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Mechanical and thermal properties of carbyne: Analytical estimates

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To describe the mechanical and thermal properties of free-standing carbyne, the Harrison's bond orbital model is used, within which the Grüneisen parameter, heat capacities and the reaction of the central interaction on force constant of the stretching deformation and temperature are considered. The results obtained are compared with available data on graphene. The nature of the influence of the metal substrate on the characteristics of epitaxial carbyne is discussed.

Keywords: cumulene, polyyne, elasticity, temperature.

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1. Introduction

The advent of graphene [1] has instigated a renewed interest in the only truly one-dimensional (1D) structure — carbyne, which is a linear chain of carbon atoms. Two kinds of carbynes are distinguished: metallic cumulene with double bonds ($\ldots{=}C{=}C{=}\ldots$) and semiconducting polyyne with alternating single and triple bonds ($\ldots{\equiv}C{-}C{\equiv}C{-}C{\equiv}\ldots$) [2–14]. The theoretically expected strength, elastic modulus, and stiffness of carbynes are greater than those of any known material, including diamond, carbon nanotubes, and graphene, allowing for new composite materials (e. g., by reinforcing the matrix with carbyne filaments). Harmonic characteristics of free and epitaxial carbynes were discussed in Ref. [8]. Here we will take anharmonicity into account and obtain analytical estimates of the characterization of the elastic and thermal properties of carbynes. Here, as in Ref. [14], we will use Harrison's binding orbitals model [15,16], which we have previously tested on graphene and graphene-like binary compounds [17].

The energy E_b of two-electron σ-bond of the sp-orbitals of carbon atoms in cumulene can be represented as follows according to Ref. [16]

$$E_b = -2V + 2SV, \tag{1}$$

where $V = \eta(\hbar^2/ma^2)$ is the covalent energy, S is the overlap integral, a is the distance between nearest neighbors, m is the electron mass, $\hbar$ is the reduced Planck constant, the coefficient $\eta = 3.19$ (here, in contrast to Ref. [16], we assume $V_2 \equiv V > 0$). In cumulene, the length of the double bond C=C is $\bar{a} = 1.282\,\text{Å}$, so $\bar{V} = 14.79\,\text{eV}$; in polyyne, the single bond C$-$C has length $\bar{a} = 1.265\,\text{Å}$, and the triple bond C$\equiv$C has length $\bar{a} = 1.301\,\text{Å}$ [18], so that in the former case $\bar{V}_1 = 15.19\,\text{eV}$, in the latter $\bar{V}_2 = 14.36\,\text{eV}$. Considering that $S \propto a^{-1}$, from the equilibrium condition $(\partial E_b/\partial a)_{\bar{a}}$ we obtain $\bar{S} = 2/3$, where hereafter the dash above the symbol indicates its magnitude under equilibrium conditions. Thus,

$$\bar{E}_b = -2\bar{V}/3. \tag{2}$$

Since ultra-long carbyne chains of 6000 atoms embedded in double-walled carbon nanotubes [2,3,7] are now available, the infinite carbon chain model we will use here is quite reasonable. The case of the free carbyne assumption is more complicated. This approximation is discussed at the end of the next section.

2. Free carbyne

Let us consider an infinite free chain of carbon atoms. In order to take anharmonism into account in the calculation of mechanical and thermal characteristics, we need to know the values of the third- and fourth-order derivatives of E_b over the interatomic distance (first- and second-order anharmonism). We obtain from (1)

$$\bar{f} \equiv E_b^{(2)} = 4\bar{V}/\bar{a}^2, \quad \bar{g} \equiv E_b^{(3)} = -32\bar{V}/\bar{a}^3,$$

$$\bar{h} \equiv E_b^{(4)} = 240\bar{V}/\bar{a}^4, \tag{3}$$

where $E_b^{(n)} \equiv (\partial^n E_b/\partial a^n)_{\bar{a}}$. Since for polyine $(\bar{a}_1+\bar{a}_2)/2 = 1.283\,\text{Å}$, which practically coincides with the interatomic distance in cumulene $\bar{a}$, then in the future, unless otherwise specified, we will simply talk about carbine. In the case of graphene, where σ-bonds are formed by sp^2-orbitals, the expressions (1) and (2) are true, but instead of $\bar{V}$ it should be $\bar{V}_{\text{Gr}} = \eta_{\text{Gr}}(\hbar^2/m\bar{a}_{\text{Gr}})$, where $\eta_{\text{Gr}} = 3.26$ [15] and $\bar{a}_{\text{Gr}} = 1.42\,\text{Å}$, so that $\bar{V}_{\text{Gr}} = 12.32\,\text{eV}$. Since the force constant of the central interaction $k_0 = \bar{f}$, we obtain

