STABLE CARBON CONFIGURATIONS

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Abstract. Molecular Mechanics models molecules as configurations of particles interacting via classical potentials. The specific geometry of covalent bonding in carbon is described by the combination of an attractive-repulsive two-body interaction and a three-body bond-orientation part. We investigate the strict local minimality of specific carbon configurations under general assumptions on the interaction potentials. Carbyne, graphene, some fullerenes, and diamond are proved to be stable.

1. Introduction

The richness of Organic Chemistry comes from the capability of carbon to constitute strong bonds to a variety of different elements. Carbon-carbon bonds form chains and rings, resulting then in basic structures for all organic molecules. This bonds are of covalent nature, for two carbon atoms share a pair of electrons. As a result, the corresponding orbitals are so-called *sp*-, sp^2-, or sp^3-hybridized, inducing indeed bonds at a given atom to align, to form $2\pi/3$ angles, or to arrange in a tetrahedral structure, respectively. In combination with hydrogen (hydrocarbon), these give correspondingly rise to *alkynes*, *alkenes*, and *alkanes* [12].

These three different bonding modes are responsible for the geometric diversity of carbon *allotropes*, namely elemental forms of pure carbon. Linear acetylenic carbon (*carbyne*) is a long chain of *sp*-bonded atoms. *Graphene* is a sp^2-based two-dimensional material consisting in a single carbon sheet. *Nanotubes* and *fullerenes* are three-dimensional closed-cage-like structures based on sp^2 bonding as well. Finally, *diamond* and *lonsdaleite* are sp^3-bonded crystals [59]. The extraordinary electromechanical and optical properties of these structures have triggered an immense amount of research over the last decades. Landmarks in this respect are the 1996 Nobel Prize in Chemistry to Curl, Kroto, and Smalley for the experimental discovery of fullerenes and the 2010 Nobel Prize in Physics to Geim and Novoselov for the realization of graphene.

Our focus is on rigorously analyzing these structures within the framework of Molecular Mechanics [1]. Carbon configurations are modeled as a

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collection of particle positions to which a *configurational energy* is associated. This energy is given in terms of classical potentials and takes into account both attractive-repulsive *two-body* interactions, minimized at some given bond length, and *three-body* terms favoring specific angles between bonds [4, 54, 56].

The tenet of Molecular Mechanics is that molecular structures and their physical properties can be ascertained by inspecting the configurational energy [23, 39]. With respect to quantum-mechanical models, this phenomenological approach has the advantage of being simpler and parametrizable, although at the expense of a certain degree of approximation. Remarkably, Molecular Mechanics delivers the only computationally amenable option as the dimension of the ensamble scales up. This advantage is indeed groundbreaking for it paves the way to the understanding of macromolecules. The development of Molecular Mechanics has been awarded the 2013 Nobel Prize in Chemistry to Karplus, Levitt, and Warshel.

Inherent to the process of molecular structuring is the concept of *stability*: among the many possible geometries only those showing some suitable stability (either thermodynamic, or electrochemical, or even mechanical, depending on the context) can be expected to be realized. This issue is formalized within this paper by interpreting

$$\text{stability} = \text{strict minimality w.r.t. the configurational energy.}$$

The aim of this note is to discuss the *stability* of specific carbon configurations. Our main result consists in identifying a minimal set of assumptions on the configurational energy entailing stability of carbyne, graphene, some fullerenes, and diamond. With respect to classical molecular-mechanical computations the novelty of our contribution resides in providing rigorous results instead of numerical assessments [1, 39, 50]. Note that a menagerie of different possible choices for energy terms has been implemented in Computational Chemistry codes [6, 11, 25, 47, 60]. A by-product of our results is hence the cross-validation of these choices in view of their capability of describing stable carbon geometries.

Our analysis follows indeed two distinct but interdependent lines. The first one consists in encoding the local geometry of the specific carbon-bonding mode directly in the structure of the three-body interaction part by suitably prescribing minimality at specific bond angles. This is indeed the traditional choice [4, 54, 56] and allows to reformulate stability as a rather geometrical rigidity-type property of the entire configuration. The price to pay is the a priori determination of the carbon-bonding mode and, correspondingly, a lack of generality.

The second line focuses on the search for a single potential describing ideally *all geometries* at once. Instead of minimality at specific bond angles we use here local convexity and monotonicity. The global topology of the configuration has to come into the picture in order to translate optimality of small atomic ensambles to stability. We sort out some minimal assumptions on the energy entailing the stability of all the mentioned carbon configurations.

Let us briefly comment on the current literature on geometry optimization in carbon. The *global minimality* of graphene in two dimensions has to be traced back to [19]. By assuming the three-body energy term to favor *sp*^{2} bonding, the *thermodynamic limit* of a large number of atoms is ascertained to correspond to a regular hexagonal lattice. This result corresponds to a three-body version of the seminal theory in [57]. In this same direction, in [20] the authors recover the hexagonal lattice in the thermodynamic limit by assuming the three-body energy term to favor *sp* bonding instead. The generically nonunique ground state for a *finite* number of atoms in two dimensions has been proved to be a graphene patch in [46] and characterized in terms a discrete isoperimetric inequality in [16]. In particular, one can quantitatively check the emergence of a hexagonal Wulff shape as the number of atoms increases. Apart from the recent [21], which however does not describe carbon geometries, no global minimality (crystallization) result in three dimensions is presently available.

As for *local minimality (stability)* one has to record the convexity argument in [46] where it is checked that the two fullerenes C_{20} and C_{60} are stable. To some extent, part of this paper corresponds to an extension of those ideas to other configurations. Stability is also employed as a selection criterion among different carbon-nanotube and fullerene geometries in [22, 44, 45]. To our knowledge, this paper presents the first stability result for carbyne and diamond.

2. Configurational energies

Carbon ensambles are modeled as collections of points, to which we refer to as *atoms*. On configurations $X = \{x_1, \dots, x_n\}$ of n atoms in $\mathbb{R}^3$ we assume to be given a *configurational energy* $E : \mathbb{R}^{3n} \to \mathbb{R} \cup \{\infty\}$ as

$$E(X) = E_2(X) + E_3(X) := \frac{1}{2} \sum_{(i,j)\in N} v_2(|x_i - x_j|) + \frac{1}{2} \sum_{(i,j,k)\in T} v_3(\theta_{ijk}).$$

This energy is the sum of a *two-body* term E_2, depending solely on the mutual distance of the atoms, and a *three-body* contribution E_3 depending instead on bond angles, see Figure 1. Reflecting the locality of covalent bonding, the two-body *interaction density* $v_2 : [0, \infty) \to \mathbb{R} \cup \{\infty\}$ is assumed to be of attractive-repulsive type and short-ranged. In particular, we ask for

$$-1 = v_2(1) < v_2(\ell) \quad \forall \ell \neq 1. \tag{1}$$

Condition (1) expresses the fact that carbon bonds have a preferential bond length, here normalized to 1. Note that this is an idealization, since bond lengths in carbon structures actually depend on chemistry (single, double, triple bonds) and geometry (molecular configuration) and usually vary consistently in the range 1.2-1.6 Å. This is however a sensible assumption in the case of the configurations here under consideration, where indeed bond lengths can be assumed to be equal.

