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# Atomic structure and mechanical properties of carbyne

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The atomic structure and mechanical properties of the carbyne (monatomic linear chains), containing from 2 to 21 carbon atoms, are theoretically investigated by *ab-initio* methods. We demonstrate the existence of a stable cumulene structure in the inner part of chains with the number of atoms $N \geqslant 10$. We present a general stress-strain diagram of chains until the moment when they break, which enables to determine their strength, elasticity, and fragility. These diagrams can be utilized to calibrate empirical potentials, especially for large deviations of the atoms from the equilibrium positions. For chains with $N \geqslant 4$, the relationship between the strength of the chain and the binding energy of the edge atom in the chain is established. The existence of scale-effect and "even-odd" effect for such properties as strength, elasticity, and fragility is observed. We demonstrate that the five-atom carbon chains show the maximum strength value.

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## I. INTRODUCTION

Carbynes (monatomic linear chains of carbon) have recently attracted much attention due to their unusual physical properties [1–3] and promising applications [4–9]. The potential implementations of these unique functional properties essentially depend on the strength and elasticity of the carbyne. Moreover, the possibility of obtaining carbyne by unraveling out of nanotubes or graphene sheets is governed by its mechanical properties [4,5,10,11]. Therefore, a lot of studies concerning the investigation of strength and stability of monatomic carbon chains have appeared recently [12–15]. At the same time, most of the studies do not present the results of targeted investigations of the dependence of the strength of chains on their atomic structure. The mechanical properties data is usually the auxiliary one when analyzing electronic, magnetic, and other functional properties. Currently, to the best of our knowledge, this information is contradictory in literature. For example, the data on the strength of monatomic carbon chains in various papers differs by the order of magnitude [16], and in most cases, the properties of chains of *infinite* length are investigated. However, the structure and properties of a finite carbon chain (carbyne) differ significantly from those for an infinite chain [17,18].

Experimental findings of tests on determination of tensile strength of carbon atomic chains (CACs) by high-field technique were published recently [19,20]. Extremely high level of strength of these chains was ascertained, which exceeds 270 GPa [20]. Besides, their high-field-evaporation stability was found. However, these experiments have enabled us to specify only the lower limit of carbyne strength. The goal of this paper is to give more comprehensive characterization of carbyne by *ab-initio* simulation, namely, to ascertain regularities of the effect of the number of atoms in carbyne on its atomic structure and mechanical properties such as strength, elasticity, and fragility.

## II. THE SUBJECT AND THE METHODS OF SIMULATION

As it was shown in Refs. [17,18], the interatomic distance in the chains of different lengths is not constant and depends on the number of atoms in the chain. In the present study we carry out a detailed analysis of this effect using *ab initio* calculations of the electronic and atomic structure of chains of different lengths with an even and odd number of atoms. The number of atoms in the chain was varied from 2 to 21. We performed comparative analysis of interatomic distances for carbynes and carbon chains of infinite length. For this purpose, the same calculation techniques should be used for simulation of atomic structure. In the present paper, *ab initio* methods with 3D translational symmetry were employed (molecule in a box), which are regularly used for calculation of atomic and electronic structure of crystals. The size of the box was $9 \times 9 \times 30$ Å, thus eliminating interactions between chains (Fig. 1). When modeling both the atomic structure of chains and their tension, size of elementary cell was kept constant. Modelling tension of chains, we fixed one edge atom and the other edge atom was displaced, allowing others atoms of the chain to relax to their equilibrium positions. Maximal increment in the chain length at each step of the simulation does not exceed 2% of its original equilibrium length. Full energies of chains were calculated by pseudopotential method (software *Quantum*-ESPRESSO (QE) [21]). This method was employed also for simulation of mechanical properties of chains. Pseudopotentials for carbon were generated according to scheme *Vanderbilt ultrasoft* using software Vanderbilt code version 7.3.4 [22]. To estimate the accuracy of calculation of full energies of CACs, control calculations for infinite chains with cumulene and polyyne structure were performed. Obtained values of interatomic distances and full energies agree with the results of paper [18]. The value of cutoff $E_{\mathrm{cut}}$ for number of plane waves in an expansion of wave function was of 450 eV. The first Brillouin zone was split by a mesh containing $1 \times 1 \times 100$ points. The structural optimization was stopped when components of forces acting on atomic nuclei became less that 0.01 eV/a.u. Accuracy of calculation of the total energy was 1 meV. It should be noted that calculation of the total energy was carried out at fixed positions of atomic nuclei, i.e., without accounting for zero oscillations of nuclei.

