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THE GEOMETRY OF C_{60}: A RIGOROUS APPROACH VIA MOLECULAR MECHANICS*

MANUEL FRIEDRICH†, PAOLO PIOVANO†, AND ULISSE STEFANELLI‡

Abstract. Molecular Mechanics describes molecules as particle configurations interacting via classical potentials. These *configurational energies* usually consist of the sum of different phenomenological terms which are tailored to the description of specific bonding geometries. This approach is followed here to model the fullerene C_{60}, an allotrope of carbon corresponding to a specific hollow spherical structure of sixty atoms. We rigorously address different modeling options and advance a set of minimal requirements on the configurational energy able to deliver an accurate prediction of the fine three-dimensional geometry of C_{60} as well as of its remarkable stability. In particular, the experimentally observed truncated-icosahedron structure with two different bond lengths is shown to be a strict local minimizer.

Key words. fullerene, C_{60}, configurational energy minimization, local stability

AMS subject classification. 82D25

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1. Introduction.

The molecule C_{60} is an allotrope of carbon formed by 60 atoms sitting at the vertices of a truncated icosahedron. Theoretically discussed in [38] and [5], its serendipitous experimental discovery in 1985 led to the attribution of the 1996 Nobel Prize in Chemistry to Curl, Kroto, and Smalley (see [30, 29]). This truly remarkable result paved the way for extending the up-to-then known allotropes, namely graphite, diamond, and amorphous carbon, to a whole new class of molecules consisting of hollow carbon cages, balls, ellipsoids, and nanotubes. The resemblance of C_{60} with the geodesic domes by the American architect Buckminster Fuller has brought to these molecules the name *fullerenes*.

Fullerenes have attracted an immense amount of attention. The identification of their three-dimensional structure; the study of their chemical properties, including aromaticity, solubility, and electrochemistry; and their application in medicine and pharmacology have developed into the new branch of *Fullerene Chemistry*. A central question concerning fullerenes is their *stability* [28], either from the thermodynamic, the electrochemical, or the mechanical standpoint. Stability is believed to be the key factor in explaining why just a few fullerene isomers out of a theoretically predicted wide variety have actually been revealed. Among these the fullerene C_{60} is remarkably stable, and considerable amounts of these molecules have been detected in interstellar space, despite the harsh radiation environment [1].

The aim of this paper is to provide a rigorous discussion of the geometric structure and the stability properties of the C_{60} molecule. This analysis is set within the vari-

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[†] Faculty of Mathematics, University of Vienna, A-1090 Vienna, Austria (manuel.friedrich@univie.ac.at, paolo.piovano@univie.ac.at).

[‡] Faculty of Mathematics, University of Vienna, A-1090 Vienna, Austria, and Istituto di Matematica Applicata e Tecnologie Informatiche "E. Magenes" - CNR, I-27100 Pavia, Italy (ulisse.stefanelli@univie.ac.at).

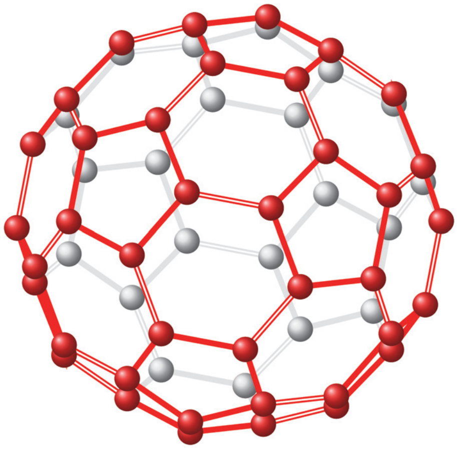

Fig. 1. *The geometry of C_{60}. The bonds shared by two hexagons are here indicated by double lines.*

ational frame of *molecular mechanics* [2, 31, 41]. This consists of modeling molecular configurations in terms of classical mechanics: atomic relations are described by classical interaction potentials between atomic positions. Although far from the quantum nature of molecular bonding, this approach has proved computationally effective, especially in the case of large molecules, leading to the award of the 2013 Nobel Prize in Chemistry to Karplus, Levitt, and Warshel. We shall express the *energy* of a carbon configuration as

$$E = E_{\text{bond}} + E_{\text{angle}} + E_{\text{dihedral}} + E_{\text{nonbond}}. \tag{1}$$

Here, E_{bond} describes two-body interactions; it is short-ranged and favors some specific bond length, here normalized to 1. The term E_{angle} is a three-body interaction energy instead [6, 45, 47], favoring the formation of $2\pi/3$ or $4\pi/3$ angles between first-neighbor bonds. This corresponds to the so-called sp^2-orbital hybridization of carbon atoms, determining indeed the geometry of approximately flat, locally two-dimensional carbon structures, such as graphene and nanotubes. Note that reducing to pure sp^2 hybridization to describe the truly three-dimensional nature of C_{60} is questionable. Still, this simplification delivers the correct geometry of the molecule, and possible extensions of this perspective are reported in Remark 2.4. The term E_{dihedral} is a four-body contribution, favoring planarity of the bonds at a given atom. Finally, the term E_{nonbond} represents *nonbonded* interactions. These may include van der Waals attraction, steric repulsion, and electrostatic effects.

Our focus is to identify a minimal set of assumptions on E delivering the local minimality of the correct geometric structure of C_{60}: the sixty atoms sit at the intersections of the edges of an icosahedron with a sphere with the same center. This results in a football-like geometry consisting of twelve equal regular planar pentagons and twenty equal planar hexagons. We call $\mathcal{X}$ all such truncated-icosahedral configurations and remark that they are uniquely determined (up to isometries) by specifying the length a of the side shared by two hexagons and the length b of the sides of the pentagons (see Figure 1). The corresponding configuration is indicated by $X_{a,b}$. These two lengths are indeed different for the C_{60} molecule: nuclear-magnetic-resonance experiments provide values of $a = 1.40 \pm 0.015$ Å and $b = 1.45 \pm 0.015$ Å, respectively [55].

The investigation of the structure of C_{60} via variational methods was initiated in [36, 44], where, under suitable convexity assumptions, the energy $E_{\text{bond}} + E_{\text{angle}}$ was proved to be locally minimized by $X_{1,1}$. The short-rangedness of this particular energy form induces this local minimizer to have all bonds of length 1, which does does not reflect the fine geometry of the C_{60}, which has two distinct bond lengths. In order to take long-range effects into account, one is tempted to consider the energy $E_{\text{bond}} + E_{\text{angle}} + E_{\text{nonbond}}$ instead. This has the effect of bringing (at least) second-neighbors into the picture, hence potentially distinguishing between bonds of types a and b. The addition of the nonbonded-interaction term, however, induces a shortening of second-neighbor bonds, and a key conclusion of our paper is the observation that without additional assumptions on the energy, local minimality of any configuration $X_{a,b}$ is eventually prevented. Our main positive result is then that the inclusion of a dihedral term in the energy, namely $E = E_{\text{bond}} + E_{\text{angle}} + E_{\text{dihedral}} + E_{\text{nonbond}}$, restores the icosahedral symmetry and entails the local minimality of a configuration X_{a^*,b^*} with $a^* < b^*$.

In the following we critically review the effect of single terms in E, by providing an accurate formalization of the above discussion. With respect to the original *computational* nature of molecular mechanics this *rigorous* approach seems unprecedented, contributing a novel justification of the variational perspective and a way of validating specific modeling choices. Indeed, a variety of different molecular mechanical codes [7, 8, 19, 37, 53] have been presented, corresponding to different phenomenological choices for the single terms in E (as well as for possible additional effects, not included in our analysis). A by-product of our results is hence the cross-validation of these choices in view of their capability in describing the actual geometry of C_{60}. Let us briefly mention that the modeling options discussed in this article are also consistent with the characterization of the geometry and stability of other carbon structures such as graphene or the fullerene C_{20}. Moreover, this variational approach has proved effective at describing a wider class of carbon structures [44], including, e.g., carbon nanotubes [32, 33].

Before moving on, we would like to contextualize the results of this paper with respect to the available literature. Our analysis is related to the classical *crystallization problem*, which consists of characterizing crystals at zero temperature as periodic ground states of suitable configurational energies that include two- and three-body interaction terms.

In one space dimension, the reader is referred with no claim of completeness to [3, 18, 22, 40, 49, 50, 51, 52] for a collection of results proving or disproving, under different choices for the energy, the minimization property of an equally spaced configuration of atoms and its stability with respect to perturbations.

Ground states in two dimensions have been proved to be subsets of the triangular lattice under pure two-body interactions in [23, 39, 52] for specific potentials. The considerably more involved case of Lennard-Jones-like potentials has been analyzed in [48] as the number of atoms of the configuration tends to infinity. The hexagonal case is addressed by including in the energy a three-body interaction term favoring wells at $2\pi/3$ and $4\pi/3$ angles both in the finite crystallization case [36] and in the thermodynamic limit [11]. The recent [14] obtains a hexagonal lattice in the thermodynamic limit under the effect of an energy favoring π angles instead. Eventually, the case of the square lattice is tackled in [34, 35]. Here the energy favors $\pi/2$, π, and $3\pi/2$ bond angles.

The only three-dimensional crystallization result presently available is in [16], where a face-centered cubic lattice was recovered as the thermodynamic limit under pairwise and three-body interactions favoring $\pi/3$ bond angles; see also [15]. All the mentioned results concern the zero-temperature setting. Finite temperatures have been tackled in the one-dimensional case only [27]. We refer the reader to [4] for an extended review on this topic.