The sum defining E_2 ranges over the set of indices N corresponding to bonded atoms. We say that the two atoms x_i and x_j are *bonded* or that the exists a *bond* between x_i and x_j iff

$$1-\varepsilon < |x_i - x_j| < \frac{3}{2}(1-\varepsilon),$$

where $\varepsilon \in (0,1/3)$ is some small parameter. Here $1-\varepsilon$ corresponds to some *minimal bond length* modeling atomic repulsion. Short-range repulsion is the effect of electrostatic interactions and is often modeled by asking $v_2(\ell)=\infty$ for $\ell < 1-\varepsilon$. The value $3(1-\varepsilon)/2$ above is the *maximal two-body interaction range.* Note that the specific form of these bounds is chosen for definiteness and could be generalized. The indices corresponding to bonded atoms are defined as

$$N = \{(i,j) \in \{1,\dots,n\}^2 \, : \, i \neq j, \ 1-\varepsilon < |x_i - x_j| < 3(1-\varepsilon)/2\}.$$

The coefficient 1/2 in front of the sum in E_2 reflects the fact that all bonds are represented twice in N.

To all configurations we associate the respective *bond graph* resulting from taking the atoms as vertices and the bonds as edges, and tacitly identify it with its three dimensional realization with bonds represented as straight segments. We shall mainly use *atom* and *bond* for *vertex* and *edge* in the following, still resorting to the graph-theory terminology in specific places. We use *hexagon* (*pentagon*, etc.) to indicate a simple cycle of the bond graph with six bonds (five bonds, etc.). A bond is called *cyclic* if it belongs to a simple cycle and *acyclic* otherwise. An acyclic bond is a *cut-edge* iff its removal disconnects the bond graph.

The three-body energy term E_3 is modulated via the interaction energy density $v_3 : [0,2\pi] \to [0,\infty)$. The angles θ_{ijk} appearing in the definition of E_3 are those formed by bonds. In particular, the index set T is defined as

$$T = \{(i,j,k) \, : \, (i,j) \in N, \, (k,j) \in N, i \neq k\}$$

and θ_{ijk} is the angle formed by the segments (x_i,x_j) and (x_k,x_j), counterclockwise oriented in the plane containing x_i, x_j, and x_k, see Figure 1. Although not strictly needed from the mathematical standpoint, we assume in the following the symmetry

$$v_3(\theta) = v_3(2\pi - \theta) \quad \forall \theta \in [0,\pi). \tag{2}$$

This ensures that the two complementary bond angles θ_{ijk} and θ_{kji} contribute the same energy to E_3. The factor 1/2 in the definition of E_3 reflects the fact that all these terms are summed. In addition, (2) yields the invariance of the energy under any relabelling of the atoms and can thus be seen

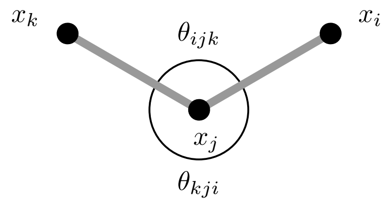

Figure 1. Notation for bond angles.

as a consistency condition. Note that (2) entails that π is a critical point of v_3 whenever differentiability holds. Different models may require π to be locally minimizing or maximizing v_3 [4, 5, 54, 56].

With the intent of keeping technicalities and notation to a minimum, we stay with assumptions (1)-(2) throughout the paper without further mentioning. On the contrary, we specify additional assumptions on v_3, especially of differentiability, convexity, or monotonicity nature, as we get along.

The energy E is invariant by translation and rotation. In the following we tacitly assume that all statements are to be considered up to isometries. Note incidentally that E is coercive whenever v_2 is. Under lower semincontinuity assumptions on the interaction densities the existence of global minimizers immediately follows. Still, the exact geometry of global minimizers is to a large extent not known.

As bonding is energetically favored, one can easily prove that ground states are necessarily *connected* configurations, i.e. configurations such that the corresponding bond graph is connected. In order to simplify our statements we will focus exclusively on connected configurations. Note that some statements, for instance Theorem 4.3 below, do not hold without assuming connectedness. Modifications in case of not connected configurations will be then straightforward.

3. Carbyne

Let us start our discussion by *sp*-bonded carbon structures where indeed atoms have two neighbors and the corresponding bonds tend to align. This local configuration is prototypical of *alkynes* (C_nH_{2n-2}) [59] where nevertheless carbon atoms are bonded to hydrogen. On the other hand, the pure-carbon reference structure in this context is *linear acetylenic carbon*, also called *carbyne*. This allotrope of carbon presents an unrestricted number of doubly-*sp*-bonded carbon atoms (together with hydrogen or metal capping, excluded from our analysis) [41]. The interest for carbyne is justified by its predicted remarkable mechanical properties. With a Young modulus of 32.7 TPa it is expected be the strongest material to date [30, 31]. Our stability result for carbyne reads as follows.

Theorem 3.1 (Carbyne is stable)**.** *Let* v_3 *be strictly minimized at* π*. Then the open carbyne chain* $S_n := \{(k,0,0) \,:\, k=1,\dots,n\}$ *is a strict local minimizer.*

Assume v_3 *to be convex and strictly decreasing in a left neighborhood of* π *and* $n \geq 5$*. Then the planar closed carbyne ring*

$$R_n := r\{(\cos(2\pi k/n), \sin(2\pi k/n), 0) \,:\, k=1,\dots,n\}$$

with radius $r = 1/(2\sin(\pi/n))$ *is a strict local minimizer.*

Proof. The first part of the assertion is straightforward. As for the closed ring R_n let us preliminarily observe that value of the radius r is such that all bonds have length 1. Let now $\widetilde{R}_n = \{\tilde{x}_1,\dots,\tilde{x}_n\}$ be a small perturbation of R_n preserving the topology of the bond graph. All bond angles of R_n which are smaller than π are indeed $\pi - 2\pi/n$, as this is the internal angle of a polygon with n sides. We indicate with $\tilde{\theta}_i$ the corresponding bond angles of $\widetilde{R}_n$. These are all smaller than π if the perturbation is small enough. The mean of all such bond angles satisfies

$$\overline{\theta} = \frac{1}{n}\sum_{i=1}^{n}\tilde{\theta}_i \leq \pi - 2\pi/n \tag{3}$$

where the occurrence of a strict inequality would be the signature of a non-planar $\widetilde{R}_n$. By using this fact we deduce that

$$\begin{aligned} E(\widetilde{R}_n) &\overset{\text{(a)}}{\geq} -n + \sum_{i=1}^{n} v_3(\tilde{\theta}_i) \overset{\text{(b)}}{\geq} -n + nv_3(\overline{\theta}) \\ &\overset{\text{(c)}}{\geq} -n + nv_3(\pi - 2\pi/n) = E(R_n). \end{aligned}$$

We have used the minimality (1) in (a), the convexity of v_3 in (b), and the monotonicity of v_3 combined with (3) in (c). In order to do this, we are assuming the perturbation to be so small that all $\tilde{\theta}_i$ belong to the convexity and strict monotonicity left-neighborhood of π.

The above chain of inequalities is strict whenever (a) a bond in $\widetilde{R}_n$ has length different from 1, (b) not all bond angles in $\widetilde{R}_n$ are equal, or (c) $\overline{\theta} < \pi - 2\pi/n$, namely iff $\widetilde{R}_n$ is not planar. We hence conclude that $E(\widetilde{R}_n) = E(R_n)$ iff $\widetilde{R}_n = R_n$ so that R_n is a strict local minimizer. Note that in order to prove the local strict minimality of R_n, no minimality of v_3 in π is needed. □

Before closing this section, let us mention that $E(R_n) < E(S_n)$ for n large enough. In particular, a long open carbyne chain is stable but not a ground state. Indeed, by comparing

$$E(R_n) = -n + nv_3(\pi - 2/n) \quad \text{and} \quad E(S_n) = -n + 1 + nv_3(\pi)$$

one finds that $E(R_n) < E(S_n)$ for

$$nv_3(\pi - 2/n) < 1 + nv_3(\pi). \tag{4}$$

Assume v_3 to be twice differentiable in π and $v_3(\pi) = 0 < v_3''(\pi)$. Then for n large we have

$$nv_3(\pi - 2/n) \sim nv_3(\pi) + \frac{2}{n} v_3''(\pi)$$

and the above right-hand side is eventually smaller than 1, so that (4) holds. This observation is remarkably corresponding, although necessarily in a very schematic way, to the current debate on the possibility of realizing very long carbyne chains [3]. In fact, under additional quantitative assumptions on the interaction densities one could prove that either S_n or R_n is the unique global minimizer in $\mathbb{R}^3$. For given n, condition (4) singles out which of the two occurs. We plan to develop these considerations in a forthcoming contribution [37].