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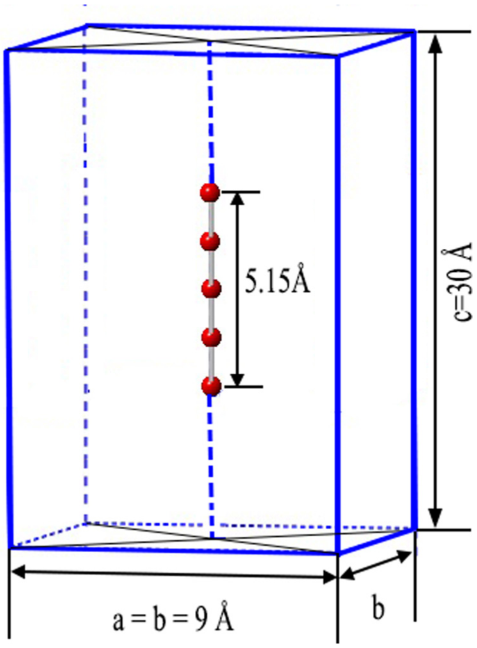

FIG. 1. (Color online) Supercell for calculation of atomic and electronic structure of finite chain containing five atoms, as an example (scheme).

To visualize spatial distribution of electron density in a chain containing seven atoms, full-electron method FLAPW (the program package WIEN2K [23]) was used. Atomic sphere radii were 1.2 a.u. The calculations were executed for 1000 $k$-space points in the first Brillouin zone. Inside the atomic spheres the wave function was expanded up to $l_{\max} = 12$. The electronic density and potential inside the spheres were expanded to $L_{\max} = 6$. For expansion of wave function the number of plane waves per atom was equal to 330. The exchange-correlation potential was GGA-PBE [24].

As the results of *ab-initio* calculations, the dependence of the tensile force $F$ on the value of total chain strain $e$ was determined, as well as the values of the "bond strain" $\varepsilon$ between the first and the second atoms from the edge of the chain (Fig. 2). The force acting on the edge atom was calculated as:

$$F = \frac{dE}{da}, \tag{1}$$

where $E$ is the total energy of the system; $a$ is the current distance between the first and the second atoms (length of the edge bond).

The strain of the whole chain $e$ was estimated as:

$$e = \ln\left(\frac{l}{l_0}\right), \tag{2}$$

where $l_0$ and $l$ are the equilibrium chain length and its length in tensile state, respectively. The strain of interatomic bonds between the first and the second atoms was calculated as

$$\varepsilon = \ln\left(\frac{a_i}{a_0}\right), \tag{3}$$

where $a_0$ and $a_i$ are the equilibrium distance between the first and the second atoms and the distance in tensile state,

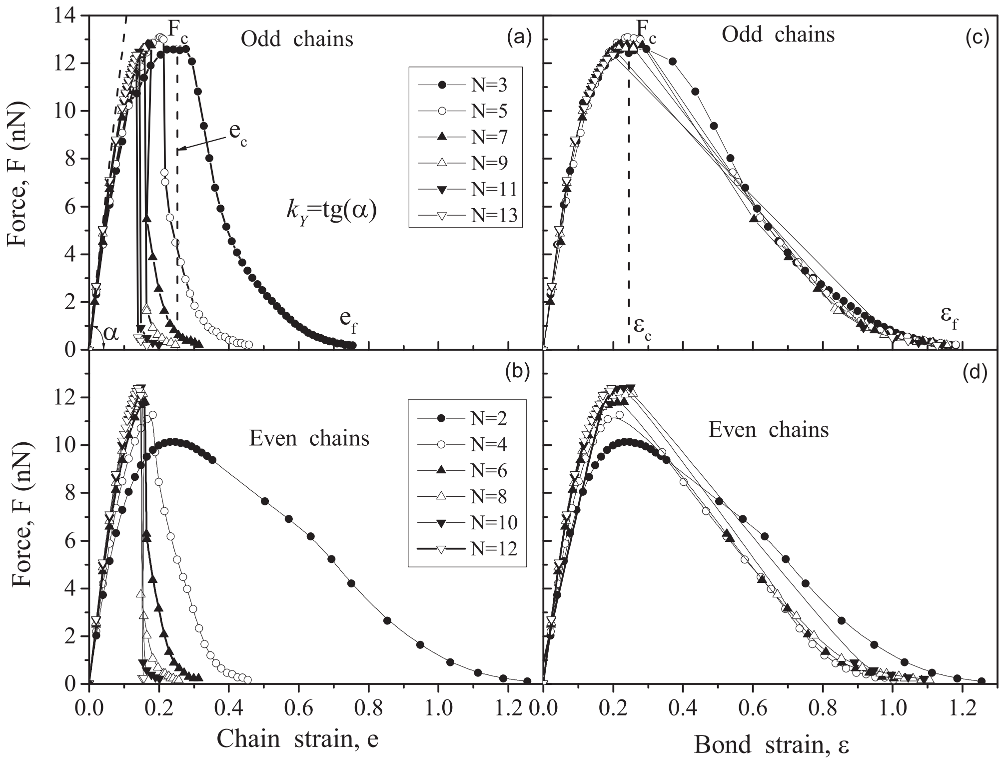

FIG. 2. The dependence of force $F$ on strain $e$ for the whole chain with odd (a) and even (b) number of atoms, and on the value of strain $\varepsilon$ at the edge atomic bond in "odd" (c) and "even" (d) chains: $F_c$ is critical stress for instability of atomic bond (bond strength); $\varepsilon_c$ and $e_c$ are critical strain of instability of atomic bond and the chain as a whole, respectively; $\varepsilon_f$ and $e_f$ are fracture strain for atomic bond and chain, respectively; $k_Y$ is coefficient of elasticity of the chain; $N$ is number of atoms.