In contrast with the classical crystallization problem, we are not concerned here with ground-state characterization but rather with the analysis of the C_{60} configuration in terms of its stability. Note that various concepts of crystal stability are available. We refer the reader to [13] for a discussion of the connections between phonon-stability, homogenized-continuum stability, and Cauchy-born stability in the case of three-dimensional crystals, and to [42] for an application at the continuum level for free-standing graphene. The validity of the Cauchy–Born assumption for crystalline solids has been also discussed in [12] and [17]. All these different stability notions are qualified via the specification of the corresponding admissible perturbations. In this regard, our stability notion seems to be the strongest, since all small perturbations of atomic positions are allowed.

The plan of the paper is the following. We formalize our setting and state our main results in section 2. We also provide a classification of all modeling options by exactly characterizing the cases in which C_{60} can be identified as a local minimizer of the energy (cf. Table 1). We report in subsection 2.3 a discussion of our assumption frame with respect to various phenomenological potentials from the literature. The proof of the results is then developed in sections 3–5. More precisely, the description of the geometry of C_{60} is addressed in section 3, and its stability under the presence of a dihedral term is contained in section 4. Thereafter, in section 5 we provide some counterexamples to stability in absence of a dihedral term. These consist of rotating one pentagonal facet or simultaneously moving the vertices of a pentagonal facet towards the center of the cage.

2. Modeling and main results.

The focus of this section is on introducing the relevant notation and stating the main results.

2.1. Mathematical setting and modeling options.

Let $X = \{x_1, \dots, x_{60}\} \in \mathbb{R}^3$ indicate a general *configuration* of sixty atoms in three-dimensional space, and let $E : (\mathbb{R}^3)^{60} \to \mathbb{R}$ be a given *configurational energy* (1). The fundamental principle of material objectivity imposes that E is invariant under rotations and translations. As such, all the following statements have to be intended *up to isometries*, unless otherwise specified.

We shall introduce some specific structure for the terms in (1) by modeling the basic chemistry of *sp*2-covalent bonding in carbon [45, 47], namely the specific bonding mode of C_{60}. We define the two-body interaction term E_{bond} as

$$E_{\text{bond}}(X) := \frac{1}{2} \sum_{(i,j) \in \mathcal{N}_1(X)} v_{\text{bond}}(|x_i - x_j|),$$

where the index set $\mathcal{N}_1(X)$ indicates *first neighbors* and is defined as

$$\mathcal{N}_1(X) := \{(i,j) \, : \, |x_i - x_j| < \sqrt{2}\}.$$

The potential $v_{\text{bond}} : [0,\infty) \to [-1,\infty)$ is assumed to be smooth in the closure of a small open neighborhood I_{bond} of 1,

$$v_{\text{bond}}(\ell) = -1 \ \text{ iff } \ell = 1 \quad \text{and} \quad v''_{\text{bond}}(\ell) > 0 \ \text{ for all } \ell \in \overline{I}_{\text{bond}}. \tag{2}$$

This basic assumption corresponds to the fact that covalent bonds in carbon atoms are characterized by some reference bond length, here normalized to 1. The choice of the cut-off value $\sqrt{2}$ in the definition of first neighbors is discretional, yet it is suggested by the planar case of graphene [36]. In the following we shall also use the notation

$$\mathcal{N}_1(x_i) := \{(i,j) \, : \, j \in \{1,\dots,60\} \text{ and } (i,j) \in \mathcal{N}_1(X)\}$$

for the set of first neighbors of the atom $x_i \in X$, and denote the tuples of lengths of the covalent bonds shared by x_i by

$$\mathcal{B}_1(x_i) := \{|x_i - x_j| \, : \, (i,j) \in \mathcal{N}_1(x_i)\}.$$

The energy E_{angle} represents three-body interactions and is defined by

$$E_{\mathrm{angle}}(X) := \frac{1}{2} \sum_{(i,j,k) \in \mathcal{T}(X)} v_{\mathrm{angle}}(\alpha_{ijk}),$$

where the index set $\mathcal{T}(X)$ is given by

$$\mathcal{T}(X) := \{(i,j,k) \, : \, i \neq k, \, (i,j) \in \mathcal{N}_1(X) \text{ and } (j,k) \in \mathcal{N}_1(X)\},$$

and α_{ijk} denotes the angle determined by the segments $x_i - x_j$ and $x_k - x_j$ (choose counterclockwise orientation, for definiteness). The potential $v_{\mathrm{angle}} : [0, 2\pi] \to [0, \infty)$ is symmetric with respect to π, attains its minimum value 0 only at $2\pi/3$ and $4\pi/3$, and is strongly convex in a small closed neighborhood I_{angle} of $[3\pi/5, 2\pi/3]$; i.e.,

$$\theta \mapsto v_{\mathrm{angle}}(\theta) - \lambda_{\mathrm{angle}}|\theta|^2 \text{ is convex on } I_{\mathrm{angle}} \text{ for some } \lambda_{\mathrm{angle}} > 0. \tag{3}$$

These properties will be assumed throughout the paper and model the fact that *sp*2-hybridized orbitals tend to form $2\pi/3$ bond angles [47]. The index set

$$\mathcal{A}(X) := \{\alpha_{ijk} \, : \, (i,j,k) \in \mathcal{T}(X) \text{ and } \alpha_{ijk} \leq \alpha_{kji}\}$$

will indicate *active angles* of the configuration X, while we will denote by

$$\mathcal{A}(x_j) := \{\alpha_{ijk} \in \mathcal{A}(X) \, : \, \text{for some } i,k = 1,\dots,60\}$$

the tuple of the active angles at x_j. In the following, we will also make use of an alternative three-body energy term E_{kink} of the form of E_{angle}, namely,

$$E_{\mathrm{kink}}(X) := \frac{1}{2} \sum_{(i,j,k) \in \mathcal{T}(X)} v_{\mathrm{kink}}(\alpha_{ijk}),$$

where v_{kink} fulfills the same assumptions as v_{angle} and is additionally differentiable in a small left neighborhood of $2\pi/3$ with

$$\lim_{\theta \uparrow 2\pi/3} v'_{\mathrm{kink}}(\theta) < 0. \tag{4}$$

Note that v_{kink} is not differentiable at $2\pi/3$ and $4\pi/3$, where indeed its graph has a *kink*. This is a mathematical assumption which has no explicit chemical justification. Still, such a nondifferentiable case is surprisingly the only one allowing us to prove that two-dimensional minimizers of $E_{\mathrm{bond}} + E_{\mathrm{kink}}$ are indeed subsets of the regular hexagonal lattice [36]. Note that such *kink assumptions* arise in all finite crystallization results to date. In particular, they have been considered in connection with the two-dimensional triangular lattice and the square lattice as well [23, 34, 35, 39, 52]; see [9, 10] for related results. As such, we believe the discussion of the term $E_{\rm kink}$ to bear some relevance.

The four-body dihedral term $E_{\rm dihedral}$ is defined by

$$E_{\rm dihedral}(X) := \eta' \sum_{i=1}^{60} v_{\rm dihedral}(\alpha_i^1, \alpha_i^2, \alpha_i^3)$$

for a potential $v_{\rm dihedral} : [0, 2\pi)^3 \to [0, \infty)$ for all configurations $X = \{x_1, \ldots, x_{60}\}$ such that $\#\mathcal{A}(x_i) = 3$ for all $i = 1, \ldots, 60$, where $\mathcal{A}(x_i) = \{\alpha_i^1, \alpha_i^2, \alpha_i^3\}$. The constant $\eta' > 0$ will be chosen to be suitably small, corresponding indeed to the smallness of four-body energy effects with respect to two- and three-body energy contributions. We will assume $v_{\rm dihedral}$ to be smooth, symmetric in its variables, and satisfying

$$\frac{\mathrm{d}}{\mathrm{d}\varphi} v_{\rm dihedral}\left(\frac{3\pi}{5}, \varphi, \varphi\right)\Big|_{\varphi = 2\pi/3} < 0. \tag{5}$$

The effect of the term $E_{\rm dihedral}$ is that of favoring the planarity of active bonds at each atom. This again corresponds to the local bonding geometry of *sp*2 covalent bonding [47].

Eventually, nonbonded interactions are included in the energy by considering the term $E_{\rm nonbond}$ defined by

$$E_{\rm nonbond}(X) := \frac{\eta}{2} \sum_{i=1}^{60} \sum_{(j,i,k) \in \mathcal{T}(X)} v_{\rm nbd}(|x_k - x_j|) \tag{6}$$

for a smooth function $v_{\rm nbd} : [0, \infty) \to [-1, \infty)$ increasing in a small neighborhood $I_{\rm nbd}$ of $[2\sin(3\pi/10), \sqrt{3}]$. The constant $\eta > 0$ will be chosen to be suitably small later on, reflecting indeed the different relevance of the effects of first and second neighbors in covalent bonding. Note that in (6) the potential $v_{\rm nbd}$ is evaluated over *second neighbors* only, namely atoms corresponding to pairs

$$\mathcal{N}_2(X) := \{(i, k) \,:\, (i, j, k) \in \mathcal{T}(X) \text{ for some } j = 1, \ldots, 60\}.$$

In particular, we assume nonbonded-interaction effects to be negligible except for second neighbors. We also denote by

$$\mathcal{B}_2(x_j) := \{|x_i - x_k| \,:\, (i, j, k) \in \mathcal{T}(X)\}$$

the tuple of distances to second neighbors related to the atom $x_j \in X$. All the above assumptions on the potentials $v_{\rm bond}$, $v_{\rm angle}$, $v_{\rm kink}$, $v_{\rm dihedral}$, and $v_{\rm nbd}$ are tacitly assumed throughout the paper.