$k_0 = 36\,\text{eV/Å}^2$ for carbyne (for the C−C and C≡C chains we have, respectively, 38 and $34\,\text{eV/Å}^2$), and for graphene (without taking into account metallicity [17]) we have $k_0 = 24.44\,\text{eV/Å}^2$.

For what follows, we need the phonon spectrum of the carbynes. As shown in Ref. [14],

$$M\omega^2_{\text{cum}} = 4k_0 \sin^2(q\bar{a}/2), \quad |q| \le \pi/\bar{a},$$

$$M\omega^2_{\text{pol}}(q) = (k_{01} + k_{02})(1 \pm R), \quad |q| \le \pi/2. \tag{4}$$

Here q is the wave vector, M is the mass of the carbon atom, $k_{01(2)} = 4\bar{V}_{1(2)}/\bar{a}^2_{1(2)}$ and $R = \sqrt{1 - 4k_{01}k_{02}\sin^2(qa)/(k_{01}+k_{02})^2}$, the plus sign before R corresponds to the optical branch of the polyene $\omega^+_{\text{pol}}(q)$, minus sign is the acoustic branch $\omega^-_{\text{pol}}(q)$. Assuming approximately $k_{01,2} \approx k_0 \pm \Delta k$, where $\Delta k \approx 2\,\text{eV/Å}^2$ [13], up to $(\Delta k/k_0)^2 \approx 3 \cdot 10^{-3}$ we obtain $(\omega^+_{\text{pol}})^2 \approx (4k_0/M)\cos^2(qa/2)$ and $(\omega^-_{\text{pol}})^2 \approx$ $\approx (4k_0/M)\sin^2(qa/2)$. The Gruneisen parameter averaged over the Brillouin zone (BZ) is

$$\langle\gamma\rangle_{BZ} = -\frac{\bar{a}}{2\langle\omega^2(q)\rangle_{BZ}}\left(\frac{\partial\langle\omega^2(q)\rangle_{BZ}}{\partial a}\right)_{\bar{a}} \tag{5}$$

(see Refs. [19,20]). Then, given that $\langle\omega^2_{\text{cum}}\rangle_{BZ} \approx \langle\omega^2_{\text{pol}}\rangle_{BZ}$ $\approx 2k_0/M$, we find for carbynes $\langle\gamma\rangle_{BZ} \approx -\kappa/4k_0$, where $\kappa = \bar{a}(\partial^2 E_d/\partial a^2)_{\bar{a}}$ is a parameter describing the response of the constant k_0 to the deformation $\varepsilon = \delta\bar{a}/\bar{a}$ of the interatomic bond, equal for cumulene $-288\,\text{eV/Å}^2$, (for the C−C and C≡C chains we have, respectively, -304 and $-271\,\text{eV/Å}^2$, and for graphene $-186\,\text{eV/Å}^2$ [17]). We obtain IFx70xxE for the averaged Grüneisen parameter in the case of carbyne, which is almost identical to the value for graphene of 2.1 [17], where the deviation from 2 is attributable to the consideration of metallicity.

The quasiharmonic approximation in lattice dynamics is that the vibrational energy F_{vib} is represented in the same form as in the harmonic approximation, but the force constants are assumed to depend on strain [19–24]. Then the free energy can be represented as $F = E_b + F_{vib}$, where

$$F_{vib} \approx 3k_B T \ln\left(2\,\text{sh}\,\frac{\hbar\langle\omega^2\rangle^{1/2}_{BZ}}{2k_B T}\right). \tag{6}$$