4. Graphene

We now move to the case of *sp*^{2} bonding, where each carbon atom shares three (pairs of) electrons with three neighboring atoms. This hybridized bonding regime arises classically in *alkenes* (C_nH_{2n}) where it gives rise to long structures [59]. Locally two-dimensional allotropic forms of carbon including graphene, nanotubes, and fullerenes, are based on *sp*^{2} bonding as well.

The specific geometry of *sp*^{2} covalent bonding favors $2\pi/3$ bonds. In case v_3 is locally strictly minimized at $2\pi/3$, namely if

$$0 = v_3(2\pi/3) < v_3(\theta) \quad \forall \theta \neq 2\pi/3, 4\pi/3, \tag{5}$$

by specifically quantifying the convexity and the monotonicity of v_3 ground states in two dimensions can be shown to be subsets of a regular hexagonal lattice and the exact value of the ground-state energy in terms of n is established [46]. This precise knowledge of the ground-state energy allows for a characterization of all the two-dimensional ground states, which are generically (with respect to n) nonunique. Their complete characterization in terms of a discrete isoperimetric inequality as well as a sharp, quantitative study of the emergence of a hexagonal Wulff shape for large n is provided in [16]. Note in particular that two-dimensional ground states for large n differ from a suitably rescaled hexagonal configuration by at most $\mathrm{O}(n^{3/4})$ atoms, exactly as in the case of the triangular [2, 15, 53] and the square lattice [43]. The so-called *thermodynamic limit* for $n \to \infty$ has been studied in [19] by extending to the case of (5) the analysis for the triangular lattice in [57]. More recently, the hexagonal lattice has been obtained in the thermodynamic limit for some qualified v_3 density not fulfilling (5) but rather being minimized at π [20].

No ground-state characterization is presently available in three dimensions. Still, the stability of some three-dimensional configurations has been already addressed in [46]. The content of this section corresponds to an extension and refinement of the arguments in [46].

Before going on, let us define $\mathcal{H}$ to be the *hexagonal lattice* with bond length 1, lying on some plane in $\mathbb{R}^3$. A possible specific choice for $\mathcal{H}$ is

$$\mathcal{H} := \{nx + my + cz \,:\, n,\, m \in \mathbb{Z},\ c = 0, 1\}$$

where $x = (\sqrt{3}, 0, 0)$, $y = (\sqrt{3}/2, 3/2, 0)$, $z = (0, 1, 0)$. We call *sp^2-regular* any configuration having solely bonds of length 1 and $2\pi/3$ bond angles and start from the following elementary observation.

Proposition 4.1 (sp^2-regular configurations)**.** *Under assumption* (5) *all sp^2-regular configurations are local minimizers.*

Proof. Let X be sp^2-regular and $\widetilde{X}$ be a small perturbation of X so that the topology of the bond graph is preserved. By indicating with b the number of bonds in X (as well as in $\widetilde{X}$) we have

$$E(\widetilde{X}) \geq -b + \frac{1}{2}\sum_j v_3(\tilde{\theta}_j) \geq -b = E(X)$$

where $\tilde{\theta}_j$ are the bond angles in $\widetilde{X}$. □

The latter proposition entails that all $X \subset \mathcal{H}$ are local minimizers. In particular, *benzene* (a hexagon) and all *alkenes*

$$A_n := \{kx \,:\, k = 1, \dots, \lceil n/2 \rceil\} \cup \{kx - y + z \,:\, k = 1, \dots, \lfloor n/2 \rfloor\}$$

where the vectors x, y, and z are defined above,

are local minimizers. Note however that local minimizers need not be sp^2-regular: Under suitable convexity conditions an isolated pentagon is stable (see Theorem 4.5 below).

Proposition 4.1 leaves open the question whether sp^2-regular configurations are *strict* minimizers, namely *stable* under our understanding. This is indeed not the case, as there exist sp^2-regular configurations which can be deformed without changing the energy. The simplest example in this class is A_4 (*butene*) which presents three bonds, forming two $2\pi/3$ angles. One can obtain a continuum of sp^2-regular configurations by rotating one lateral bond around the central one, by keeping the other lateral bond fixed. Note that all these configurations but A_4 are not planar.

Moving from this example, we call *angle-rigid* a configuration which cannot be continuously deformed without changing the bond lengths or bond angles. More precisely, given the configuration $X \in \mathbb{R}^{3n}$, we say that the continuous deformation $\varphi : X \to \mathbb{R}^{3n}$ is *angle-rigid* for X if it leaves all bond lengths and all bond angles unchanged. We define the configuration X to be *angle-rigid* iff its only angle-rigid deformation is the identity (as well as all isometries).

Examples of angle-rigid configurations are planar hexagons (see Theorem 4.3) and pentagons. On the other hand, configuration A_4 is not angle-rigid. An immediate consequence of Proposition 4.1 is the following.

Proposition 4.2 (Angle-rigidity + sp^2-regularity = stability)**.** *Under assumption* (5) *all angle-rigid, sp^2-regular configurations are stable.*

In case v_3 is locally strictly minimized at $2\pi/3$ and $4\pi/3$ the problem of identifying which sp^2-regular configurations are indeed stable is hence reduced to the analysis of their angle-rigidity. We unfortunately do not have a complete characterization of angle-rigid configurations. In the following, we present some partial results.

Theorem 4.3 (Graphene is stable)**.** *Assume* (5) *and that $X \subset \mathcal{H}$ is a union of hexagons and single-bonded atoms. Then X is angle-rigid, hence strictly minimizing.*

On the other hand, assume that the bond graph of X has a cut-edge connecting two components with at least two atoms. Then X is not angle-rigid, hence not strictly minimizing.

Proof. Let us start by checking that the benzene cycle C_6, a single hexagon, is angle-rigid. Assume φ to be a nontrivial angle-rigid deformation of C_6. Then clearly φ cannot be planar. On the other hand, if $\varphi(C_6)$ is not planar the sum of its bond angles (namely, those smaller than π) is necessarily strictly smaller than 4π, entailing that at least one bond angle has changed. We conclude that the only angle-rigid deformation of C_6 is the identity.

Consider now a configuration whose bond graph is the union of hexagons. Since each hexagon is angle-rigid, a nontrivial angle-rigid deformation must necessarily be angle-rigid for each hexagon. As the configuration is connected, this means that at least two hexagons must rotate about a common bond. This would however change the two bond angles relative to the vertices of this bond and not internal to the hexagons, contradicting the fact that the deformation is angle-rigid. Having proved the angle-rigidity of a configuration whose bond graph is the union of hexagons the treatment of additional single-bonded atoms is straightforward.

Assume now that the bond graph of X has a cut-edge between atoms x' and x'' disconnecting X into two subconfigurations $X' \ni x'$ and $X'' \ni x''$, each of which contains at least two atoms. By keeping X' fixed and rotating X'' around the axis $x' - x''$ we obtain a continuum of nonplanar configurations with the same energy of X. Hence, the minimality of X is not strict. $\square$

Before moving on let us remark that the two topological conditions of Theorem 4.3 are sufficient but not necessary as some configurations whose bond graph is not a union of hexagons and single-bonded atoms can be angle-rigid as well. An example is the left configuration in Figure 2. On the other hand, not angle-rigid configurations need not have cut-edges, see for instance the right configuration in Figure 2.