In the following we discuss the effect of the various terms in (1). For the sake of definiteness we introduce here a more specific notation for the configurational energy by letting

$$\begin{aligned} E_c(X) := {} & E_{\rm bond}(X) + c_{\rm angle} E_{\rm angle}(X) + c_{\rm kink} E_{\rm kink}(X) \\ & + c_{\rm dihedral} E_{\rm dihedral}(X) + c_{\rm nbd} E_{\rm nonbond}(X). \end{aligned} \tag{7}$$

The constants c_{angle}, c_{kink}, c_{dihedral}, and c_{nbd} take values in $\{0,1\}$ and are hence intended to switch on and off the different energy terms. Correspondingly, different energies in (7) will be indicated by different vectors:

$$c = (c_{\text{angle}}, c_{\text{kink}}, c_{\text{dihedral}}, c_{\text{nbd}}) \in \{0,1\}^4.$$

In the following, c_{angle} and c_{kink} are never simultaneously equal to 1, since the two energies E_{angle} and E_{kink} indeed correspond to the same three-body contribution but distinguish the case without or with the kink, respectively. Moreover, it seems natural to consider the four-body contribution E_{dihedral} only in the case where also three-body terms are present, namely either for $c_{\text{angle}} = 1$ or $c_{\text{kink}} = 1$. Under these restrictions, the discussion of all possible vectors c of coefficients reduces to exactly ten cases, all of which are addressed in Theorem 2.2; see also Table 1.

Table 1

Illustration of ten possible cases in Theorem 2.2. *The first two from the top are already considered in* [36, 44]. *Cases* 5–7 *are the core result of the paper: the fine geometry of* C_{60} *with two different bond lengths can be modeled by allowing nonbonded interactions in combination with a kink-angle or a dihedral term. By providing explicit perturbations, we will see that* X_{a^*,b^*} *is not stable in the last three cases.*

c_{angle}	c_{kink}	c_{dihedral}	c_{nbd}	Local minimizer	Ref. in Theorem 2.2
1	0	0	0	$X_{1,1}$	Assertion 3.1
0	1	0	0	$X_{1,1}$	Assertion 3.1
1	0	1	0	$X_{1,1}$	Assertion 3.1
0	1	1	0	$X_{1,1}$	Assertion 3.1
0	1	0	1	X_{a^*,b^*}	Assertion 3.2
0	1	1	1	X_{a^*,b^*}	Assertion 3.3
1	0	1	1	X_{a^*,b^*}	Assertion 3.3
0	0	0	0	not in $\mathcal{X}$	Assertion 4.1
0	0	0	1	not in $\mathcal{X}$	Assertion 4.2
1	0	0	1	not in $\mathcal{X}$	Assertion 4.2

2.2. Main results.

Among all configurations a specific subclass $\mathcal{X}$ of *objective* [26] configurations with icosahedral symmetry will play a major role. These correspond to truncated icosahedra with two possibly distinct bond lengths and are defined as follows.

Definition 2.1 (icosahedral configurations). *The set* $\mathcal{X}$ *is the family of configurations* $X_{a,b} := \{x_1, \dots, x_{60}\}$, $a, b \in I_{\text{bond}}$, *corresponding to the intersections of the edges of a regular icosahedron with a sphere with the same center, where* $\mathcal{B}_1(x_i) = \{a, b, b\}$ *for all* $i = 1, \dots, 60$.

The set $\mathcal{X}$ is hence a two-parameter family of configurations: by connecting first neighbors of $X_{a,b}$ by a straight segment, one obtains a polyhedron with twelve regular pentagonal facets with side b and twenty hexagonal facets with three sides of length a and three of length b, alternating (see Figure 1). In particular, $X_{a,a}$ is a regular truncated icosahedron with side a, and we have that, for all $x_i \in X_{a,b}$,

$$\mathcal{A}(x_i) = \{3\pi/5, 2\pi/3, 2\pi/3\}$$

and

$$\mathcal{B}_2(x_i) = \{p, h, h\},$$

where

$$p := 2b\sin(3\pi/10) \quad \text{and} \quad h := \sqrt{a^2 + b^2 + ab}. \tag{8}$$

Note that the *angular part* of the energy E_c given by

$$c_{\rm angle}E_{\rm angle} + c_{\rm kink}E_{\rm kink} + c_{\rm dihedral}E_{\rm dihedral}$$

is constant over $\mathcal{X}$ so that the minimization of E_c on $\mathcal{X}$ reduces to the two-dimensional problem

$$\min_{a,b\in I_{\rm bond}} \big(E_{\rm bond}(X_{a,b}) + c_{\rm nbd}E_{\rm nonbond}(X_{a,b})\big). \tag{9}$$

In section 3 we will show that the latter energy is convex with respect to (a,b) whenever η is chosen small enough.

Our tenet is that the analysis of the above two-dimensional problem actually delivers information on the 180-dimensional problem $\min E_c$. In particular, some choices of the vector c entail the local stability of specific configurations in $\mathcal{X}$ with respect to all (small) perturbations in $(\mathbb{R}^3)^{60}$.

In order to investigate such stability, let us introduce perturbations of configurations $X_{a,b} = \{x_1,\dots,x_{60}\}\in\mathcal{X}$ with respect to the energy E_c as

$$\mathcal{P}(X_{a,b}) := \{\{x_1',\dots,x_{60}'\} \,:\, x_i' := x_i + \delta x_i \text{ with } |\delta x_i| < \delta_0 \text{ for all } i=1,\dots,60\}, \tag{10}$$

where $\delta_0 > 0$ is chosen to be small enough. In particular, we choose δ_0 so small that every $P=\{x_1',\dots,x_{60}'\}\in\mathcal{P}(X_{a,b})$ is such that

$$\mathcal{B}_1(x_i') = \{a_i, b_i^1, b_i^2\} \tag{11}$$

with $a_i, b_i^1, b_i^2 \in I_{\rm bond}$;

$$\mathcal{A}(x_i') = \{\theta_i, \varphi_i^1, \varphi_i^2\}$$

with $\theta_i \in \mathit{\Theta}_\varepsilon$ and $\varphi_i^1,\varphi_i^2\in\mathit{\Phi}_\varepsilon$, where $\mathit{\Theta}_\varepsilon := (3\pi/5-\varepsilon, 3\pi/5+\varepsilon)$ and $\mathit{\Phi}_\varepsilon := (2\pi/3-\varepsilon, 2\pi/3+\varepsilon)$ for every every $x_i'\in P$; and for ε small depending on δ_0 and

$$\mathcal{B}_2(x_i') = \{p_i, h_i^1, h_i^2\} \tag{12}$$

with $p_i, h_i^1, h_i^2 \in I_{\rm nbd}$, where

$$p_i = \sqrt{(b_i^1)^2 + (b_i^2)^2 - 2b_i^1b_i^2\cos(\theta_i)} \quad \text{and} \quad h_i^j = \sqrt{a_i^2 + (b_i^j)^2 - 2a_ib_i^j\cos(\varphi_i^j)} \tag{13}$$

for $j=1,2$ (see Figure 2). In the following we say that P and $X_{a,b}$ have the same *geometry* if and only if $\mathcal{B}_1(x_i) = \mathcal{B}_1(x_i')$, $\mathcal{B}_2(x_i)=\mathcal{B}_2(x_i')$, and $\mathcal{A}(x_i)=\mathcal{A}(x_i')$ for all $i=1,\dots,60$.

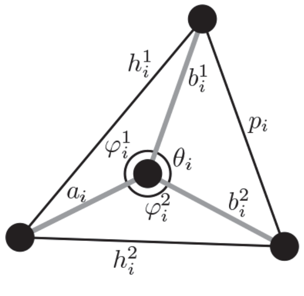

FIG. 2. *Angles, bonds (thick gray lines), and second neighbors (thin black lines) at an atom* $x_i'\in\mathcal{P}(X_{a,b})$.

We are now in a position to state our main result.

THEOREM 2.2 (geometry of C_{60}). *Under the above assumptions on the potentials* v_{bond}*,* v_{angle}*,* v_{kink}*,* v_{dihedral}*, and* v_{nbd}*, the following assertions hold:*

1. (Minimality in $\mathcal{X}$) *For all* c *and for* η *small enough there exists a unique minimizer* X_{a^*,b^*} *of* E_c *in* $\mathcal{X}$*. All configurations in* $\mathcal{X}$ *different from* X_{a^*,b^*} *are not locally stable.*
2. (Nonbonded-interaction effects) *If* $c_{\mathrm{nbd}} = 0$*, then* $a^* = b^* = 1$*. If* $c_{\mathrm{nbd}} = 1$ *and*

$$\sqrt{3}v'_{\mathrm{nbd}}(\sqrt{3}) \neq \sigma v'_{\mathrm{nbd}}(\sigma) \quad \text{with } \sigma = 2\sin(3\pi/10), \tag{14}$$

then $a^*, b^* \leq 1$*,* $a^* \neq b^*$*, and* $\operatorname{sgn}(b^*-a^*) = \operatorname{sgn}\big(\sqrt{3}v'_{\mathrm{nbd}}(\sqrt{3})-\sigma v'_{\mathrm{nbd}}(\sigma)\big)$*.*

3. (Local stability) *Let* η *be small enough.*
   - 3.1 *If* $c_{\mathrm{nbd}} = 0$ *and* $c_{\mathrm{angle}} \vee c_{\mathrm{kink}} = 1$*, then* $X_{1,1}$ *is locally stable with respect to perturbations in* $\mathcal{P}(X_{1,1})$*.*
   - 3.2 *If* $c_{\mathrm{kink}} = c_{\mathrm{nbd}} = 1$ *and* $c_{\mathrm{angle}} = c_{\mathrm{dihedral}} = 0$*, then* X_{a^*,b^*} *is locally stable with respect to perturbations in* $\mathcal{P}(X_{a^*,b^*})$*.*
   - 3.3 *If* $c_{\mathrm{dihedral}} = c_{\mathrm{nbd}} = 1$ *and* $c_{\mathrm{angle}} \vee c_{\mathrm{kink}} = 1$*, and* η' *and* η/η' *are small enough, the configuration* X_{a^*,b^*} *is locally stable with respect to perturbations in* $\mathcal{P}(X_{a^*,b^*})$*.*
4. (Instability)
   - 4.1 *If* $c = (0,0,0,0)$*, then there exists* $P_1 \in \mathcal{P}(X_{a^*,b^*})$ *whose geometry differs from* X_{a^*,b^*} *such that* $E_c(P_1) = E_c(X_{a^*,b^*})$*.*
   - 4.2 *If* $c = (0,0,0,1)$ *or* $c = (1,0,0,1)$ *and* $v'_{\mathrm{angle}}(2\pi/3) = 0$*,* $v'_{\mathrm{nbd}}(x) > 0$ *for* $x \in I_{\mathrm{nbd}}$*, then there exists* $P_2 \in \mathcal{P}(X_{a^*,b^*})$ *such that* $E_c(P_2) < E_c(X_{a^*,b^*})$*.*