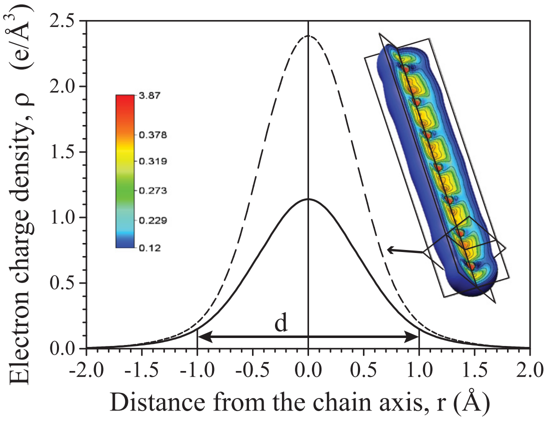

FIG. 3. (Color online) The distribution of the electron density in the bulk of the chain and its cross section passing through the middle of the edge atomic bond in the unloaded state (dashed line) and at the moment of instability of the chain (solid line).

respectively. Dependencies of force on strain (Fig. 2) have enabled us to calculate the maximum force, which chain can withstand (chain strength $F_c$), and corresponding values of the critical strain of an edge bond $\varepsilon_c$ and strain of a whole chain $e_c$. At loadings higher than $F_c$, the chain instability occurs. Complete failure of a chain ($F = 0$) takes place at the strains $\varepsilon_f$ and $e_f$ (Fig. 2).

The values of the elasticity coefficient (stiffness) $k_Y$ and of the elastic $Y$ modulus were calculated as:

$$k_Y = \left.\frac{dF}{de}\right|_{e=0}, \tag{4}$$

$$Y = \frac{k_Y}{S}, \tag{5}$$

where $S$ is the effective cross-sectional area of the chain, through which the atoms interact with each other.

Estimation of "diameter" of monatomic chain is one of the key problems in the theory of 1D-crystal strength. Values given in references differ by the order of magnitude from each other [16]. Typically, the value of the effective diameter is determined by comparison of the results of atomistic simulations and calculations obtained in the framework of continuum mechanics [15]. In the present paper we have demonstrated the relation between a chain diameter and distribution of electron density in the cross section of the chain. Figure 3 shows the electron charge density in the cross section of the chain in the unloaded state and at the critical strain $e_c$ of chain. The cross section for the unloaded state was chosen in the middle of the distance between first and second atoms. For the critical state of the chain the cross section was chosen at a distance from the edge atom, at which the magnitude of the electron charge in a plane perpendicular to the axis of the chain reaches its minimum value. Calculations have been carried out by FLAPW method.

This approach enables us to give an estimate for the transverse size of the area of the force interaction between the first and the second atoms in the chain, whose value was found to be $d \approx 2$ Å. We note that the same diameter of the chain has been used in Ref. [25] to simulate the formation of carbyne by unraveling. This value coincides with the effective magnitude $d$ obtained in Ref. [26] to analyze the thermal conductivity of chains. Furthermore, this value enables us to obtain the calculated value of strength of carbyne, which correlates reasonably well with its experimental value, as established in Ref. [20].

## III. RESULTS AND DISCUSSION

Figure 4 shows distances between the two nearest neighboring atoms $a_{i,i+1} (i = 1, \ldots, N)$ in carbon chains of different lengths. According to these results, the distances between the atoms depends on their positions in the chain, as well as on the length of the chain itself. This represents the principle difference between the atomic structure of carbyne and that of infinite carbon chains. The distance between the the first and the second atoms, $a_{1,2}$, appeared to be the largest one, while the smallest distance was observed between the third and the fourth atoms. In chains with less than 16 atoms, the distance $a_{1,2}$ depends on both the total number of atoms in the chain and on whether this number is odd or even. Therefore the "scale" and "even-odd" effects occur simultaneously. Our calculations showed that in carbynes with more than 10 atoms, the interatomic distances within the chain (starting from the fourth atom) are equal to those in cumulenes, i.e., the internal structure of carbyne is a cumulene one. It should be noted that the cumulene structure is unstable in the chains of infinite length, and for such chains a polyyne structure is energetically favorable [27]. Therefore, the existence of a cumulene structure in the inner part of the chain is a specific characteristic of the atomic structure of carbyne. The presence of the edge atoms appears to be the reason for stability of