Corollary 4.4 (Stability of alkenes). *Assume* (5). *Then,* A_1*,* A_2 *(ethene or ethylene), and* A_3 *(propene) are strict local minimizers. All other* A_n *with* $n \geq 4$ *are not strict minimizers.*

The corollary nicely reflects, although necessarily in a very schematic way, the richness of geometries in alkens with $n \geq 4$. These are known to exhibit complex nonplanar configurations [58], a fact which is usually referred to as *structural isomerism* and originates from the interplay of the planarity of the three sp^2 bonds (connecting indeed neighboring carbon atoms and hydrogen) with the remaining fourth orbital, which establishes a weaker and antiplanar so-called π-bond.

Assumption (5) is surely needed for the local minimality of alkenes: if v_3 is not minimized in $2\pi/3$ one can find a perturbation of A_n with lower energy. The situation for graphene is however different. As we have already seen, the hexagonal structure of the configurations entails angle-rigidity and assumption (5) can be dropped and replaced by strict convexity and monotonicity. In particular, specific graphene patches are stable with respect to possibly more general potentials.

Theorem 4.5 (Graphene is stable 2). *Assume* v_3 *to be strictly convex in a neighborhood of* $2\pi/3$ *and strictly decreasing in a left neighborhood of* $2\pi/3$*. Let* $X \subset \mathcal{H}$ *be angle-rigid and such that all atoms either have one or three neighbors. Then* X *is a strict local minimizer.*

Proof. Let $\widetilde{X}$ be a small perturbation of X preserving the bond-graph topology and indicate with b the number of bonds in X (and in $\widetilde{X}$). To each three-bonded atom x_i in $\widetilde{X}$ correspond three bond angles smaller than π which we indicate with $\tilde{\theta}_i^1, \tilde{\theta}_i^2$, and $\tilde{\theta}_i^3$. As

$$\tilde{\theta}_i^1 + \tilde{\theta}_i^2 + \tilde{\theta}_i^3 \leq 2\pi,$$

the latter being an equality iff all bonds in x_i are coplanar, we indicate by $\overline{\theta}$ the mean

$$\overline{\theta} = \frac{1}{3m} \sum_{i=1}^{m} \left(\tilde{\theta}_i^1 + \tilde{\theta}_i^2 + \tilde{\theta}_i^3 \right) \leq \frac{2\pi}{3}$$

where m is the number of three-bonded atoms, and compute

$$\begin{aligned} E(\widetilde{X}) &\overset{\text{(a)}}{\geq} -b + \sum_{i=1}^{m} \Big(v_3(\tilde{\theta}_i^1) + v_3(\tilde{\theta}_i^2) + v_3(\tilde{\theta}_i^3) \Big) \overset{\text{(b)}}{\geq} -b + 3m v_3(\overline{\theta}) \\ &\overset{\text{(c)}}{\geq} -b + 3m v_3(2\pi/3) = E(X). \end{aligned}$$

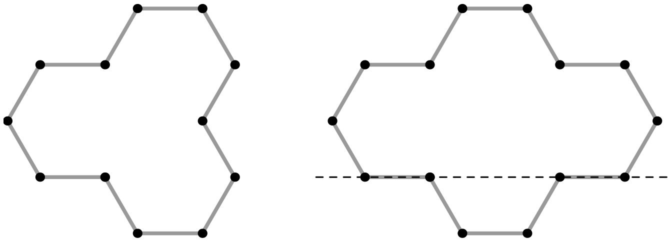

Figure 2. Left: An angle-rigid configuration which is not the union of hexagons. Right: a nonstrict local minimizer under (5): by rotating part of the configuration around the dashed axis the energy is unchanged.

Here, we are assuming that the perturbation is so small that we can exploit the convexity and the monotonicity of v_3. Inequality (a) is strict whenever the length of a bond in $\widetilde{X}$ differs from 1 whereas (b) is strict if a bond angle differs from the mean $\overline{\theta}$. Eventually, inequality (c) is strict if $\overline{\theta} < 2\pi/3$, namely if some triplet of bonds at a point is nonplanar. If $E(\widetilde{X}) = X$ then necessarily $\widetilde{X}$ has all bonds of length 1 and all its bond angles are $2\pi/3$. Since X is angle-rigid, we necessarily have $\widetilde{X} = X$ so that the local strict minimality follows. $\square$

The assumption in Theorem 4.5 on the topology of the bond graph can be relaxed and more configurations can be proved to be stable. In particular, the benzene cycle C_6 is stable. By indicating with $\tilde{\theta}_i$ the bond angles smaller than π of the small perturbation $\widetilde{C}_6$ we readily check that

$$\begin{aligned} E(\widetilde{C}_6) &\overset{\text{(a)}}{\geq} -6 + \sum_{i=1}^{6} v_3(\tilde{\theta}_i) \overset{\text{(b)}}{\geq} -6 + 6v_3\left(\frac{1}{6}\sum_{i=1}^{6}\tilde{\theta}_i\right) \\ &\overset{\text{(c)}}{\geq} -6 + 6v_3(2\pi/3) = E(C_6). \end{aligned}$$

Here we have used the convexity of v_3 in (b) and the fact that

$$\frac{1}{6}\sum_{i=1}^{6}\tilde{\theta}_i \leq 2\pi/3,$$

this being an equality iff $\widetilde{C}_6$ is planar, combined with monotonicity of v_3 in (c). The above chain of inequalities is strict whenever $\widetilde{C}_6 \neq C_6$.

On the other hand, some restriction on topology of the bond graph is needed in order to establish a stability result in the spirit Theorem 4.5. The requirement on the angle-rigidity of the configuration is of course necessary: as E depends on bonds and bond angles only, if X is not angle-rigid then it is necessarily not a strict minimizer. Even under assumption (5) one can find configurations which are not strictly minimizing. An example is in Figure 2 below.

The assumptions on v_3 in the statement of Theorem 4.5 are on the contrary somehow optimal, at least in relation with benzene. Assume v_3 to convex and monotone in a neighborhood of $2\pi/3$. By dropping the strict convexity assumption one would include the case of a locally affine v_3. This would however allow to construct a nontrivial perturbation of the benzene cycle by reducing three bond angles and increasing the other three by the same small quantity leaving the energy unchanged. On the other hand, if we drop the strict monotonicity assumption we can obtain a nontrivial nonplanar perturbation with the same energy by reducing all bond angles (smaller than π) by the same small amount. In both cases the benzene cycle would be unstable.

5. FULLERENES

Theorem 4.5 is concerned with stable *planar* configurations in three dimensions. On the other hand, sp^2-bonded configurations may be nonplanar. Relevant examples in this directions are *fullerenes*, namely configurations whose bond graph contains exactly 12 pentagons and an unrestricted number of hexagons [35, 36]. Fullerenes are usually indicated by the symbol C_n, where n is the number of carbon atoms, and are believed to exist for arbitrary (even) $20 \leq n \neq 22$. One has however to note that, with the exception of $n = 20$, a number of topologically different bond graphs can be generated for the same n. These are what are usually referred to as different *isomers*. As such, the symbol C_n does not directly define the topology of the bond graph of the configuration and some care has to be taken in order to specify the object in study.

We can ascertain the stability of two specific fullerenes, namely C_{20} (unsaturated *dodecahedrane*) and (a specific isomer of) C_{60}. The dodecahedrane C_{20} is the smallest fullerene and it is expected to possibly show a variety of interesting properties including superconductivity [40]. On the other hand, C_{60} is by far the most common fullerene. Usually the first one to cluster, probably due to its evenly distributed strain energy [36], it is to be found in interstellar space as well [9]. For the purposes of this analysis we specify these two configurations as follows

$$C_{20} := \big\{x_1, \dots, x_{20} \in \mathbb{R}^3 \text{ vertices of a regular}\\ \text{dodecahedron with side } 1\big\}.$$

On the other hand, we indicate with C_{60} the configuration

$$C_{60} := \big\{x_1, \dots, x_{60} \in \mathbb{R}^3 \text{ vertices of a truncated}\\ \text{regular icosahedron with side } 1\big\}$$

where the *truncation* of the definition of C_{60} is realized by intersecting the edges of a regular icosahedron with a sphere with the same center. The stability of C_{20} and C_{60} has been discussed in [46, Thm. 7.3]. We report here a slightly refined version of that statement, along with its elementary proof.