Depending on which term is active in E_c, Theorem 2.2 asserts that different situations may occur; see Table 1. By including nonbonded-interaction effects in the picture ($c_{\mathrm{nbd}} = 1$) as well as a kink-angular or a dihedral term ($c_{\mathrm{kink}} \vee c_{\mathrm{dihedral}} = 1$), the unique minimizer X_{a^*,b^*} in $\mathcal{X}$ is locally stable and has two different bond lengths under the generic condition (14). This corresponds to the actual geometry of the C_{60} molecule and is our main result. As already mentioned in the introduction, two distinct bond lengths $a^* < b^*$ are experimentally observed. This is reflected in assertion 2 of Theorem 2.2. Indeed, for v_{nbd} convex and increasing in I_{nbd} we have that $t \mapsto tv'_{\mathrm{nbd}}(t)$ is increasing as well, so that $a^* < b^*$.

If nonbonded interactions are neglected ($c_{\mathrm{nbd}} = 0$) and either angle term is present, namely $c_{\mathrm{angle}} = 1$ or $c_{\mathrm{kink}} = 1$, the configuration $X_{1,1}$ is stable instead. These cases, already addressed in [36, 44], are unsatisfactory, as they fail to deliver the correct geometry of C_{60}, featuring indeed two different bond lengths. This shortcoming was the main motivation for the present study. Let us stress, however, that the extension of the argument of [36, 44] to the case of nonbonded interactions is nontrivial, as noted in section 4 below.

Finally, by neglecting both kink-angular and dihedral terms ($c_{\mathrm{kink}} = c_{\mathrm{dihedral}} = 0$), we find that no icosahedral configuration in $\mathcal{X}$ is locally stable. Indeed, we provide an explicit perturbation P_2 lowering the energy, which consists of simultaneously moving the vertices of a pentagonal facet towards the center of the cage so to reduce the length of second neighbors.

Our result focuses on the case where η and η' are small, reflecting that the terms of E_{nonbond} and E_{dihedral} can be supposed to be of lower order with respect to the two- and three-body parts of the energy [2]. In case both dihedral and nonbonded-interaction terms are present (assertion 3.3 of Theorem 2.2), we additionally assume

η/η' to be small, namely that the dihedral term dominates, which again is well motivated by the basic chemistry of covalent bonding in carbon. If this is not the case, for $c = (1, 0, 1, 1)$ the same perturbation P_2 of assertion 4.2 of Theorem 2.2 proves that the configuration X_{a^*,b^*} is not locally stable.

Remark 2.3. An alternative, equivalent approach would have been that of considering a single $v_{\text{two-body}} := [0,\infty) \to [-1,\infty)$ for all two-body effects, namely for both first and second neighbors, instead of using the two potentials v_{bond} and v_{nbd}. More precisely, one could introduce the energy term $E_{\text{two-body}}$ defined by

$$E_{\text{two-body}}(X) := \frac{1}{2} \sum_{(i,j)\in \mathcal{N}_1 \cup \mathcal{N}_2} v_{\text{two-body}}(|x_i - x_j|). \tag{15}$$

Then, the statements of Theorem 2.2 with $c_{\text{nbd}} = 1$ can be reformulated by replacing $E_{\text{bond}} + E_{\text{nonbond}}$ by $E_{\text{two-body}}$ and letting

$$v_{\text{two-body}} = \psi_{\text{bond}} v_{\text{bond}} + \eta \psi_{\text{nbd}} v_{\text{nbd}},$$

where ψ_{bond} and ψ_{nbd} are suitable cut-off functions supported in I_{bond} and I_{nbd}, respectively. This approach would in particular allow $v_{\text{two-body}}$ to have the Lennard-Jones form $v_{\text{two-body}}(r) = kr^{-12} - k'r^{-6}$ for suitable positive constants k and k'. We, however, prefer to keep our notation, as we believe that it delivers a clearer argument.

Remark 2.4. The reference to sp^2 hybridization, that is, the assumption that v_{angle} is minimized solely at $2\pi/3$ and $4\pi/3$, is here chosen for definiteness only. This assumption could be weakened in order to encompass more general bonding regimes. In particular, potentials with negative slope at $2\pi/3$, such as Brenner-like potentials favoring π bond angles (see [6]), could be considered as well. In this case, the results correspond to those of Theorem 2.2 along with the choice $c_{\text{kink}} = 1$. Moreover, the case of v_3 having a (small) positive slope at $2\pi/3$ could be addressed as well. Depending on the contribution of E_{dihedral}, we get either a stability or an instability result as in assertions 3 and 4, respectively, of Theorem 2.2. We prefer to present the results under the slightly more restrictive assumptions of section 2.1, which allow a clearer exposition.

2.3. Examples of admissible potentials.

The assumption frame of subsection 2.1 is sufficiently weak to include virtually all the specific choices for the potentials which have been introduced in the literature [2]. The aim of this subsection is to illustrate some concrete examples. In the following, we shall use the indexed symbol k to indicate different positive parameters.

Let us start by observing that the classical potentials

$$\begin{aligned} &\text{(harmonic)} && \frac{1}{2} k_h (r-1)^2 - 1, \\ &\text{(Morse)} && k_M \left(\mathrm{e}^{-k'_M (r-1)} - 1\right)^2 - 1, \\ &\text{(Lennard-Jones)} && \frac{1}{r^{12}} - \frac{2}{r^6} \end{aligned}$$

fulfill assumption (2) for v_{bond}. The Morse and the Lennard-Jones potentials, possibly modulated by suitable additional parameters, can give account of nonbonded interactions as well [24, 54]. In particular, they can be chosen as v_{nbd} and calibrated in such a way that assumption (6) can be met. In addition, nonbonded interactions can be described by the classical potential [25]

$$\text{(Buckingham)} \qquad k_B \mathrm{e}^{-k'_B r} - \frac{k''_B}{r^6},$$

which again fulfills (6) for a suitable choice of the coefficients. Combinations of these potentials can also be considered in order to model two-body interactions in the spirit of (15).

The angle potential v_{angle} is usually defined to be quadratic around $2\pi/3$ and $4\pi/3$, which ideally fits with assumption (3) but not with (4). Note, however, that the latter, as already noted above, has no direct chemical justification.

Various formulations for the dihedral term appear in the literature. We mention the molecular dynamics computational libraries AMBER [53], CHARMM [7], GROMOS [19], Tripos 5.2 [8], DREIDING [37], and AIREBO [46] and refer the reader also to [41, subsection 3.2.2] for the detailed geometric account of different choices.

In AMBER the contribution of the atom x_i with bonds $\mathcal{B}_1(x_i) = \{a_i, b_i^2, b_i^2\}$ to the dihedral term v_{dihedral} is

$$v_{\text{AMBER}}(\gamma_i) := k_{\text{AMBER}} \left[1 - \cos\left(3(\gamma_i - \pi)\right)\right],$$

where γ_i is the angle formed by the two planes π_i^j, containing the bonds with lengths a_i and b_i^j, respectively, for $j = 1, 2$ [41] (see Figure 3).

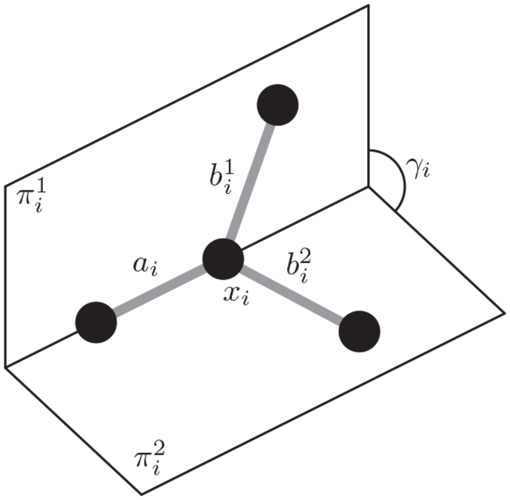

FIG. 3. *The dihedral potential employed in AMBER depends at every atom x_i on the corresponding angle γ_i shown in the picture.*

In [20, 43] yet another definition for the dihedral term is introduced. This is based on the notion of the π-orbital axis vector (POAV), namely the axis which forms equal angles with the three covalent bonds centered at a given atom (see [21, Appendix] for a detailed definition). Both the AMBER and the POAV dihedral terms can be proved to satisfy assumption (5). For example, in the AMBER case we observe that if $\varphi_i^j = \varphi_i$ for $j = 1, 2$, then

$$\sin\frac{\gamma_i}{2} \sin\varphi_i = \sin\frac{\theta_i}{2},$$

as computed in [32, Proposition 3.2], and hence assumption (5) follows from verifying that

$$\frac{\mathrm{d}}{\mathrm{d}\gamma} v_{\mathrm{AMBER}}(\gamma)\Big|_{\gamma=\gamma_0} < 0$$

for $\gamma_0 \in (2\pi/3, \pi)$ such that

$$\sin\frac{\gamma_0}{2}\sin\frac{2}{3}\pi = \sin\frac{3}{10}\pi.$$

3. The geometry of C_{60}.

In this section we specify the geometry of C_{60} by minimizing the energy in the class of icosahedral configurations $\mathcal{X}$. In particular, we prove the first and second assertions of Theorem 2.2.