We have $F_{vib} \approx 3\hbar\langle\omega^2\rangle^{1/2}_{BZ}/2$ at temperatures of $T \ll \Theta = \hbar\langle\omega^2\rangle^{1/2}_{BZ}/k_B \approx 1500\,\text{K}$, while at temperatures $T \gg \Theta$

$$F_{vib} \approx \frac{3k_B T}{2}\ln\left(\frac{\hbar^2\langle\omega^2\rangle_{BZ}}{k_B^2 T^2}\right). \tag{7}$$

This is the approximation used to describe the temperature effects in graphene [17,20]. The coefficient of thermal expansion $\alpha = -\bar{g}k_B/2\bar{f}^2\bar{a}$ [17,19], whence we have $\alpha = k_B/\bar{V}$, where k_B is the Boltzmann constant, which for carbynes gives $\alpha \approx 6 \cdot 10^{-6}\,\text{K}^{-1}$, whereas for graphene $\alpha \approx 8 \cdot 10^{-6}\,\text{K}^{-1}$. Temperature coefficient of the central interaction force constant $\text{TK}(k_0) = k_0^{-1}(\partial k_0/\partial T) = \kappa\alpha \approx -0.5 \cdot 10^{-4}\,\text{K}^{-1}$. The analog of this characteristic for graphene is the coefficient $\text{TK}(B) = B^{-1}(\partial B/\partial T) \approx -0.75 \cdot 10^{-4}\,\text{K}^{-1}$, where B is the two-dimensional analog of the all-round compression modulus [16] (one and a half times the excess of —TK(B)— over —TK(k_0)— is equal to the ratio $\bar{a}/\bar{a}_{\text{Gr}} = 1.5$). Using the results [18] for the heat capacities C_p and C_V, we have $C_p \approx Nk_B[1 + 3k_B T/\bar{V}]$ and $C_p - C_V = 4Nk_B^2 T/\bar{V}$, where under $C_{p(V)}$ we should understand the heat capacity at constant chain tension (length) (the relation $k_B T/\bar{V} \sim 10^{-2}$ at $T = 1500\,\text{K}$). For convenience, a summary of the formulas defining the considered parameters is summarized in Table 1. The results of the estimations for cumulene are summarized in comparison with those for graphene in Table 2.

Table 1. Analytical results (captionk_0 is the force constant of the central interaction, $\kappa = \bar{a}\bar{g}$ is the bond response to its elongation, α is the coefficient of thermal expansion, TC(k_0) is the temperature coefficient of the force constant k_0)

Symbol	k_0	κ	$\langle\gamma\rangle_{BZ}$	α	TC(k_0)
Formula	$\bar{f}$	$\bar{a}\bar{g}$	$\bar{a}\bar{g}/4\bar{f}$	$-\bar{g}k_B/2\bar{f}^2\bar{a}$	$\kappa\alpha + k_B(\bar{h} - \bar{g}^2/\bar{f})/\bar{f}$

3. Epitaxial carbyne

So far we have considered free carbyne, but now we will turn to epitaxial carbyne (epicarbyne). The possibility of chain formation on the grooved faces of transition metals is discussed in detail in Ref. [25]. These facets (e.g., facets (112) of the BCC lattice and (110) of the FCC lattice) are constructed from parallel densely packed rows of atoms separated by „grooves“ of atomic depth. According to Ref. [15] (Chapter 19), matrix element of σ-bonds of p_z-states of carbon with d-states of metal substrate

$$\tilde{V}_1 \equiv V_{pd\sigma} = 2.95\left(\hbar^2 r_d^{3/2}/md^{3/2}\right), \tag{8}$$

where r_d is the radius of d-shell, equal for W and Mo, respectively, 1.27 and 1.20 Å and d is the length of the adsorption bond. Assuming $d \sim 2.5$ Å, we obtain $\tilde{V}_1 \sim 1$ eV. A matrix element was used for the same purpose in Ref. jcite26

$$\tilde{V}_2 = 1.85(\hbar^2/m)(r_p r_d^3)^{1/2}/d^4, \tag{9}$$

where „radius of“ of carbon $r_p = 6.59$ Å [27]. We have $\tilde{V}_2 = 2.77$ eV for carbine on Co and Ni substrates ($d = 2.1$ Å, $r_p = 0.76$ Å) [26]. Thus, the matrix elements of the bond carbine-substrate $\tilde{V}_{1,2}$ are much smaller than the matrix elements of the interatomic interaction in carbine $\bar{V}$, $\bar{V}_{1,2}$, since $d \gg \bar{a}$, ($\bar{a}_{1,2}$). It already follows from this inequality that the effect of the substrate on the mechanical and anharmonic properties of carbine, which results in the appearance of additional interaction of carbon adatoms

