hill* angle  $\alpha_i^{\text{ch}}$  are minimizers of the energy-per-particle  $\widehat{E}_i$ . On the contrary, one finds the optimal angles  $\alpha_i^*$ . To these angles one associate the corresponding configurations in  $\mathcal{F}_i$  which are hence global minimizers of the energy  $E$  in  $\mathcal{F}_i$ .

**6.2. Stability.** Let  $i = a, z$ . In order to provide numerical evidence of the fact that the optimal angles  $\alpha_i^*$  describe locally stable geometries, we compare their energies with those corresponding to general perturbations. As these perturbations obviously brake the symmetry of the configuration, we are forced to work with the actual energy  $E$  instead of the angle energies  $\widehat{E}_i$ . In particular, we need to fix the topology of the bond graph of the configurations under consideration. In order to check the robustness of our findings with respect to nanotubes of different aspect-ratios, we will concentrate on the following six topologies:

- Zigzag topologies:
  - Z1)  $n = 10$  atoms on the cross section,  $T = 8(1 + s)$ .
  - Z2)  $n = 20$  atoms on the cross section,  $T = 8(1 + s)$ .
  - Z3)  $n = 10$  atoms on the cross section,  $T = 16(1 + s)$ .
- Armchair topologies:
  - A1)  $n = 10$  atoms on the cross section,  $T = 8(1 + s)$ .

A2)  $n = 20$  atoms on the cross section,  $T = 8(1 + s)$ .

A3)  $n = 10$  atoms on the cross section,  $T = 16(1 + s)$ .

Note that the above notation recalls that all configurations are considered under periodicity in the axis direction. In particular, we impose to all random perturbation the specific period determined by the corresponding optimal configuration. In case of Z1, for instance, one computes the period  $L_{Z1}$  to be the period of the configurations in  $\mathcal{F}_z$  corresponding to Z1 along with their optimal angle  $\alpha_z^*$ .

In all cases we generate random perturbations of the optimal configuration and compute the corresponding energy. The results of the simulations are collected in Figure 7 and prove that indeed the optimal configurations are local strict energy minimizers.

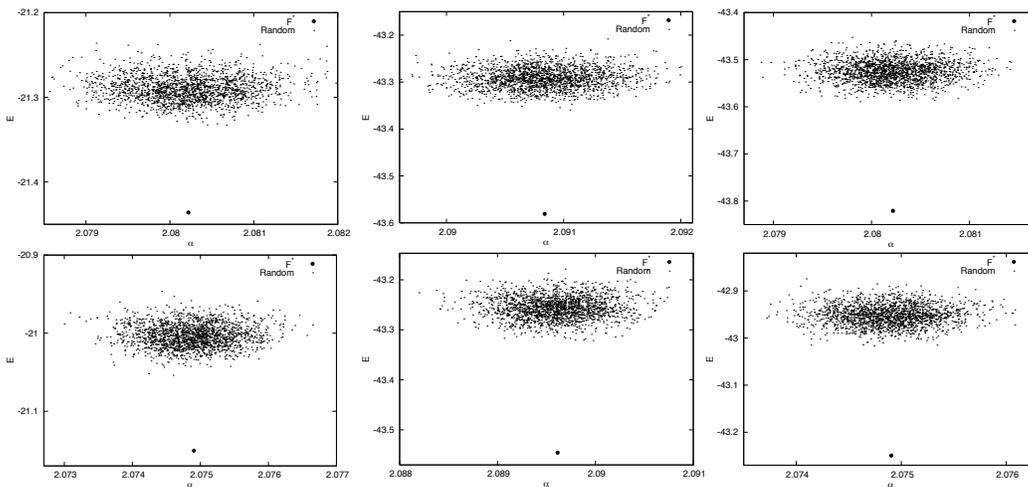


FIGURE 7. Comparison between energies of the optimal configurations and energies of their perturbations in the cases Z1, Z2, Z3 (top, from left) and A1, A2, A3 (bottom, from left).

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