Proof of assertion 1 *of Theorem* 2.2. For every vector c the energy $E_c(X_{a,b})$ coincides (up to an additive constant not depending on $a, b \in I_{\mathrm{bond}}$) with (recall (8) and (9))

$$\begin{aligned} E_\eta(X_{a,b}) &:= 30v_{\mathrm{bond}}(a) + 60v_{\mathrm{bond}}(b) + c_{\mathrm{nbd}}\eta\Bigg(60v_{\mathrm{nbd}}\left(2b\sin\left(\frac{3\pi}{10}\right)\right) \\ &\qquad + 120v_{\mathrm{nbd}}(\sqrt{a^2+b^2+ab})\Bigg) \\ &= 30v_{\mathrm{bond}}(a) + 60v_{\mathrm{bond}}(b) + \eta f(a,b) \qquad (16) \end{aligned}$$

for a suitable function f being C^2 on $I_{\mathrm{nbd}} \times I_{\mathrm{nbd}}$ (see below (6)). We first observe that $E_\eta(X_{a,b})$ is strictly convex as a function of $a, b \in I_2$. Indeed, the Hessian reads as $\mathrm{D}^2E_\eta(X_{a,b}) = 30v''_{\mathrm{bond}}(a)\; e_1 \otimes e_1 + 60v''_{\mathrm{bond}}(b)\; e_2 \otimes e_2 + \eta\mathrm{D}^2 f(a,b)$, and the assertion follows from (2) for η small enough.

Consequently, for such η small enough there exists a unique minimizer $X_{a^*_\eta, b^*_\eta}$ of E_η in $\overline{I}_{\mathrm{bond}} \times \overline{I}_{\mathrm{bond}}$. We observe that for small η we have $a^*_\eta, b^*_\eta \in I_{\mathrm{bond}}$. In fact, as E_η is a continuous perturbation of E_0, one has $(a^*_\eta, b^*_\eta) \to (a^*_0, b^*_0)$ as $\eta \to 0$ and $(a^*_0, b^*_0) = (1,1)$ by (2). Consequently, $X_{a^*_\eta, b^*_\eta}$ is also the unique minimizer of E_c over the family $\mathcal{X}$. For given fixed η we drop the subscript η and indicate the minimizer as the minimizer (a^*, b^*), for the sake of notational simplicity. Note that the strict convexity and $a^*, b^* \in I_{\mathrm{bond}}$ imply

$$\mathrm{D}E_\eta(X_{a,b}) = 0 \quad \text{for } a, b \in I_{\mathrm{bond}} \text{ iff } (a,b) = (a^*, b^*). \qquad (17)$$

To conclude the proof of assertion 1 of Theorem 2.2, it remains to show that $X_{a,b} = \{x_1, \ldots, x_{60}\} \in \mathcal{X} \setminus \{X_{a^*,b^*}\}$ is not locally stable for small perturbations. Since $\mathrm{D}E_\eta(X_{a,b}) \neq 0$ by (17), we find $a', b' \in I_{\mathrm{bond}}$ with $|a - a'|$, $|b - b'|$ arbitrarily small such that $E_c(X_{a',b'}) < E_c(X_{a,b})$. It now suffices to observe that $X_{a',b'}$ can be realized by a configuration $\{x'_1, \ldots, x'_{60}\} \in \mathcal{X}$ with $|x_i - x'_i| < \delta_0$ for $i = 1, \ldots, 60$. Indeed, this corresponds to moving the facets of the pentagons and hexagons (infinitesimally) inwardly or outwardly without changing the bond angles. ☐

In the following let $a^*, b^* \in I_{\mathrm{bond}}$ be the length of the bonds of X_{a^*,b^*}, and denote by

$$p^* := 2b^*\sin\left(\frac{3\pi}{10}\right) = b^*\sigma, \qquad h^* := \sqrt{(a^*)^2 + (b^*)^2 + a^*b^*} \qquad (18)$$

the lengths between its second neighbors, where $\sigma = 2\sin(3\pi/10)$. We now prove the second assertion of Theorem 2.2.

Proof of assertion 2 *of Theorem* 2.2. First, if $c_{\mathrm{nbd}} = 0$ or, equivalently, $\eta = 0$ in E_η (see (16)), we have already proved in (17) that $(a^*, b^*) = (1, 1)$. Suppose now that $c_{\mathrm{nbd}} = 1$ and $\eta > 0$. By computing the derivative of $E_\eta(X_{a,b})$, we obtain

$$\begin{aligned}(19)\qquad \mathrm{D}E_\eta(X_{a,b}) = \bigg(&30v'_{\mathrm{bond}}(a) + 120\eta\frac{2a+b}{2h}v'_{\mathrm{nbd}}(h),\\ &60v'_{\mathrm{bond}}(b) + 60\eta\sigma v'_{\mathrm{nbd}}(\sigma b) + 120\eta\frac{a+2b}{2h}v'_{\mathrm{nbd}}(h)\bigg),\end{aligned}$$

where, similarly as above, we have set $h = \sqrt{a^2+b^2+ab}$. Since by the assumption on v_{nbd} (see below (6)) we have $0 \le v'_{\mathrm{nbd}}(p^*), v'_{\mathrm{nbd}}(h^*)$, equation (17) implies that

$$v'_{\mathrm{bond}}(a^*), v'_{\mathrm{bond}}(b^*) \le 0,$$

and thus $a^*, b^* \le 1$ by (2).

Assume that (14) holds, and observe that this implies $\sqrt{3}v'_{\mathrm{nbd}}(\sqrt{3}d) \neq \sigma v'_{\mathrm{nbd}}(\sigma d)$ for all $d \in I_{\mathrm{bond}}$ if we choose the neighborhood I_{bond} small enough (depending on v_{nbd}). Now suppose that $(a^*, b^*) = (d, d)$ for some $d \in I_{\mathrm{bond}}$. Then (17) yields $\mathrm{D}E_\eta(X_{d,d}) = 0$, and thus by the previous computation we get

$$\begin{aligned}&30v'_{\mathrm{bond}}(d) + 120\eta\frac{\sqrt{3}}{2}v'_{\mathrm{nbd}}(\sqrt{3}d)\\ &\quad = 60v'_{\mathrm{bond}}(d) + 60\eta\sigma v'_{\mathrm{nbd}}(\sigma d) + 120\eta\frac{\sqrt{3}}{2}v'_{\mathrm{nbd}}(\sqrt{3}d) = 0,\end{aligned}$$

which leads to $\sqrt{3}v'_{\mathrm{nbd}}(\sqrt{3}d) = \sigma v'_{\mathrm{nbd}}(\sigma d)$. This contradicts assumption (14) and eventually shows that $a^* \neq b^*$. Finally, again by using the first order optimality condition, we derive

$$v'_{\mathrm{bond}}(b^*) - v'_{\mathrm{bond}}(a^*) = 3\eta\frac{a^*}{h^*}v'_{\mathrm{nbd}}(h^*) - \eta\sigma v'_{\mathrm{nbd}}(\sigma b^*).$$

As v'_{bond} is increasing on I_{bond} by (2), we get

$$\mathrm{sgn}(b^* - a^*) = \mathrm{sgn}\left(3\frac{a^*}{h^*}v'_{\mathrm{nbd}}(h^*) - \sigma v'_{\mathrm{nbd}}(\sigma b^*)\right).$$

Note that we can assume that $|a^* - 1|$, $|b^* - 1|$, and $|h^* - \sqrt{3}|$ are arbitrarily small by simply choosing the neighborhood I_{bond} sufficiently small. Consequently, by the regularity of the potentials, the term on the above right-hand side has the same sign as $\sqrt{3}v'_{\mathrm{nbd}}(\sqrt{3}) - \sigma v'_{\mathrm{nbd}}(\sigma)$. This concludes the proof. ☐

4. Stability of C_{60} with the kink or the dihedral term. The section is devoted to the proof of the stability results of assertion 3 of Theorem 2.2. We follow the general strategy proposed in [36, Theorem 7.3], which is based on convexity and monotonicity arguments for the energy E_c. In our context, however, a more elaborate analysis of the properties of the phenomenological energy E_c is required. Indeed, the original argument in [36] is based on the possibility of treating bonded and angle effects *separately*. This is not possible here, as both first-neighbor bond lengths and angles contribute to the length of second neighbors, and hence to the term $E_{\mathrm{nonbonded}}$. The strategy is hence to exploit the smallness of $E_{\mathrm{nonbonded}}$, that is of η, in order to keep this additional intricacy under control.