Theorem 5.1 (C_{20} and C_{60} are stable)**.** *Assume* v_3 *to be strictly convex in a neighborhood of* $3\pi/5$ *and* $2\pi/3$ *and strictly decreasing in a left neighborhood of* $3\pi/5$ *and* $2\pi/3$*. Then* C_{20} *and* C_{60} *are strict local minimizers.*

Proof. We give the detail of the proof for C_{60}, the adaptation for C_{20} being trivial. Let $\widetilde{C}_{60}$ be a small perturbation of C_{60} preserving the topology of the bond graph. We indicate by $\{\tilde{h}_1^k,\dots,\tilde{h}_6^k\}$, $k=1,\dots,20$ and $\{\tilde{p}_1^k,\dots,\tilde{p}_5^k\}$, $k=1,\dots,12$ the *internal* bond angles of hexagons and pentagons in the bond graph of $\widetilde{C}_{60}$ (that is, the angles which correspond to internal angles of the undeformed planar simple cycles of C_{60}). By using

$$\frac{1}{6}\sum_{i=1}^{6}\tilde{h}_i^k \le 2\pi/3, \quad \frac{1}{5}\sum_{i=1}^{5}\tilde{p}_i^k \le 3\pi/5$$

which holds for each simple cycle, we compute

$$\begin{aligned} E(\widetilde{C}_{60}) &\overset{(a)}{\ge} -90 + \sum_{k=1}^{20}\sum_{i=1}^{6} v_3(\tilde{h}_i^k) + \sum_{k=1}^{12}\sum_{i=1}^{5} v_3(\tilde{p}_i^k) \\ &\overset{(b)}{\ge} -90 + 6\sum_{k=1}^{20} v_3\left(\frac{1}{6}\sum_{i=1}^{6}\tilde{h}_i^k\right) + 5\sum_{k=1}^{12} v_3\left(\frac{1}{5}\sum_{i=1}^{5}\tilde{p}_i^k\right) \\ &\overset{(c)}{\ge} -90 + 120 v_3(2\pi/3) + 60 v_3(3\pi/5) = E(C_{60}). \end{aligned}$$

We have assumed here that the perturbation is so small that we can exploit the convexity and monotonicity of v_3. In the above chain of inequalities, relation (a) is strict whenever the length of a bond of $\widetilde{C}_{60}$ is different from 1 and (b) is strict if a bond angle corresponding to a simple cycle of $\widetilde{C}_{60}$ is different from the mean of the bond angles in that cycle. Then inequality (c) is strict whenever a simple cycle of $\widetilde{C}_{60}$ is nonplanar. If $E(\widetilde{C}_{60}) = E(C_{60})$ then all pentagons and hexagons of the bond graph of $\widetilde{C}_{60}$ are planar and regular with bond length 1, namely $\widetilde{C}_{60} = C_{60}$. we conclude that C_{60} is a strict local minimizer. □

Theorem 5.1 delivers a variational model for the geometry of C_{20} and C_{60}. In the specific case of C_{60} actual experiments show that the molecule has indeed two distinct bond lengths, depending on the fact that the bond connects two different pentagons or not [14]. This level of detail cannot be described within the current simplified frame but can be reproduced by taking into account second-neighbor interactions or additional four-body terms [22].

By inspecting the proof of Theorem 5.1 one realizes that planarity of the simple cycles is crucial in order to establish stability. This however restricts the applicability of the proof to the *only two* fullerenes with planar cycles, which are exactly C_{20} and C_{60} [52]. On the other hand, we mention that the planarity of simple cycles has been argued to have a relevant role in sorting out the observed isomers [34]. Note that planarity alone does not entail stability (nor minimality). An example in this direction is *corannulene*, a three-dimensional configuration whose bond graph is a pentagon surrounded by five hexagons. Measurements show that the hexagons in corannulene are not planar [27]. Quite remarkably this corresponds to the following.

Proposition 5.2 (Corannulene has nonplanar hexagons)**.** *Assume v_3 to be twice differentiable with $v_3'(3\pi/5) < 0 = v_3(2\pi/3)$. Let the configuration K have all bonds of length 1 as well as a bond graph consisting of a pentagon surrounded by five hexagons, all of which being planar. Then K is not a minimizer.*

Proof. We describe a small perturbation of K which lowers the energy. This is achieved by making the five hexagons of the bond graph of K nonplanar. Each hexagon has exactly two atoms belonging to the pentagon, two three-bonded atoms which do not belong to the pentagon, and two two-bonded atoms. The small perturbation consists, in each hexagon, in keeping the first four atoms fixed and displace the last two out of plane by rotating them along the diagonal connecting the two three-bonded atoms x_j not belonging to the pentagon. For the sake of definiteness let us indicate by θ the internal angle of the hexagon at x_j and by φ the external angle at x_j, namely the only bond angle in x_j which is not internal to a hexagon. The above-described deformation changes the bond angles θ to $\tilde\theta = \theta - \delta\theta$ and φ to $\tilde\varphi = \varphi + \delta\varphi$, by some $\delta\theta$ and $\delta\varphi$ positive and small. In particular, the energy contribution corresponding to θ increases while the one corresponding to φ decreases. It is readily seen that

$$2\tilde\theta + \tilde\varphi > 2\theta + \varphi$$

so that $\delta\varphi > 2\delta\theta > 0$. As v_3 is linear around $3\pi/5$ and quadratic in $2\pi/3$, small deformations result in a global energy drop. ☐

Single-walled carbon nanotubes constitute another important class of three-dimensional sp^2 configurations having nonplanar simple cycles. These can be be visualized as the result of the roll-up of a graphene strip [17]. Depending on the direction of the roll-up with respect to the reference frame of $\mathcal{H}$, carbon nanotubes have different bond-graph topologies (so-called *zigzag, armchair*, and *chiral*) resulting in different electro-mechanical properties. These remarkable effects are believed to be possibly playing a major technological role in the near future.

The investigation of rolled-up structures via configurational-energy analysis is already quite classical. The reader is referred, for instance to [32, 51] for geometries, to [24, 61] for mechanical response, and to [10, 48] for discrete to continuum limits. In [46] it is argued that sufficiently large graphene patches have higher energy with respect to their roll-up in a tube-like structure and that a constant aspect ratio for nanotubes can be expected, as the number n of atoms increases. This in particular reflects the experimental observation that carbon nanotube can grow as long as 10^6 times their diameter.

On the other hand the fine geometry of carbon nanotubes is currently still debated and two competing models, namely the *rolled-up* [17, 18, 33] and the *polyhedral* model [13, 38], have been advanced. Both models assume atoms to be arranged on the surface of a cylinder by prescribing different bond angles. It has been proved in [44, 45] that none of these models give rise to a configurational-energy minimizer (when referred to armchair and zigzag nanotubes). Note however that a stable periodic configuration exists and can be characterized by solving a single scalar nonlinear equation [44, 45].