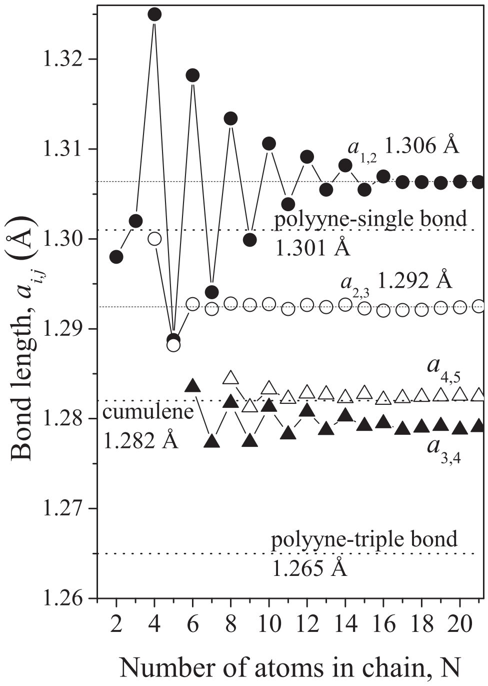

FIG. 4. The dependence of the length of interatomic bond $a_{i,j}$ on the number of atoms in the chain $N$.

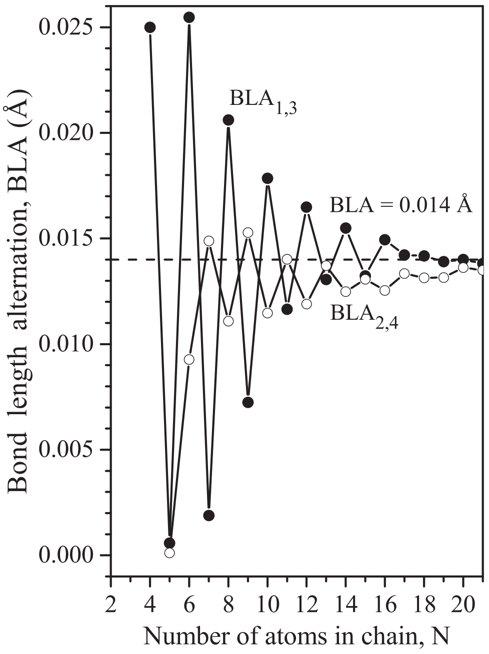

FIG. 5. The dependence of the value of bond length alternation (BLA) on the number of atoms in the chain $N$: $\mathrm{BLA}_{1,3}$ and $\mathrm{BLA}_{2,4}$ are the values of BLA for atomic bonds $a_{1,2}$ and $a_{2,3}$; $a_{2,3}$ and $a_{3,4}$, respectively.

a cumulene structure in the central part of the finite length chains.

Similar to the case of the infinite chains, the ratio of the bond lengths in finite chains can be characterized using the $\mathrm{BLA}_{i,j}$ (bond length alternation) quantity. The regularities of changes in $\mathrm{BLA}_{1,3} = a_{1,2} - a_{2,3}$ and $\mathrm{BLA}_{2,4} = a_{2,3} - a_{3,4}$ values in chains of different lengths are presented in Fig. 5. General regularity of changes in the $\mathrm{BLA}_{1,3}$ and $\mathrm{BLA}_{2,4}$ values lies in the fact that the chains with an even number of atoms show maximum values of these quantities, while the chains having an odd number of atoms show the minimum ones. In addition, the opposite trends in BLA change with the growth of the number of atoms $N$ that are observed. In even-numbered chains the values of $\mathrm{BLA}_{1,3}$ and $\mathrm{BLA}_{2,4}$ decrease with $N$ (at $N \geqslant 6$), while in odd-numbered chains, they are increasing. At $N \geqslant 19$, these values no longer depend on the total number/parity of atoms, and they approach a constant value of $\mathrm{BLA} \approx 0.014$ Å. This value is significantly smaller than the BLA for the infinite polyyne chain (0.070–0.090 Å) [18].

Significant changes in the interatomic distances along the chain (Fig. 4) indicate that the interatomic interaction energy must also vary depending on the position of the atom in the chain. Therefore, to describe interatomic interaction in the carbyne, the binding energy of each atom with the rest of the chain, $E_i^b(N)$, should be estimated. The total energy of a finite chain $E(N)$, consisting of $N$ atoms, can be represented as:

$$E(N) = \sum_{i}^{N} E_i^b(N) + N E_{at}, \tag{6}$$

where $E_{at}$ is the energy of a free carbon atom. In carbyne structures with the number of atoms $N \geqslant 6$, three types of carbon atoms with different binding energies can be identified. Our analysis of the interatomic distances (Fig. 4) shows that the first (from the edge) atom should have the lowest binding energy, as the distances $a_{1,2}$ between the first and the second atoms are the largest ones in carbyne. At the same time, the atoms in the central part of the carbyne are expected to have the highest values of the binding energies, as the distances between those atoms are approximately the same and are close to the bond length in cumulenes. The second atoms from the edge are expected to have intermediate values of the binding energies. This allows us to represent total energy [Eq. (6)] as follows:

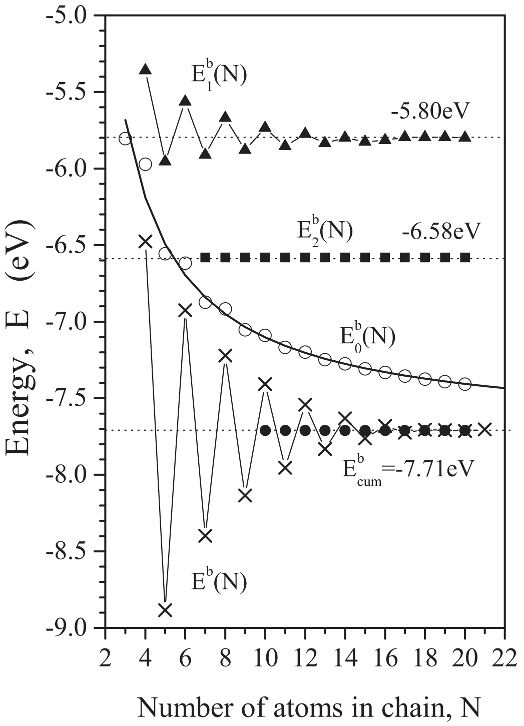

FIG. 6. The dependence of the binding energy on the number of atoms: $E_1^b(N)$ and $E_2^b(N)$ for the first and second atoms from chain edge, $E_{\mathrm{cum}}^b$ for inner atoms, $E^b(N)$ for energy of separation, calculated in the Eq. (8), $E_0^b(N)$ for the average binding energy per atom [solid line—calculated in Eq. (11)].

$$E(N) = N E_{at} + 2\left[E_1^b(N) + E_2^b(N)\right] + (N-4)E_{\mathrm{cum}}^b, \tag{7}$$

where $E_1^b(N)$ and $E_2^b(N)$ are binding energies of first and second atoms from chain edge, and $E_{\mathrm{cum}}^b = -7.71$ eV is a binding energy of the carbon atom in cumulene structure. The total energy calculations of finite chains with different numbers of atoms allowed us to evaluate the binding energy of carbon atoms with a different location inside the chain. The results of the calculations are presented in Fig. 6. In the first approximation, the value of $E_1^b(N)$ in chains with $N \geqslant 16$ is equal to the average binding energy of carbon atom in a chain of three atoms $E_1^b = -5.80$ eV (Fig. 6). Such approximation is based on the fact that interatomic distances in the chain are close to the value $a_{1,2}$ in the chain with number of atoms $N \geqslant 16$ (Fig. 4). Binding energy of the near-edge atom ($E_2^b = -6.58$ eV) was obtained from the expression (7) for the total energy of the chain containing 16 atoms using the $E_1^b = -5.80$ eV value. Interestingly, the average energy of the atom in the five-atom chain is equal to 6.55 eV and is close to the value of $E_2^b$. This can be explained by the fact that the interatomic distances in a five-atom chain are equal and are close to the value of $a_{2,3}$ in the chains with $N \geqslant 16$ (see Fig. 4). According to our calculations, the value of $E_1^b$ depends both on the total number of atoms in carbyne and on the parity of this number (see Fig. 6). In chains with an odd number of atoms, the values of $E_1^b$ are greater in magnitude and decrease with an increasing number of atoms in the chain, approaching the value of $E_1^b = -5.80$ eV. The situation is different for even-numbered chains, where binding energy of the edge atoms increase with $N$ (see Fig. 6). It is interesting to note the fact that the stronger odd-numbered carbynes are insulators, and even-numbered ones are conducting systems. However, a detailed study of the electronic structure of carbyne systems is beyond the scope of the present paper and should be a topic of a separate investigation.

The data presented in Fig. 6 demonstrates that the atomic bonds of the edge atoms are the weakest ones. As we show below, this fact leads to the edge atoms tearing off upon the stress application. Formally, the energy of separation of one atom from a chain can be written as follows:

$$E^b(N) = E(N) - E(N-1) - E_{at}, \tag{8}$$

where $E(N)$ and $E(N-1)$ are the total energies of chains with $N$ and $N-1$ atoms, respectively. The regularities of change in this value with increasing of the number of atoms in carbyne are presented in Fig. 6. By substituting $E(N)$ and $E(N-1)$ from Eq. (7) to Eq. (8), while taking into account that $E_2^b(N) = const$, one can see that the nonmonotonic change in $E^b(N)$ value is mainly due to the change in the binding energy of the edge atom, $E_1^b(N)$:

$$E^b(N) = 2\left[E_1^b(N) - E_1^b(N-1)\right] + E_{\text{cum}}^b, \tag{9}$$

At $N \geqslant 16$ the $E_1^b(N)$ value is almost equal to $E_1^b(N-1)$. Therefore, with increasing of $N$, the value of $E^b(N)$ approaches the value of binding energy of the carbon atom in cumulene, $E_{\text{cum}} = -7.71$ eV, which agrees well with the results of *ab initio* calculations (Fig. 6). Therefore, the equation (8) describes the energy balance in the separation of one atom from the chain, so it can be used to determine the binding energy in the infinite chain. However, it does not take into account specific features of interatomic interaction in the chains of finite length.