Let us start by rewriting the energy corresponding to a small perturbation $P = \{x'_1, \dots, x'_{60}\} \in \mathcal{P}(X_{a^*,b^*})$ (see (10)) as a sum

$$E_c(P) = \sum_{i=1}^{60} \widehat{E}_c(x'_i),$$

where $\widehat{E}_c(x'_i)$ is the energy contribution associated to a single atom. In view of (11)–(13), each $\widehat{E}_c(x'_i)$ can be expressed as a function in terms of the covalent bonds and the angles, i.e., with a slight abuse of notation $\widehat{E}_c(a_i, b_i^1, b_i^2, \theta_i, \varphi_i^1, \varphi_i^2) = \widehat{E}_c(x_i)$, and is defined by (set $y_i = (a_i, b_i^1, b_i^2, \theta_i, \varphi_i^1, \varphi_i^2)$ for shorthand)

$$\begin{aligned}\widehat{E}_c(y_i) := {}& \widehat{E}_{\text{bond}}(y_i) + c_{\text{angle}}\widehat{E}_{\text{angle}}(y_i) + c_{\text{kink}}\widehat{E}_{\text{kink}}(y_i)\\ &+ \eta'\, c_{\text{dihedral}}\widehat{E}_{\text{dihedral}}(y_i) + \eta\, c_{\text{nbd}}\widehat{E}_{\text{nonbond}}(y_i)\end{aligned} \tag{20}$$

for every $x_i \in P$, where we have

$$\begin{aligned}&\widehat{E}_{\text{bond}}(y_i) := \frac{1}{2}v_{\text{bond}}(a_i) + \frac{1}{2}v_{\text{bond}}(b_i^1) + \frac{1}{2}v_{\text{bond}}(b_i^2),\\ &\widehat{E}_{\text{angle}}(y_i) := v_{\text{angle}}(\theta_i) + v_{\text{angle}}(\varphi_i^1) + v_{\text{angle}}(\varphi_i^2),\\ &\widehat{E}_{\text{kink}}(y_i) := v_{\text{kink}}(\theta_i) + v_{\text{kink}}(\varphi_i^1) + v_{\text{kink}}(\varphi_i^2),\\ &\widehat{E}_{\text{dihedral}}(y_i) := v_{\text{dihedral}}(\theta_i, \varphi_i^1, \varphi_i^2), \quad \text{and}\\ &\widehat{E}_{\text{nonbond}}(y_i) := v_{\text{nbd}}(p_i) + v_{\text{nbd}}(h_i^1) + v_{\text{nbd}}(h_i^2).\end{aligned}$$

Note that the factor $1/2$ in the definition of $\widehat{E}_{\text{bond}}$ takes into account the fact that each bond is shared by two atoms. We first use the convexity properties in (2) and (3) to show the convexity of $\widehat{E}_c$.

Proposition 4.1 (strict convexity of $\widehat{E}_c$). *If η, η' are taken small enough, then for every vector $c \in \{0,1\}^4$ with $c_{\text{angle}} \vee c_{\text{kink}} = 1$ the energy $\widehat{E}_c$ is strictly convex on $I_{\text{bond}}^3 \times I_{\text{angle}}^3$. If $c_{\text{nbd}} = 0$ or $c_{\text{dihedral}} = 0$, the choice of η or η', respectively, is arbitrary.*

Proof. We split $\widehat{E}_c = f_1 + f_2 + f_3$ into the parts $f_1 = \widehat{E}_{\text{bond}}$, $f_2 = \eta\, c_{\text{nbd}}\widehat{E}_{\text{nonbond}} + \eta'\, c_{\text{dihedral}}\widehat{E}_{\text{dihedral}}$, and $f_3 = c_{\text{angle}}\widehat{E}_{\text{angle}} + c_{\text{kink}}\widehat{E}_{\text{kink}}$. We consider two points $y_1, y_2 \in I_{\text{bond}}^3 \times I_{\text{angle}}^3$ and distinguish the bond and angle part by writing $y_i = (y_i^1, y_i^2)$ for $i = 1, 2$ with $y_i^1, y_i^2 \in \mathbb{R}^3$. We let $\lambda_{\text{bond}} = \min_{\ell \in \overline{I}_{\text{bond}}} v''_{\text{bond}}(\ell)/2$, and by the smoothness of $\widehat{E}_{\text{nonbond}}$ and $\widehat{E}_{\text{dihedral}}$ we can choose $\lambda^* \in \mathbb{R}$ such that for each $y \in I_{\text{bond}}^3 \times I_{\text{angle}}^3$ the smallest eigenvalue of $\mathrm{D}^2\widehat{E}_{\text{nonbond}}(y)$ and $\mathrm{D}^2\widehat{E}_{\text{dihedral}}(y)$ is larger than λ^*. It is a well-known fact in the theory of convex functions that this implies for $t \in [0,1]$

$$\begin{aligned}&f_1(ty_1 + (1-t)y_2) \le tf_1(y_1) + (1-t)f_1(y_2) - \frac{1}{2}\lambda_{\text{bond}}t(1-t)|y_1^1 - y_2^1|^2,\\ &f_2(ty_1 + (1-t)y_2) \le tf_2(y_1) + (1-t)f_2(y_2)\\ &\qquad\qquad + \frac{1}{2}|\lambda^*|(\eta c_{\text{nbd}} + \eta' c_{\text{dihedral}})t(1-t)|y_1 - y_2|^2.\end{aligned}$$

Moreover, by the strong convexity of f_3 in the angle variables (see (3)), we have for $t \in [0,1]$

$$f_3(ty_1 + (1-t)y_2) \le tf_3(y_1) + (1-t)f_3(y_2) - \lambda_{\text{angle}}t(1-t)|y_1^2 - y_2^2|^2.$$

Thus, since $\lambda_{\text{bond}} > 0$ by (2) and $\lambda_{\text{angle}} > 0$, we derive for η, η' small enough that

$$\min\left\{\frac{1}{2}\lambda_{\text{bond}}, \lambda_{\text{angle}}\right\} - \frac{1}{2}|\lambda^*|(\eta c_{\text{nbd}} + \eta' c_{\text{dihedral}}) > 0,$$

and we conclude that $\widehat{E}_c$ is strictly convex. ☐

We now derive a monotonicity property which can be recovered from the kink assumption (4) or from assumption (5). Note that in both cases the argument is based on the fact that the planarity of the faces is energetically favored by $\widehat{E}_{\text{kink}}$ or $\widehat{E}_{\text{dihedral}}$.

PROPOSITION 4.2 (monotonicity of $\widehat{E}_c$). *Assume that η is small enough. If*

1. $c = (1,0,0,0)$ *or*
2. $c \in \{(0,1,0,1),(0,1,0,0)\}$ *or*
3. $c \in \{(1,0,1,1),(0,1,1,1),(1,0,1,0),(0,1,1,0)\}$ *and η/η' small enough,*

then we have for all $a, b \in I_{\text{bond}}$, $\theta \in \Theta_\varepsilon$, $\varphi \in \Phi_\varepsilon$ with $\theta \le 3\pi/5$ and $\varphi \le 2\pi/3$ that

$$\widehat{E}_c(a,b,b,\theta,\varphi,\varphi) \ge \widehat{E}_c(a^*,b^*,b^*,3\pi/5,2\pi/3,2\pi/3), \tag{21}$$

where equality holds only if $a = a^*$, $b = b^*$, $\theta = 3\pi/5$, and $\varphi = 2\pi/3$.

Proof. We first observe that in case 1 one has $a^* = b^* = 1$, and the assertion follows directly from (2) and (3) (cf. also the arguments in [36, Theorem 7.3]).

For cases 2 and 3 we split $\widehat{E}_c = f_1 + f_2$ into the parts $f_1(a,b,\theta,\varphi) = \widehat{E}_{\text{bond}}(y) + \eta\, c_{\text{nbd}}\widehat{E}_{\text{nonbond}}(y)$ and $f_2(\theta,\varphi) = c_{\text{angle}}\widehat{E}_{\text{angle}}(y) + c_{\text{kink}}\widehat{E}_{\text{kink}}(y) + \eta'\, c_{\text{dihedral}}\widehat{E}_{\text{dihedral}}(y)$, where for brevity we write $y = (a,b,b,\theta,\varphi,\varphi)$. By the smoothness of v_{bond} and v_{nbd} and by (13) we can find a constant C_1 independent of η such that $|\mathrm{D}_{\theta,\varphi} f_1(a,b,\theta,\varphi)| \le C_1\eta$ for all $a, b \in I_{\text{bond}}$ and $\theta \in \Theta_\varepsilon$, $\varphi \in \Phi_\varepsilon$. Let for brevity $\theta_0 = 3\pi/5$ and $\varphi_0 = 2\pi/3$. Then we get by Taylor's formula for all $a, b \in I_{\text{bond}}$, $\theta \in \Theta_\varepsilon$, and $\varphi \in \Phi_\varepsilon$ that

$$\begin{aligned}|f_1(a,b,\theta,\varphi) - f_1(a,b,\theta_0,\varphi_0)| &\le C_1\eta(|\theta-\theta_0| + |\varphi-\varphi_0|) + C_1(|\theta-\theta_0| + |\varphi-\varphi_0|)^2\\ &\le C_1(\eta+\varepsilon)(|\theta-\theta_0| + |\varphi-\varphi_0|),\end{aligned} \tag{22}$$

passing possibly to a larger constant C_1 without introducing new notation. We now show that there exists a constant $C_2 > 0$ such that for all $\theta \in \Theta_\varepsilon$, $\varphi \in \Phi_\varepsilon$ with $\theta \le \theta_0$, and $\varphi \le \varphi_0$ one has

$$f_2(\theta,\varphi) - f_2(\theta_0,\varphi_0) \ge C_2(c_{\text{kink}} + \eta'\, c_{\text{dihedral}})((\theta_0-\theta) + (\varphi_0-\varphi)). \tag{23}$$

In case 2 we use the convexity of v_{kink} in I_{angle} and condition (4) to derive $v_{\text{kink}}(\theta) - v_{\text{kink}}(\theta_0) \ge \lambda(\theta_0 - \theta)$ and $v_{\text{kink}}(\varphi) - v_{\text{kink}}(\varphi_0) \ge \lambda(\varphi_0 - \varphi)$, where we set $\lambda := -\lim_{\theta\uparrow 2\pi/3} v'_{\text{kink}}(\theta) > 0$ by (4). This implies (23). In case 3 we first observe that the strong convexity of v_{angle} assumed in (3) and the fact that the minimum value is attained at $\theta_0 = 2\pi/3$ implies $v_{\text{angle}}(\theta) - v_{\text{angle}}(\theta_0) \ge C_3(\theta_0 - \theta)$ for a constant $C_3 > 0$ depending only on λ_{angle}. Moreover, the smoothness of v_{dihedral} implies $v_{\text{dihedral}}(\theta,\varphi,\varphi) - v_{\text{dihedral}}(\theta_0,\varphi,\varphi) \ge -C_4(\theta_0-\theta)$ for a constant $C_4 > 0$ large enough. Now we use (5) and Taylor's formula to compute

$$v_{\text{dihedral}}(\theta_0,\varphi,\varphi) - v_{\text{dihedral}}(\theta_0,\varphi_0,\varphi_0) \ge \lambda'(\varphi_0-\varphi) - C_5(\varphi_0-\varphi)^2 \ge (\lambda' - C_5\varepsilon)(\varphi_0-\varphi)$$

for $C_5 > 0$ large enough, where

$$\lambda' = -\frac{\mathrm{d}}{\mathrm{d}\varphi} v_{\text{dihedral}}(\theta_0,\varphi,\varphi)\Big|_{\varphi=2\pi/3} > 0,$$

by assumption (5). Collecting the last estimates and using $v_{\mathrm{angle}}(\varphi) \geq v_{\mathrm{angle}}(\varphi_0)$, we conclude

$$f_2(\theta,\varphi) \geq f_2(\theta_0,\varphi_0) + (C_3 - C_4\eta')(\theta_0 - \theta) + \eta'(\lambda' - C_5\varepsilon)(\varphi_0 - \varphi),$$

which for η' and ε small enough implies (23).