It has been recently argued that a new allotrope of sp^2 carbon could possibly have the form of a so-called K_4 crystal [29, 55]. This consists of a 3-regular graph (all atoms have three bonds) with all bond lengths 1 and all bond angles $2\pi/3$. Differently from $\mathcal{H}$ where all bond planes (namely, given an atom, the plane containing its three bonds) are coplanar, the bond plane of two bonded atoms in the K_4 crystal graph are orthogonal. This gives rise to a chiral, three-dimensional structure. Owing to Proposition 4.1 this structure is a local minimizer. The complete characterization of angle-rigid subsets of K_4 crystals is currently not available. Still, results in the spirit of Theorems 4.3 and 4.5 can be obtained.

Eventually, let us mention that a variety of other locally two-dimensional sp^2 carbon structures have been theoretically proposed and experimentally investigated. Among these we could mention *nanobuds* [49] (resulting from the junction of nanotubes and fullerenes), *nanofunnels* [26] (graphene and nanotube), *nanosieves* (joining two nanofunnels) [26], *Mackay crystals* [42], as well as the theoretical wealth of three-dimensional carbon architectures which may be possibly generated by combining these. Although all of these configurations can be addressed by variational methods and, in particular, a global minimizer within a specific bond-graph-topology class may exist under fairly general lower semicontinuity assumptions, such minimizers cannot be expected to share properties as planarity or regularity of simple cycles. Indeed, nonplanar heptagons and octagons seem also to come into the picture. As such, the investigation of the stability of these structures (or, better, of the optimal geometry within the corresponding bond-graph-topology class, an object which is still to be identified) is currently beyond the reach of our methods.

Another interesting class of carbon nanostructures emerges as stratification of many two-dimensional substructures. These include *multiwalled nanotubes* [28] and *carbon onions* [8]. The underlying two-dimensional substructures can be interpreted as sp^2-bonded configurations and the overall stratification is classically assumed to be governed by the weaker, antiplanar π-bonds as well. This finer description is currently not included in our simplified variational frame. For some initial result in the direction of the variational modelization of π-bonds we refer the reader to [22].

6. DIAMOND

Let us now move to the analysis of sp^3-bonded configurations. This is the basic bonding mode in *alkanes*, a reference structure being *pentane* (C_5H_{12}) where the four neighbors of the central atom sit at the vertices of a regular tetrahedron. Correspondingly, the four bonds form six *tetragonal* angles of

$$\theta_\tau = 2\arctan(\sqrt{2}) = \arccos(-1/3).$$

sp^3-bonded configurations are genuinely three-dimensional. An important example are subconfigurations of the *diamond* lattice $\mathcal{D}$ corresponding indeed to the face-centered-cubic structure of tetrahedra

$$\mathcal{D} = \mathcal{T} \cup (\mathcal{T}{+}v) + \mathbb{Z}w.$$

Here, $\mathcal{T}$ stands for the triangular lattice

$$\mathcal{T} = \{kx + jy \,:\, k,\, j \in \mathbb{Z}\}$$

with $x = (\ell, 0, 0)$, $y = (\ell/2, \sqrt{3}\ell/2, 0)$, $\ell = 2\sin(\theta_\tau/2) \sim 1.633$, and we have used the short-hand notation for the shifts $v = (\ell/2, \ell/(2\sqrt{3}), 1/3)$ and $w = v + (0, 0, 1)$. Note that all bonds in $\mathcal{D}$ have length 1 and all bond angles are θ_τ. We shall refer to configurations having these two properties as *sp^3-regular.*

The sp^3 geometry can be enforced by imposing the minimality

$$0 = v_3(\theta_\tau) < v_3(\theta) \quad \forall \theta \neq \theta_\tau,\, 2\pi - \theta_\tau. \tag{6}$$

The latter entails the local minimality of sp^3-regular configurations. Indeed, we have the analogue of Proposition 4.1.

Proposition 6.1 (sp^3-regular configurations)**.** *Under assumption* (6) *all sp^3-regular configurations are local minimizers.*

In the same spirit of Theorem 4.3, angle-rigidity characterizes stability within the class of sp^3-regular configurations. We have the following.

Theorem 6.2 (Diamond is stable)**.** *Assume* (5) *and that $X \subset \mathcal{D}$ is a union of hexagons and single bonded atoms. Then X is angle-rigid, hence strictly minimizing.*

On the other hand, assume that the bond graph of $X \subset \mathcal{D}$ has a cut-edge connecting two components with at least two atoms. Then X is not angle-rigid, hence not strictly minimizing.

Proof. The assertion follows along the very same lines as that of Theorem 4.3 upon noticing that hexagons with bond length 1 and bond angles θ_τ are angle-rigid. $\square$

Once again, we remark that the topological assumptions of Theorem 6.2 are not necessary conditions: angle-rigid configurations with cut-edges connecting two components with at least two atoms and not angle-rigid configurations with no cut-edge can be found in $\mathcal{D}$ in the spirit of Figure 2.

Let us now consider the possibility of dropping assumption (6) and replacing it by monotonicity and convexity requirements, in analogy with Theorem 4.5. Note that sp^3-regular configurations are not planar. In particular, isolated hexagons in $\mathcal{D}$ cannot be minimal if $v_3'(\theta_\mathcal{T}) \neq 0$. This motivates a restriction of possible subconfigurations of $\mathcal{D}$ as in the following.

Theorem 6.3 (Diamond is stable 2)**.** *Assume that* v_3 *is* C^2 *in a neighborhood of* $\theta_\mathcal{T}$ *and* $0 < -0.334\, v_3'(\theta_\mathcal{T}) < v_3''(\theta_\mathcal{T})$. *Let* $X \subset \mathcal{D}$ *be angle-rigid and such that all atoms have either one or four neighbors. Then* X *is a strict local minimizer.*

Proof. The local geometry of the configuration at a four-bonded atom is described by six bond angles and four bond lengths. Equivalently, instead of the six bond angles one could consider the three bond angles θ^1, θ^2, θ^3 formed by one specific bond and the three incidence angles γ^1, γ^2, γ^2 formed by the planes containing θ^1 and θ^2, θ^2 and θ^3, and θ^1 and θ^3, respectively. In particular, given θ^1, θ^2, and γ^1, the third bond angle can be computed via basic trigonometry as

$$\beta(\theta^1,\theta^2,\gamma^1) := 2\arcsin\left(\frac{1}{\sqrt{2}}\sqrt{1-\cos\gamma^1\sin\theta^1\sin\theta^2-\cos\theta^1\cos\theta^2}\right),$$

see Figure 3. By recalling that $\gamma^1+\gamma^2+\gamma^3=2\pi$, the three-body part of

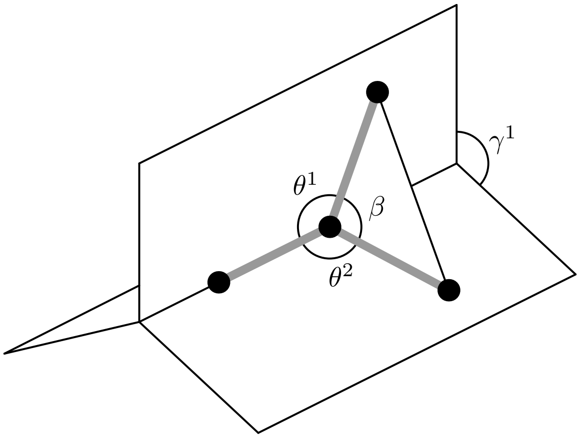

Figure 3. The function $\beta = \beta(\theta^1,\theta^2,\gamma^1)$.

the energy contribution of a four-bonded atom whose geometry is described by the quintuple $(\theta^1,\theta^2,\theta^3,\gamma^1,\gamma^2)$ can be expressed as

$$\begin{aligned}\widehat{E}(\theta^1,\theta^2,\theta^3,\gamma^1,\gamma^2) &= v_3(\theta^1)+v_3(\theta^2)+v_3(\theta^3)\\ &\quad + v_3\big(\beta(\theta^1,\theta^2,\gamma^1)\big)+v_3\big(\beta(\theta^2,\theta^3,\gamma^2)\big)\\ &\quad + v_3\big(\beta(\theta^3,\theta^1,2\pi{-}\gamma^1-\gamma^2)\big).\end{aligned}$$

In particular, the local geometry of $\mathcal{D}$ corresponds to the quintuple of *tetragonal values* $(\theta_\tau,\theta_\tau,\theta_\tau,2\pi/3,2\pi/3)$. Note that indeed one has the identity $\beta(\theta_\tau,\theta_\tau,2\pi/3)=\theta_\tau$.