Equation (7) for the total energy of the chain allows us to write down analytical expression for the average binding energy $E_0^b(N)$ per atom:

$$E_0^b(N) = \frac{2\left[E_1^b(N) + E_2^b(N) - 2E_{\text{cum}}^b\right]}{N} + E_{\text{cum}}^b. \tag{10}$$

When $N \geqslant 16$ the values $E_1^b(N)$ and $E_2^b(N)$ do not depend on the number of atoms in a chain, and are equal to $E_1^b(N) = -5.80$ eV and $E_2^b(N) = -6.58$ eV. In this case the average value of binding energy per atom can be found using the following expression:

$$E_0^b(N) = \frac{A}{N} + E_{\text{cum}}^b, \tag{11}$$

where $A = 6.08$ eV.

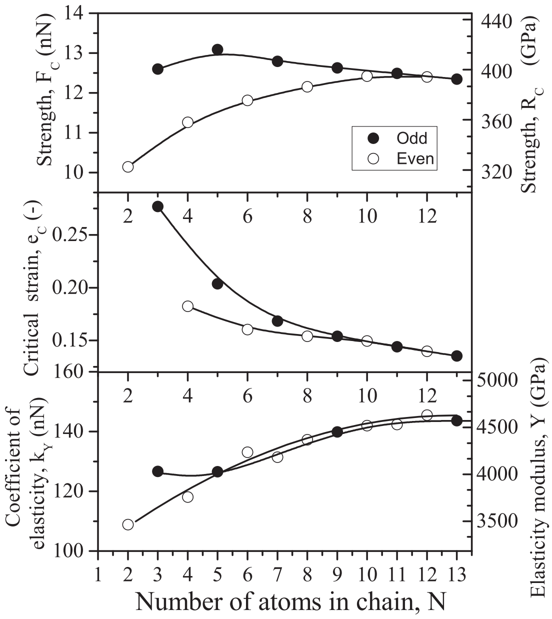

FIG. 7. The effect of the number of atoms in carbyne on its strength $F_c$, fragility $e_c$, and hardness $k_Y$.

According to Fig. 6 this relation agrees well with the results of our *ab initio* calculations and can be used to predict the average value of the binding energy per atom in carbynes containing a different number of atoms. The difference between $E(N)$ for the chain of finite length and infinite chain with a cumulative structure is due to the presence of the edge atoms (edge effect), and in the case of $N = \infty$ we have $E_0^b(N) = E_{\text{cum}}^b$.

To calculate the mechanical properties of carbyne, we performed modeling of tension of chains of various lengths up to their complete break. As the result of these calculations, the values of elasticity coefficient $k_Y$ and the elasticity modulus $Y$, the value of the maximum force $F_c$ as well as the respective values of critical strains of the whole chain $e_c$ [Figs. 2(a) and 2(b)] and the edge bond $\varepsilon_c$ [Figs. 2(c) and 2(d)] were determined. Besides these values, the breaking strain of the whole chain $e_f$ [Figs. 2(a) and 2(b)] and the edge bond $\varepsilon_f$ [Figs. 2(c) and 2(d)] were found. The $F_c$ value defines the level of strength of carbyne, and $e_c$ characterizes its fragility.

According to the results of our *ab initio* simulations, the magnitude of strength of the carbyne is determined by the strength of atomic bond of the edge atom. The value of this strength depends both on the total number of atoms in the chain and on whether this number is odd or even. We observe that the strength of carbynes with an odd number of atoms is higher in comparison with the strength of even-numbered carbynes. Carbyne containing five atoms has a maximum strength of $F_c = 13.09$ nN. Chains with an odd number of atoms not only show higher strength, but they are also less fragile because their instability takes place at higher values of critical strain $e_c$. The simulation results, presented in Fig. 7, show that the difference between the strength of even-numbered and odd-numbered chains decreases with an increase of the number of atoms in the chain, and at $N \geqslant 12$ this difference practically disappears. The increase in the number of atoms in the chains gives rise