We are now in the position to show (21). By combining (22) and (23), we derive for η/η' small and ε small with respect to η and η'

$$\widehat{E}_c(a,b,b,\theta,\varphi,\varphi) \geq \widehat{E}_c(a,b,b,\theta_0,\varphi_0,\varphi_0),$$

where equality holds only if $\theta = \theta_0$ and $\varphi = \varphi_0$. Recalling (16) and the fact that (a^*,b^*) minimizes $E_\eta(X_{a,b})$, we conclude

$$\widehat{E}_c(a,b,b,\theta,\varphi,\varphi) \geq \frac{1}{60}E_\eta(X_{a,b}) \geq \frac{1}{60}E_\eta(X_{a^*,b^*}) = \widehat{E}_c(a^*,b^*,b^*,\theta_0,\varphi_0,\varphi_0),$$

where due to the uniqueness of the minimizer of E_η, equality holds only if $a = a^*$ and $b = b^*$. ∎

We are now in the position to prove the stability of $X_{a^*b^*}$ under small perturbations. In the following proof we will treat assertions 3.1, 3.2, and 3.3 of Theorem 2.2 simultaneously.

Proof of assertion 3 *of Theorem* 2.2. Let $P = \{x_1',\ldots,x_{60}'\} \in \mathcal{P}(X_{a^*,b^*})$ be given, and suppose that the assumptions stated in assertion 3.1, 3.2, or 3.3 are satisfied. Recalling (11)–(13), to each x_i', $i = 1,\ldots,60$, we associate $a_i, b_i^1, b_i^2, \theta_i$, φ_i^1, φ_i^2. Let us assume that P does not have the same geometry as X_{a^*,b^*}; i.e., not all bond lengths and angles coincide with the corresponding values of X_{a^*,b^*}. We show that then indeed $E_c(P) > E_c(X_{a^*,b^*})$.

Define the mean values

$$\bar{a} = \frac{1}{60}\sum_{i=1}^{60} a_i, \quad \bar{b} = \frac{1}{120}\sum_{i=1}^{60}(b_i^1 + b_i^2), \quad \bar{\theta} = \frac{1}{60}\sum_{i=1}^{60}\theta_i, \quad \text{and } \bar{\varphi} = \frac{1}{120}\sum_{i=1}^{60}(\varphi_i^1 + \varphi_i^2).$$

Then we apply Proposition 4.1 for η and η' small enough (if $c_{\mathrm{nbd}} = 1$ or $c_{\mathrm{dihedral}} = 1$, respectively) and use the strict convexity of $\widehat{E}_c$ twice to obtain

$$\begin{aligned} E_c(P) &= \sum_{i=1}^{60} \widehat{E}_c\left(a_i, b_i^1, b_i^2, \theta_i, \varphi_i^1, \varphi_i^2\right) \\ &\geq \sum_{i=1}^{60} \widehat{E}_c\left(a_i, \frac{b_i^1 + b_i^2}{2}, \frac{b_i^1 + b_i^2}{2}, \theta_i, \frac{\varphi_i^1 + \varphi_i^2}{2}, \frac{\varphi_i^1 + \varphi_i^2}{2}\right) \\ &\geq 60\,\widehat{E}_c\left(\bar{a}, \bar{b}, \bar{b}, \bar{\theta}, \bar{\varphi}, \bar{\varphi}\right), \end{aligned} \tag{24}$$

where we have equality iff each bond and each angle coincides with the corresponding mean value. As the five angles of each pentagon sum up to at most to 3π, we obtain $\bar{\theta} \leq 3\pi/5$. A similar argument for the angles of a hexagon, whose sum does not exceed 4π, yields $\bar{\varphi} \leq 2\pi/3$. We observe that for each vector c in the assertions 3.1–3.3 one of the assumptions 1–3 of Proposition 4.2 is satisfied. Consequently, we obtain

$$60\widehat{E}_c(\bar{a},\bar{b},\bar{b},\bar{\theta},\bar{\varphi},\bar{\varphi}) \geq 60\widehat{E}_c\left(a^*, b^*, b^*, \frac{3\pi}{5}, \frac{2\pi}{3}, \frac{2\pi}{3}\right) = E_c(X_{a^*,b^*}), \tag{25}$$

where equality holds only if $\bar{a} = a^*$, $\bar{b} = b^*$, $\bar{\theta} = 3\pi/5$, and $\bar{\varphi} = 2\pi/3$. As, by assumption, P does not have the same geometry as X_{a^*,b^*}, equations (24)–(25) yield $E_c(P) > E_c(X_{a^*,b^*})$. ∎

5. Nonstability results. In this section we establish assertion 4 of Theorem 2.2. After translation and rotation of $X_{a^*,b^*} = (x_1^*, \dots, x_{60}^*)$, we may assume that $x_i^* \in \mathbb{R} \times \mathbb{R} \times [0, \infty)$ for all indexes $i = 1, \dots, 60$, and that one pentagon of X_{a^*,b^*} is contained in $\mathbb{R} \times \mathbb{R} \times \{0\}$ with vertices

$$V_i := (\cos(2i\pi/5), \sin(2i\pi/5), 0)$$

for $i = 1, \dots, 5$. Let us relabel the atoms of X_{a^*,b^*} so that, for $i = 1, \dots, 5$, we have $x_i^* := V_i$, and, for $i = 6, \dots, 10$, the atom x_i^* is the only neighboring atom of x_{i-5}^* not lying in $\{V_1, \dots, V_5\}$. By $H_1^*, \dots, H_5^*$ we denote the planes in $\mathbb{R}^3$ containing the five hexagonal faces of X_{a^*,b^*} adjacent to the pentagon formed by $\{V_1, \dots, V_5\}$.

The perturbation $P_1 = \{x_1', \dots, x_{60}'\}$ is defined by setting $x_i' := x_i^*$ for $i \geq 6$ and

$$x_i' := (\cos(2i\pi/5 + t_1), \sin(2i\pi/5 + t_1), t_2)$$

for $i = 1, \dots, 5$ and for some positive (small) constants t_1 and t_2 to be specified; i.e., the transformation rotates one of the twelve pentagonal faces of the molecule.

Proof of assertion 3.1 *of Theorem* 2.2. First we see that for t_1, t_2 sufficiently small, $P_1 \in \mathcal{P}(X_{a^*,b^*})$. Moreover, the geometries of P_1 and X_{a^*,b^*} are clearly different as, e.g., the hexagons adjacent to the pentagon formed by $x_1', \dots, x_5'$ are not planar. Recall that by assertion 2 of Theorem 2.2 we have $X_{a^*,b^*} = X_{1,1}$. Consequently, to prove $E_c(P_1) = E_c(X_{1,1})$ for $c = (0,0,0,0)$, it suffices to show that each bond has length 1.

We observe that the only bonds that can present a different length in P_1 with respect to X_{a^*,b^*} are the ones in $\bigcup_{i=1}^5 \mathcal{B}_1(x_i')$. As the pentagon contained in $\mathbb{R}\times\mathbb{R}\times\{0\}$ is just rotated, we find $|[x_1, x_2]| = |[x_2, x_3]| = \cdots = |[x_5, x_1]| = 1$. Finally, for a suitable choice of t_2 with respect to t_1 one can additionally obtain $|[x_i, x_{i+5}]| = 1$ for $i = 1, \dots, 5$. This concludes the proof. ◻

The definition of perturbation P_2 is more involved. One pentagonal face of X_{a^*,b^*} is moved in such a way that the length of the bonds in $\bigcup_{i=1}^{60} \mathcal{B}_1(x_i^*)$ shared by two hexagons does not change to first order. More precisely, for each $i = 1, \dots, 5$ we find a unique vector

$$v_i = (a\cos(2i\pi/5), a\sin(2i\pi/5), b) \in \mathbb{R}^3$$

for suitable constants $a, b \in (0,1)$ such that

$$|v_i| = 1 \quad \text{and} \quad v_i \cdot (x_i^* - x_{i+5}^*) = 0. \tag{26}$$

Then we define $P_2 = \{x_1', \dots, x_{60}'\}$ by setting $x_i' := x_i^*$ for $i \geq 6$ and $x_i' := x_i^* + tv_i$ for $i = 1, \dots, 5$ and for a small constant $t > 0$. By (26), each segment $[x_i^*, x_i'] \subset \mathbb{R}^3$ is not contained in the planes H_j^*, $j = 1, \dots, 5$, and therefore the five hexagons of P_2 adjacent to the pentagon $\{x_1', \dots, x_5'\}$ are not planar, but each one is kinked along the corresponding segment with endpoints in $\{x_6', \dots, x_{10}'\}$. Observe that the essential point of the transformation P_2 is the nonplanarity of these hexagons since hereby (i) the length of the second neighbors can be reduced and (ii) the energy increase due to the modification of the angles is negligible since $v'_{\text{angle}}(2\pi/3) = 0$.