Table 2. Estimates for cumulene and graphene ($\bar{a}$ is the distance between nearest carbon atoms, $\bar{V}$ is the Harrison's covalent energy)

Structure	$\bar{a}$, Å	$\bar{V}$, eV	k_0, eV/Å^2	κ, eV/Å^2	$\langle\gamma\rangle_{BZ}$	α, $10^{-6}\,\mathrm{K}^{-1}$	TC(k_0), $10^{-4}\mathrm{K}^{-1}$
cumulene	1.282	14.79	36	−288	2	6	−0.50
graphene	1.42	12.32	24	−186	2	8	−0.75

through the electronic states of the transition metal (indirect exchange) of the form

$$t_{ind}^{met} \approx -\frac{\tilde{V}_{1,2}^2 \bar{a}^2 m^*}{\pi \hbar^2} \cos(\bar{a} k_{met}^*), \quad (10)$$

where $k_{met}^* = \sqrt{2m^* E_F}/\hbar$ and the Fermi energy E_F is calculated from the bottom of the metal conduction band with the law of dispersion $\varepsilon_{\mathbf{k}_{met}} = \hbar^2 k_{met}^2/2m^*$, it will be quite limited (see details in Ref. [26]). An indirect proof of this statement is the smallness of the ratio $\Delta\omega_{\mathrm{Gr}}(\Gamma)/\omega_{\mathrm{Gr}}(\Gamma) \approx 0.01$, where $\Delta\omega_{\mathrm{Gr}}(\Gamma)$ is the red shift of the G-peak of the epigraphen formed on the polytype $6H$-SiC, $\omega_{\mathrm{Gr}}(\Gamma)$ is the frequency of the G-peak of free graphene at the point Γ of the Brillouin zone [28].

4. Conclusion

Using the Harrison's theory and scaling ($V \propto a^{-2}$ and $S \propto a^{-1}$) [16], we showed that the coefficients of expansion of the elastic binding energy E_b are equal to $f \propto a^{-4}$, $g \propto -a^{-5}$ and $h \propto a^{-6}$. Thus, all elastic characteristics associated with the central interaction of graphene atoms are smaller than the corresponding characteristics of cumulene (see Table 2). The same can be said about hypothetical one-dimensional structures consisting of Si and Ge atoms [17]. Moreover, the observed decrease increases as $\bar{a}$ increases. The second point to note is that due to the small ratio $|\bar{a}_2 - \bar{a}_1|/\bar{a} \approx 3 \cdot 10^{-2}$, the results obtained for cumulene can serve as estimates of the elastic and thermoelastic characteristics of polyine. And, thirdly, the values of $B \approx 100\,\mathrm{N/m}$ for graphene obtained in Ref. [17] turned out to be significantly underestimated compared to the experimental value of $B \approx 170\,\mathrm{N/m}$ [29]. The analysis showed that the reason for this discrepancy is the weak repulsion $2SV \propto a^{-3}$ is the second term in equation (1). If additional repulsion $\Delta E_{rep} \propto a^{-12}$ [30,31] is included in (1), then the agreement of the calculated and measured values B can be significantly improved, but the values of the anharmonic characteristics increase excessively. Thus, expressions (1)−(3) are best suited for evaluating the anharmonic properties of both low-dimensional and bulk structures. We emphasize that the Harrison's calculation scheme [16] used in this study does not use any fitting parameter: all values are expressed through the equilibrium distance between nearest neighbors $\bar{a}$ and the dimensionless multiplier η, which determines the type of hybridization of s and p states of carbon atoms.

In conclusion, we would like to note that the quantitative differences between the elastic and thermoelastic characteristics of cumulene and polyyne are relatively small, whereas their electronic properties are qualitatively different: cumulene is a metal and polyyne is a semiconductor.

Conflict of interest

The author declares that he has no conflict of interest.

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