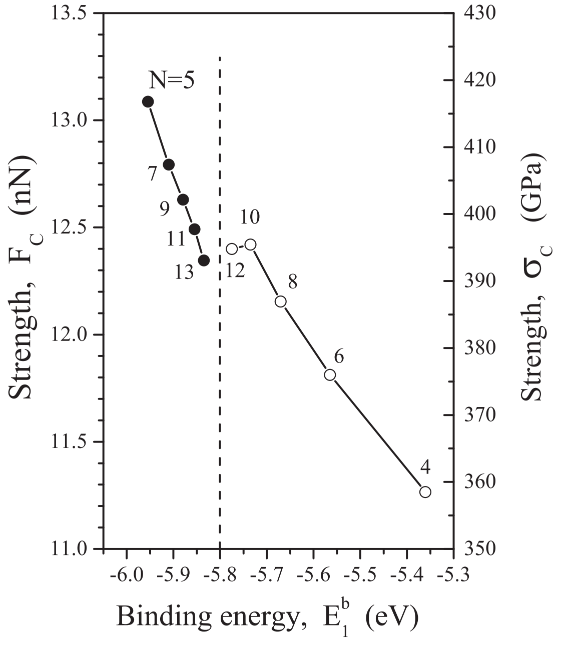

FIG. 8. The relationship between the strength of the chain $F_c$ and the binding energy $E_1^b$ of the edge atom: •—odd chains; ○—even chains.

to an increase in the stiffness of the chain $k_Y$ and to a steep (1.3–1.5 times) increase in their fragility (decrease in $e_c$). The latter is due to the inhomogeneous deformation of the chain, which shows itself as the localization of deformation in the bond between the first and second atoms because the edge bond is the weakest one. This effect is enhanced with increasing the chain length. Quantitatively, it shows itself in a significant difference between the value of fracture strain of the *whole chain* $e_f$ and the critical fracture strain of the *atomic bond* between the first and second atoms $\varepsilon_f$ (Fig. 2).

It should be noted that the disappearance of the "scale" and the "even-odd" effects for strength occurs at the reaching of a smaller number of atoms in the chain (12 atoms) instead of 16 atoms for the interatomic interaction energy. For the coefficient of elasticity $k_Y$, the difference between "even" and "odd" chains vanishes starting from $N \geqslant 5$ atoms.

Usually the strength of interatomic bonds is not estimated directly but by using the value of binding energy. Therefore, we did a comparison between the binding energy of the edge atom $E_1^b$ and the value of the critical force of instability of the edge bond $F_c$ which defines the strength of the whole chain. As is shown in Fig. 8, for chains containing more than three atoms, the increase in the binding energy of the edge atom $E_1^b$ is accompanied by the increase in strength of the chain.

According to our results, the strength of carbyne ranges from 11.3 nN (360 GPa) to 13.1 nN (417 GPa). These values are higher than the experimental strength of 270 GPa [20]. It is probably due to the fact that the experimental value of 270 GPa is a lower bound of strength of carbyne as it determines the strength of the contact atomic bond between the chain and graphene from which this chain was drawn out.

The distinction in mechanical properties of the chains with an even and odd number of atoms is due to difference in their electronic structure. This difference was observed by Pitzer and Clementi [28]. They have shown that the energy spectrum of electrons in chains with an odd and even number of carbon atoms differ in the number of filled $\pi$ orbitals. In this case the chains with an odd number of atoms are energetically more favorable.

Detailed quantitative analysis of the electronic structure of "even" and "odd" carbynes in the ground and stretched states is beyond the scope of this paper. It is the topic of a special publication.

## IV. CONCLUSION

We performed a detailed theoretical study of atomic and mechanical properties of the carbyne chains using the *ab initio* methods. Our results demonstrate that in carbynes with number of atoms $N \geqslant 10$ the length of the "inner" interatomic bonds (starting from the fourth from the edge) becomes equal to the bond length in cumulenes (1.282 Å). The existence of this "inner" structure is one of the most fundamental differences between the atomic structure of carbyne and that of the infinite chains, which show stable polyyne structure.

It is shown that unlike the carbon chains of infinite length, the interatomic distance in carbynes varies along the chain. The bond length between the first and the second (from the edge) atoms is the largest one, while the bond length between the third and the fourth atoms has the smallest value (1.279 Å). These atoms are effectively separating the inner part of carbyne from the first and second atoms. In short carbynes ($N \leqslant 16$), the distance between the first and second atoms depends both on the total number ($N$) of atoms in the carbyne and on whether $N$ is odd or even. With the growing number of atoms in carbyne, the length of the edge interatomic bond in even-numbered carbynes decreases, while this bond is increasing in odd-numbered carbynes. When the total number of carbon atoms is $N \geqslant 16$, these values approach 1.306 Å, which is only 0.005 Å greater than the length of a single bond in polyyne.

The total energy calculation showed that the energy of interatomic interaction in carbynes depends on the position of the atom in the chain. Depending on the value of the binding energy, one can distinguish three types of atoms: (i) the edge atoms that have the lowest binding energy (Å $= -5.80$ eV for $N \geqslant 16$), (ii) inner atoms whose binding energy in chains with $N \geqslant 10$ is equal to the binding energy in cumulenes ($E = -7.71$ eV), and (iii) the intermediate atoms with a binding energy of $E = -6.58$ eV. In short carbynes ($N \leqslant 16$) the binding energy of the edge atoms depends on both the total number of atoms in the carbyne and the parity of this number. The binding energy of these atoms in the even-numbered carbynes is always lower. Its value increases with the number of atoms, and in the odd-numbered carbynes, it, on the contrary, decreases.