Proof of assertion 3.2 *of Theorem* 2.2. Let P_2 be defined as above, and note that for t sufficiently small we have that $P_2 \in \mathcal{P}(X_{a^*,b^*})$. We now proceed in two steps. In Step I we analyze the modification of bond lengths and angles induced by the perturbation. In Step II, we calculate the energy difference of the two configurations X_{a^*,b^*} and P_2, which in view of the first order optimality condition derived in (17) depends only on the angles (see (30) below). We will then be able to conclude, since the sum over all angles strictly decreases due to the nonplanarity of the five hexagons (see (29) below).

Step I. The transformation changes only the bond lengths $\bigcup_{i=1}^{5}\mathcal{B}_1(x_i)\cup\mathcal{B}_2(x_i)$, the angles $\bigcup_{i=1}^{10}\mathcal{A}(x_i)$, and the second neighbors $\bigcup_{i=6}^{10}\mathcal{B}_2(x_i)$. In particular, there exist $\delta_b, \delta_\varphi \in \mathbb{R}$ such that for the covalent bonds and the angles associated to $x_1', \dots, x_5'$ we have for $i = 1, \dots, 5$

$$a_i = a^* + \mathrm{O}(t^2), \tag{27a}$$

$$b_i^j = b^* + t\delta_b + \mathrm{O}(t^2), \quad j = 1, 2, \tag{27b}$$

$$\theta_i = 3\pi/5, \tag{27c}$$

$$\varphi_i^j = 2\pi/3 + t\delta_\varphi + \mathrm{O}(t^2). \tag{27d}$$

Note that, due to the symmetry of the transformation, all these quantities are actually independent of i and j, and the pentagon $\{x_1', \dots, x_5'\}$ is regular and planar. Moreover, (27a) follows from the fact that the length of the bonds shared by two hexagons does not change in first order by (26). Likewise, for the second neighbors an elementary computation yields, in view of (13), (18), (27), and $\cos'(2\pi/3) = -\sqrt{3}/2$ for $i = 1, \dots, 5$, $j = 1, 2$ (we again set $\sigma = 2\sin(3\pi/10)$ for brevity),

$$\begin{aligned}
p_i &= \sqrt{2(1-\cos(\theta_i))}(b^* + t\delta_b + \mathrm{O}(t^2)) = p^* + t\delta_b\sigma + \mathrm{O}(t^2),\\
h_i^j &= \sqrt{a_i^2 + (b_i^j)^2 - 2a_ib_i^j\cos(\varphi_i^j)}\\
&= \sqrt{(a^*)^2 + (b^*)^2 + a^*b^* + 2t\delta_b b^* - 2ta^*(\cos(2\pi/3)\delta_b - b^*\sqrt{3}\delta_\varphi/2) + \mathrm{O}(t^2)}\\
&= h^* + (t/h^*)\Big(\delta_b\,(b^* + a^*/2) + \sqrt{3}a^*b^*\delta_\varphi/2\Big) + \mathrm{O}(t^2).
\end{aligned}$$

Moreover, for $i = 6, \dots, 10$, $j = 1, 2$, we find for $\delta_\varphi' \in \mathbb{R}$ by a similar computation

$$a_i = a^*, \quad b_i^j = b^*, \quad \theta_i = 3\pi/5, \quad p_i = p^*, \tag{28a}$$

$$\varphi_i^j = 2\pi/3 + t\delta_\varphi' + \mathrm{O}(t^2), \tag{28b}$$

$$\begin{aligned}
h_i^j &= \sqrt{a_i^2 + (b_i^j)^2 - 2a_ib_i^j\cos(\varphi_i^j)} = \sqrt{(a^*)^2 + (b^*)^2 - 2a^*b^*\cos(\varphi_i^j)}\\
&= \sqrt{(a^*)^2 + (b^*)^2 + a^*b^* + \sqrt{3}ta^*b^*\delta_\varphi') + \mathrm{O}(t^2)}\\
&= h^* + \sqrt{3}t/(2h^*)a^*b^*\delta_\varphi' + \mathrm{O}(t^2).
\end{aligned} \tag{28c}$$

We close the discussion about the modification of bonds and angles by showing

$$\delta_\varphi + \delta_\varphi' < 0. \tag{29}$$

To see this, we recall that the five hexagons adjacent to $\{x_1', \dots, x_5'\}$ are kinked along the corresponding segment with endpoints in $\{x_6', \dots, x_{10}'\}$. Each hexagon consists of two planar quadrangles Q_i^1, Q_i^2 with angles $2\pi/3$, $2\pi/3$, $\pi/3$, $\pi/3$ and $\varphi, \varphi, \pi-\varphi, \pi-\varphi$, with $\varphi := \varphi_1^1$ as given in (27d).

We have already noticed below (26) that the segment $[x_i^*, x_i']$ is not contained in H_j^*, $i, j = 1, \dots, 5$. Consequently, the angle enclosed by the the two planes containing Q_i^1 and Q_i^2 is larger than Ct for a sufficiently small universal constant $C > 0$. By an elementary trigonometric argument, this implies that φ_i^j is smaller than the sum of the two corresponding angles $\pi - \varphi$, $\pi/3$ of the quadrangles at x_i'. More precisely,

$\varphi_i^j \leq (\pi - \varphi) + \pi/3 - C't$ for $C' > 0$ small enough for all $i = 6, \dots, 10$, $j = 1, 2$. Therefore, in view of (27d) and (28b), we derive

$$\frac{2\pi}{3} + t\delta'_\varphi + \mathrm{O}(t^2) \leq \frac{2\pi}{3} - t\delta_\varphi - C't + \mathrm{O}(t^2)$$

and see that (29) holds true since $t > 0$.

Step II. We now estimate the difference between $E_c(X_{a^*,b^*})$ and $E_c(P_2)$. Let us start from the case $c = (1,0,0,1)$. By (27), (28) and the fact that $v'_{\mathrm{angle}}(2\pi/3) = 0$, we get $v_{\mathrm{bond}}(a_i) = v_{\mathrm{bond}}(a^*) + \mathrm{O}(t^2)$ and $v_{\mathrm{angle}}(\varphi_i^j) = v_{\mathrm{angle}}(2\pi/3) + \mathrm{O}(t^2) = \mathrm{O}(t^2)$ for $i = 1, \dots, 10$, $j = 1, 2$. Consequently, recalling (20) and (27)–(28), we obtain $E_c(P_2) - E_c(X_{a^*,b^*}) = A + B + C$ with

$$\begin{aligned}
A &:= \sum_{i=1}^{5} \left(\widehat{E}_{\mathrm{bond}}(x_i) - \widehat{E}_{\mathrm{bond}}(x_i^*) \right) = \sum_{i=1}^{5} \sum_{j=1}^{2} \left(\frac{1}{2} v_{\mathrm{bond}}(b_i^j) - \frac{1}{2} v_{\mathrm{bond}}(b^*) \right) + \mathrm{O}(t^2) \\
&\qquad\qquad\qquad\qquad\qquad\quad = 5 v'_{\mathrm{bond}}(b^*) t \delta_b + \mathrm{O}(t^2), \\
B &:= \sum_{i=1}^{10} \left(\widehat{E}_{\mathrm{angle}}(x_i) - \widehat{E}_{\mathrm{angle}}(x_i^*) \right) = \mathrm{O}(t^2), \\
C &:= \sum_{i=1}^{10} \eta \left(\widehat{E}_{\mathrm{nonbond}}(x_i) - \widehat{E}_{\mathrm{nonbond}}(x_i^*) \right) \\
&= 5 v'_{\mathrm{nbd}}(p^*) \eta t \delta_b \sigma + 10 v'_{\mathrm{nbd}}(h^*) \eta \frac{\sqrt{3}t}{2h^*} a^* b^* \delta'_\varphi \\
&\qquad + 10 v'_{\mathrm{nbd}}(h^*) \eta \frac{t}{h^*} \left(\delta_b \left(b^* + \frac{a^*}{2} \right) + \sqrt{3} a^* b^* \frac{\delta_\varphi}{2} \right) + \mathrm{O}(t^2).
\end{aligned}$$

In case $c = (1,0,0,0)$ we obtain the same estimate with $B = 0$. Recall that we have identified the geometry of X_{a^*,b^*} by optimizing the energy $E_\eta(X_{a,b})$ defined in (16) in terms of a, b. In particular, the first order optimality condition

$$\frac{\mathrm{d}}{\mathrm{d}b} E_\eta(X_{a^*,b}) \Big|_{b=b^*} = 0$$

yields (cf. (19))

$$v'_{\mathrm{bond}}(b^*) + \eta \sigma v'_{\mathrm{nbd}}(p^*) + 2\eta \frac{a^* + 2b^*}{2h^*} v'_{\mathrm{nbd}}(h^*) = 0.$$

Combining the last two estimates, we derive

$$E_c(P_2) - E_c(X_{a^*,b^*}) = 10 v'_{\mathrm{nbd}}(h^*) \eta \frac{\sqrt{3}t}{2h^*} a^* b^* (\delta_\varphi + \delta'_\varphi) + \mathrm{O}(t^2). \tag{30}$$

In view of (29) and the fact that $v'_{\mathrm{nbd}}(h^*) > 0$ and $t > 0$, we conclude that $E_c(P_2) - E_c(X_{a^*,b^*}) < 0$. ∎

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