We now proceed in proving that

$$\widehat{E} \text{ is uniformly convex in a neighb. of the tetragonal values.} \tag{7}$$

This follows by checking that $\mathrm{D}^2\widehat{E}$ is positive definite in the tetragonal values. Elementary computations ensure that in such points we have

$$\mathrm{D}^2_{\theta\theta}\widehat{E} = v_3''(\theta_\tau)I + v_3''(\theta_\tau)\sum_{i=1}^3 \mathrm{D}_\theta\beta^i{\otimes}\mathrm{D}_\theta\beta^i + v_3'(\theta_\tau)\sum_{i=1}^3 \mathrm{D}^2_{\theta\theta}\beta^i \tag{8}$$

where I stands for the identity matrix in $\mathbb{R}^{3\times3}$, D_θ denotes differentiation with respect to the three variables $(\theta^1,\theta^2,\theta^3)$, and we have used the notation

$$\begin{aligned}\beta^1(\theta^1,\theta^2,\theta^3,\gamma^1,\gamma^2) &= \beta(\theta^1,\theta^2,\gamma^1),\\ \beta^2(\theta^1,\theta^2,\theta^3,\gamma^1,\gamma^2) &= \beta(\theta^2,\theta^3,\gamma^2),\\ \beta^3(\theta^1,\theta^2,\theta^3,\gamma^1,\gamma^2) &= \beta(\theta^3,\theta^1,2\pi{-}\gamma^1{-}\gamma^2).\end{aligned}$$

At the tetragonal values $(\theta_\tau,\theta_\tau,\theta_\tau,2\pi/3,2\pi/3)$ one can directly compute

$$v_3''(\theta_\tau)I + v_3''(\theta_\tau)\sum_{i=1}^3 \mathrm{D}_\theta\beta^i\otimes\mathrm{D}_\theta\beta^i = \frac14 v_3''(\theta_\tau)\begin{pmatrix}6&1&1\\1&6&1\\1&1&6\end{pmatrix}.$$

On the other hand, one has that

$$v_3'(\theta_\tau)\sum_{i=1}^3 \mathrm{D}^2_{\theta\theta}\beta^i = -\frac{3v_3'(\theta_\tau)}{8\sqrt2}\begin{pmatrix}2&3&3\\3&2&3\\3&3&2\end{pmatrix}$$

so that $\mathrm{D}^2_{\theta\theta}\widehat{E}$ at the tetragonal values reads from (8) as

$$\mathrm{D}^2_{\theta\theta}\widehat{E} = \frac14 v_3''(\theta_\tau)\begin{pmatrix}6&1&1\\1&6&1\\1&1&6\end{pmatrix} - \frac{3v_3'(\theta_\tau)}{8\sqrt2}\begin{pmatrix}2&3&3\\3&2&3\\3&3&2\end{pmatrix}.$$

In particular, it has the form

$$\begin{pmatrix}a&b&b\\b&a&b\\b&b&a\end{pmatrix} \tag{9}$$

with

$$a = \frac{3}{2}v_3''(\theta_\tau) - \frac{3}{4\sqrt{2}}v_3'(\theta_\tau), \quad b = \frac{1}{4}v_3''(\theta_\tau) - \frac{9}{8\sqrt{2}}v_3'(\theta_\tau).$$

The matrix in (9) is positive definite $a > b > 0$. This condition can be rewritten as $0 < -3v_3'(\theta_\tau) < 10\sqrt{2}v_3''(\theta_\tau)$ which follows under the quantitative assumption of the statement. Hence, $\mathrm{D}^2_{\theta\theta}\widehat{E}$ is positive definite at the tetragonal values. In particular we also have that

$$\theta \mapsto \widehat{E}(\theta, \theta, \theta, 2\pi/3, 2\pi/3) \text{ has a strict local minimum in } \theta_\tau. \tag{10}$$

Indeed, we can compute that

$$\begin{aligned} &\frac{\mathrm{d}}{\mathrm{d}\theta}\widehat{E}(\theta, \theta, \theta, 2\pi/3, 2\pi/3)|_{\theta=\theta_\tau} \\ &= 3v_3'(\theta_\tau) + 3v_3'(\beta(\theta_\tau, \theta_\tau, 2\pi/3))\frac{\mathrm{d}}{\mathrm{d}\theta}\beta(\theta, \theta, 2\pi/3)|_{\theta=\theta_\tau} \\ &= 3v_3'(\theta_\tau)\left(1 + \frac{\mathrm{d}}{\mathrm{d}\theta}\beta(\theta, \theta, 2\pi/3)|_{\theta=\theta_\tau}\right) = 0 \end{aligned}$$

so that θ_τ is critical. The strict minimality in (10) follows from the positive definiteness of $\mathrm{D}^2_{\theta\theta}\widehat{E}$ at the tetragonal values.

By computing the hessian of $\widehat{E}$ with respect to the variables $\gamma = (\gamma^1, \gamma^2)$ at the tetragonal values $(\theta_\tau, \theta_\tau, \theta_\tau, 2\pi/3, 2\pi/3)$ we get

$$\mathrm{D}^2_{\gamma\gamma}\widehat{E} = \left(\frac{2}{3}v_3''(\theta_\tau) - \frac{1}{3\sqrt{2}}v_3'(\theta_\tau)\right)\begin{pmatrix} 2 & 1 \\ 1 & 2 \end{pmatrix}.$$

Finally, one directly computes $\mathrm{D}^2_{\theta\gamma}\widehat{E}$ at the tetragonal values as

$$\mathrm{D}^2_{\theta\gamma}\widehat{E} = \left(\frac{1}{\sqrt{6}}v_3''(\theta_\tau) + \frac{\sqrt{3}}{4}v_3'(\theta_\tau)\right)\begin{pmatrix} 0 & 1 \\ -1 & -1 \\ 1 & 0 \end{pmatrix}.$$

In order to check for the positive definiteness of the block matrix

$$\mathrm{D}^2\widehat{E} = \begin{pmatrix} \mathrm{D}^2_{\theta\theta}\widehat{E} & \mathrm{D}^2_{\theta\gamma}\widehat{E} \\ \mathrm{D}^2_{\theta\gamma}\widehat{E}^\top & \mathrm{D}^2_{\gamma\gamma}\widehat{E} \end{pmatrix}$$

at the tetragonal values we exploit the following equivalence

$$\mathrm{D}^2\widehat{E} > 0 \quad \Longleftrightarrow \quad \mathrm{D}^2_{\gamma\gamma}\widehat{E} > 0 \text{ and } \mathrm{D}^2_{\theta\theta}\widehat{E} - \mathrm{D}^2_{\theta\gamma}\widehat{E}(\mathrm{D}^2_{\gamma\gamma}\widehat{E})^{-1}\mathrm{D}^2_{\theta\gamma}\widehat{E}^\top > 0.$$