We show that the mechanical properties of carbyne containing more than four and less than 12 atoms are governed by the scale and "even-odd" effects. The chains with an odd number of atoms are stronger and less fragile than the even-numbered chains. However, these effects vanish when the number of atoms in the chain is more than 10.

Carbyne is the strongest material in the world. Lower experimental estimation of its strength is equal to 270 GPa at

3 K. Our *ab initio* calculations demonstrate that the five-atom carbyne chains show the maximum strength of 13.1 nN (417 GPa), while 392 GPa was obtained for this value for the carbynes with $N \geqslant 12$.

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[1] F. Banhart, Beilstein J. Nanotechnol. **6**, 559 (2015).
[2] L. Ravagnan, N. Manini, E. Cinquanta, G. Onida, D. Sangalli, C. Motta, M. Devetta, A. Bordoni, P. Piseri, and P. Milani, Phys. Rev. Lett. **102**, 245502 (2009).
[3] E. Cinquanta, L. Ravagnan, I. E. Castelli, F. Cataldo, N. Manini, G. Onida, and P. Milani, J. Chem. Phys. **135**, 194501 (2011).
[4] E. E. Durgun, R. T. Senger, H. Mehrez, S. Dag, and S. Ciraci, Europhys. Lett. **73**, 642 (2006).
[5] Y. Wang, X.-J. Ning, Z.-Z. Lin, P. Li, and J. Zhuang, Phys. Rev. B **76**, 165423 (2007).
[6] E. Erdogan, I. Popov, C. G. Rocha, G. Cuniberti, S. Roche, and G. Seifert, Phys. Rev. B **83**, 041401(R) (2011).
[7] G. Rinzler, J. Hafner, P. Nikolaev, P. Nordlander, D. T. Colbert, R. E. Smalley, L. Lou, S. G. Kim, and D. Tomanek, Science **269**, 1550 (1995).
[8] N. D. Lang and P. Avouris, Phys. Rev. Lett. **81**, 3515 (1998).
[9] N. L. Yazdani and D. M. Eigler, Science **272**, 1921 (1996).
[10] T. Ragab and C. Basaran, J. Electron. Packag. **133**, 020903 (2011).
[11] C. Ataca and S. Ciraci, Phys. Rev. B **83**, 235417 (2011).
[12] L. Kavan, J. Hlavatý, J. Kastner, and H. Kuzmany, Carbon **33**, 1321 (1995).
[13] C. S. Casari, A. LiBassi, L. Ravagnan, F. Siviero, C. Lenardi, P. Piseri, G. Bongiorno, C. E. Bottani, and P. Milani, Phys. Rev. B **69**, 075422 (2004).
[14] C. Jin, H. Lan, L. Peng, K. Suenaga, and S. Iijima, Phys. Rev. Lett. **102**, 205501 (2009).
[15] M. Liu, V. I. Artyukhov, H. Lee, F. Xu, and B. I. Yakobson, ACS Nano **7**, 10075 (2013).
[16] Y. Huang, J. Wu, and K. C. Hwang, Phys. Rev. B **74**, 245413 (2006).
[17] X. F. Fan, L. Liu, J. Lin, Z. X. Shen, and J.-L. Kuo, ACS Nano **3**, 3788 (2009).
[18] S. Cahangirov, M. Topsakal, and S. Ciraci, Phys. Rev. B **82**, 195444 (2010).
[19] S. Kotrechko, A. A. Mazilov, T. I. Mazilova, E. V. Sadanov, and I. M. Mikhailovskij, Tech. Phys. Lett. **38**, 132 (2012).
[20] I. M. Mikhailovskij, E. V. Sadanov, S. Kotrechko, V. A. Ksenofontov, and T. I. Mazilova, Phys. Rev. B **87**, 045410 (2013).
[21] P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, A. Dal Corso, S. Fabris, G. Fratesi, S. de Gironcoli, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G. Sclauzero, A. P. Seitsonen, A. Smogunov, P. Umari, and R. M. Wentzcovitch, J. Phys.: Condens. Matter. **21**, 395502 (2009).
[22] Original QE PP library, http://www.quantum-espresso.org.
[23] P. Blaha, K. Schwarz, G. Madsen, D. Kvasnicka, and J. Luitz, *WIEN2K, An Augmented Plane Wave + Local Orbital's Program for Calculating Crystal Properties* (Technische Universitat Wien, Austria, 2001).
[24] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
[25] T. I. Mazilova, S. Kotrechko, E. V. Sadanov, V. A. Ksenofontov, and I. M. Mikhailovskij, Int. J. Nanosci. **09**, 151 (2010).
[26] G. Wu and J. Dong, Phys. Rev. B **71**, 115410 (2005).
[27] R. E. Peierls, *Quantum Theory of Solids* (Oxford University Press, New York, 1955), p. 108.
[28] K. S. Pitzer and E. Clementi, J. Am. Chem. Soc. **81**, 4477 (1959).