Since $v_3'(\theta_\tau) < 0 < v_3''(\theta_\tau)$ the matrix $\mathrm{D}^2_{\gamma\gamma}\widehat{E} > 0$ is positive definite. On the other hand, the matrix $\mathrm{D}^2_{\theta\theta}\widehat{E} - \mathrm{D}^2_{\theta\gamma}\widehat{E}(\mathrm{D}^2_{\gamma\gamma}\widehat{E})^{-1}\mathrm{D}^2_{\theta\gamma}\widehat{E}^\top > 0$ has form (9) along with the choices

$$\begin{aligned}
a &= \frac{3}{2}v_3''(\theta_\mathcal{T}) - \frac{3}{4\sqrt{2}}v_3'(\theta_\mathcal{T}) \\
&\quad - \frac{2}{3}\left(\frac{1}{\sqrt{6}}v_3''(\theta_\mathcal{T}) + \frac{\sqrt{3}}{4}v_3'(\theta_\mathcal{T})\right)^2 \left(\frac{2}{3}v_3''(\theta_\mathcal{T}) - \frac{1}{3\sqrt{2}}v_3'(\theta_\mathcal{T})\right)^{-1}, \\
b &= \frac{1}{4}v_3''(\theta_\mathcal{T}) - \frac{9}{8\sqrt{2}}v_3'(\theta_\mathcal{T}) \\
&\quad + \frac{1}{3}\left(\frac{1}{\sqrt{6}}v_3''(\theta_\mathcal{T}) + \frac{\sqrt{3}}{4}v_3'(\theta_\mathcal{T})\right)^2 \left(\frac{2}{3}v_3''(\theta_\mathcal{T}) - \frac{1}{3\sqrt{2}}v_3'(\theta_\mathcal{T})\right)^{-1}.
\end{aligned}$$

One can check that the condition $a > b > 0$ for positive definiteness can be rewritten as

$$v_3''(\theta_\mathcal{T}) > \frac{2-\sqrt{19}}{5\sqrt{2}}v_3'(\theta_\mathcal{T}) > 0$$

which is slightly weaker than the quantitative assumption of the statement. We conclude that $\mathrm{D}^2\widehat{E}$ is positive definite at the tetragonal values. The local uniform convexity (7) of $\widehat{E}$ follows.

Let $\widetilde{X}$ be a small perturbation of X preserving the bond-graph topology and indicate with b the number of bonds in X (and in $\widetilde{X}$). We indicize by $i = 1, \dots, m$ the four-bonded atoms and describe the local geometry of $\widetilde{X}$ at these atoms via the quintuples $(\tilde\theta_i^1, \tilde\theta_i^2, \tilde\theta_i^3, \tilde\gamma_i^1, \tilde\gamma_i^2)$ which can be assumed to be arbitrarily close to the tetragonal values $(\theta_\mathcal{T}, \theta_\mathcal{T}, \theta_\mathcal{T}, 2\pi/3, 2\pi/3)$. By indicating by $\bar\theta$ the mean value

$$\bar\theta = \frac{1}{3m}\sum_{i=1}^{m}(\tilde\theta_i^1 + \tilde\theta_i^2 + \tilde\theta_i^3)$$

and using the symmetries

$$\beta(a, b, \gamma) = \beta(b, a, \gamma) = \beta(b, a, 2\pi - \gamma) \tag{11}$$

one can compute

$$
\begin{aligned}
E(\widetilde{X}) &\geq -b + \sum_{i=1}^{m} \widehat{E}(\tilde{\theta}_i^1, \tilde{\theta}_i^2, \tilde{\theta}_i^3, \tilde{\gamma}_i^1, \tilde{\gamma}_i^2) \\
&\overset{(11)}{=} -b + \frac{1}{3}\sum_{i=1}^{m} \widehat{E}(\tilde{\theta}_i^1, \tilde{\theta}_i^2, \tilde{\theta}_i^3, \tilde{\gamma}_i^1, \tilde{\gamma}_i^2) \\
&\qquad + \frac{1}{3}\sum_{i=1}^{m} \widehat{E}(\tilde{\theta}_i^2, \tilde{\theta}_i^3, \tilde{\theta}_i^1, \tilde{\gamma}_i^2, 2\pi - \tilde{\gamma}_i^1 - \tilde{\gamma}_i^2) \\
&\qquad + \frac{1}{3}\sum_{i=1}^{m} \widehat{E}(\tilde{\theta}_i^3, \tilde{\theta}_i^1, \tilde{\theta}_i^2, 2\pi - \tilde{\gamma}_i^1 - \tilde{\gamma}_i^2, \tilde{\gamma}_i^1) \\
&\overset{(7)}{\geq} -b + m\widehat{E}(\overline{\theta}, \overline{\theta}, \overline{\theta}, 2\pi/3, 2\pi/3) \\
&\overset{(10)}{\geq} -b + m\widehat{E}(\theta_\mathcal{T}, \theta_\mathcal{T}, \theta_\mathcal{T}, 2\pi/3, 2\pi/3) = E(X).
\end{aligned}
$$

Note that the first inequality is strict whenever the length of a bond of $\widetilde{X}$ is different from 1 while the second is strict iff $\tilde{\theta}_i^j \neq \overline{\theta}$ or $\gamma_i^k \neq 2\pi/3$ for some $i = 1, \ldots, m$ and $j = 1, 2, 3$ or $k = 1, 2$. Finally, the last inequality is strict iff $\overline{\theta} \neq \theta_\mathcal{T}$. We have proved that $E(\widetilde{X}) = E(X)$ implies that $\widetilde{X}$ and X have the same bonds and the same bond angles. As X is angle-rigid, we necessarily have $\widetilde{X} = X$. $\square$

An analogous stability result holds for specific subconfigurations of the *lonsdaleite* or *hexagonal-diamond* lattice [7]

$$\mathcal{T} \cup (\mathcal{T}+v) \cup (\mathcal{T}+w) \cup (\mathcal{T}+(0, 0, 1-2\cos(\theta_\mathcal{T})) + \mathbb{Z}(0, 0, 2-2\cos\theta_\mathcal{T}).$$

This possibility follows from the fact that the local topology of $\mathcal{L}$ is exactly the same as that of $\mathcal{D}$.

Let us remark that, in order some stability in the diamond (or the lonsdaleite) lattice to hold, the angle-rigidity assumption in the statement of Theorem 6.3 is necessary, for the energy is constant along angle-rigid deformations. At the same time, some quantitative assumption relating the convexity and the monotonicity of v_3 in a neighborhood of $\theta_\mathcal{T}$ is necessary. Indeed, assume that $v_3' < 0$ but $-3v_3' > 10\sqrt{2}v_3''$ in a neighborhood of $\theta_\mathcal{T}$. By following the argument of the proof of Theorem 6.3 one realizes that, in this case, even pentane, namely a single tetragon, is not a minimizer, for the function

$$(\theta^1, \theta^2, \theta^3) \mapsto \widehat{E}(\theta^1, \theta^2, \theta^3, 2\pi/3, 2\pi/3)$$

is not minimized at $(\theta_\mathcal{T}, \theta_\mathcal{T}, \theta_\mathcal{T})$.

Let us conclude this discussion by recording that, by assuming v_3 to be strictly convex and strictly decreasing in a neighborhood of $(3\pi/5, \pi)$ with $-0.334\, v_3'(\theta_\mathcal{T}) < v_3''(\theta_\mathcal{T})$, carbyne chains and rings, graphene patches (under the topological assumptions of Theorem 4.5), the fullerenes C_{20} and C_{60}, and diamond and lonsdaleite subconfigurations (under the topological assumptions of Theorem 6.3) are stable. By letting v_3 be homogeneous in a neighborhood of $(3\pi/5, \pi)$, namely

$$v_3(\theta) \sim |\pi - \theta|^\alpha,$$

and choosing $\alpha > -(2-\sqrt{19})(\pi-\theta_\tau)/(5\sqrt{2})+1 \sim 1.411$ the density v_3 would then fulfill all the above-mentioned assumptions. This is compatible with the classical behavior of the so-called *Brenner* potential [4, 5], and [20, App. A].

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