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# Elastic Properties of the Single-Walled Carbon Nanotubes

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In this paper the elastic properties of two main types of single-walled carbon nanotubes (armchair and zigzag) were simulated by analytical molecular mechanics models. The aim of this work is investigation and comparison of Young's modulus, shear modulus and Poisson's ratio variations of different types of tubes as functions of diameter. We obtained a set of closed-form expressions for the size-dependent elastic properties of armchair ($n$, $n$) and zigzag ($n$, 0) tubes, which are basic for constructing mathematical models. Using those models elastic properties of single-walled nanotubes were evaluated. It was predicted that zigzag tube is more sensitive to chirality then armchair. Young's and shear modules of both tubes were decreasing with diameter increasing. Poisson's ratio was ranging from 0.16 to 0.29 and from 0.32 to 0.42 for an armchair and zigzag tubes respectively, but it was independent on chirality. It can be seen that predicted values of elastic characteristics for zigzag tube are larger then that for armchair tube, especially for smaller tubes. Results of this research can be used for design, analysis and evaluating of functioning and creating new materials based on carbon nanotubes.

**Keywords:** Carbon nanotube, Chirality, Armchair, Zigzag, Young's modulus, Shear modulus, Poisson's ratio.

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## 1. INTRODUCTION

Carbon nanotubes (CNTs) have stimulated great interest and extensive research with regard to the measurement of their exact mechanical properties [1-3] and the search for potential structural applications [1] since their discovering by Iijima [2] in 1991. There are a lot of possible applications of nanotubes in different fields of science, technique, electronic, optic and even medicine. CNTs are ideal reinforcing material for a new class of superstrong nano-composites due to their extraordinary properties, such as the exceptionally high stiffness and strength, which are in the range of TPa, the extreme resilience, the ability to sustain large elastic strain as well as the high aspect ratio and low density [2]. But the main reason for studying of the CNTs mechanical properties is their tremendous strength. For example, addition of just 1wt.% CNTs to polystyrene leads to increase of Young's modulus and strength by approximately 35 %-42 % and 25 %, respectively [4]. The carbon nanotubes have high stiffness and axial strength as a result of the carbon–carbon $sp^2$ bonding. Some reviews on CNTs properties can be found in the papers [1, 3]. The accurate assessment of the mechanical properties of the nanotubes is an important first step towards the potential development of the structural composites.

Investigations of the CNTs properties have focused both on experimental and theoretical study. First one has a lot of difficulties arising from the tube's nanoscale, necessity for complicated and expensive equipment and apparatus with large resolution. Experimental methods for measuring the mechanical properties of CNTs are mainly based on the techniques of transmission electron microscopy (TEM) and atomic force microscopy (AFM) [1]. Another way of CNTs studying is theoretical [3]. Computational simulation is a powerful tool relative to the experimental difficulties.

In this paper we present two mathematical models, based on the link between solid mechanics and molecular mechanics approach, for theoretical simulation the elastic properties of armchair and zigzag single-walled CNTs (SWNTs) and the difference between them. Based on molecular mechanics it was obtained that total system potential energy associated with bond stretching and angle variation. It was considered SWNT as a thin cylinder subjected to an axial tension loading or torsion loading. Research was based on the assumption that system potential energy is equal to the strain energy. As a result expressions for calculation of Young's modulus, shear modulus and Poisson's ratio for armchair and zigzag tubes were derived.

## 2. METHODS OF INVESTIGATION

The methods of molecular dynamics (MD) and molecular mechanics (MM) are often used for the theoretical simulation [4-7] of the CNTs mechanical properties. They both are based on the molecular nature of nanotube's structure. In this work we used MM approach. It allows to calculate the geometry of the frame with sufficient accuracy and to model some physical processes in nanotubes under influence of external factors: the deforming forces, external electromagnetic fields, etc.

We used some basics of molecular mechanics [8] which is based on the concept of molecular force field for this investigation. This approach was based on a link between molecular and solid mechanics. Using the harmonic energy functions the nanotube was modeled as a frame structure and a closed-form elastic solution was obtained.

SWNT is formed by rolling a single grapheme sheet to form a hollow tube composed of carbon hexagons. Let $a_1$ and $a_2$ be unit vectors of the two-dimensional graphene sheet, ($n$, $m$) be a pair of integers that indexes the atomic structure of CNT uniquely determining the size of the SWNT. Then a pair ($n$, $m$) corresponds to a lattice vector $C_h = na_1 + ma_2$ on the graphite plane. The

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fundamental structure of carbon nanotubes can be classified into three categories: if $m = 0$, then such a tube is called zigzag, and when $n = m$ it is an armchair tube and if $n \neq m$ for $n \neq 0$, $m \neq 0$, such tube called chiral [1, 2]. Based on rolling graphene sheer model the diameter $D$ of nanotube can be determined as follows:

$$D = \frac{\sqrt{3}b}{\pi}\sqrt{n^2 + m^2 + mn}\ , \qquad (1)$$

where $b$ is the carbon-to-carbon bond length. This parameter was taken as 0.142 nm [4].

For armchair and zigzag tubes diameter is equal to $D_1$ and $D_2$ respectively:

$$D_1 = \frac{3bn}{\pi},\ D_2 = \frac{\sqrt{3}bn}{\pi}. \qquad (2)$$

Given the effective wall thickness $t$ of SWNTs which corresponds to the thickness of the graphene layer, the effective diameter $D_{eff}$ is equal to $D_{eff} = D_i + t$, where the parameter $D_i$ ($i = 1, 2$) is taken by $D_1$ for an armchair tube, and $D_2$ for a zigzag tube. Effective thickness $t$ was taken as 0.066 nm [4].

A SWNT can be regarded as a two dimensional continuum-shell model which is consist of the discrete molecular structures linked by carbon-to-carbon bonds. The molecular mechanics model is substituted with a frame structure model. The main geometrical relations of the armchair SWNT's structure are shown in Fig.1.

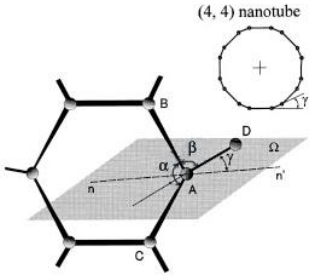


**Fig. 1** – Element of a frame structure of armchair tube [4]

Figure 1 shows the three-dimensional schematic illustration of the geometrical relationship among the atoms in armchair tube's structure. Ω is the plane perpendicular to the axes of the nanotube, and $n-n'$ is a line of intersection between the Ω plane and BAC plane.

For the zigzag tube, the frame structure has similar relations as in armchair tube, but there are some features (see Fig. 2).

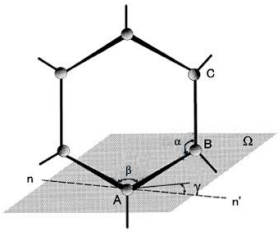


**Fig. 2** – Element of a frame structure of zigzag tube [4]

We have analyzed the forces and geometrical relations of armchair and zigzag SWNTs. Also we have used the assumption that all atomic interactions in a molecular structure of nanotubes satisfy the potential laws, so they can be described by using molecular mechanics [8]. Regarding aforementioned we have build the following relations which comprise our model of elastic properties of armchair and zigzag SWNT.

According to the geometrical relations in tube the axial strain ($\varepsilon_a$) and the hoop strain ($\varepsilon_a$) of the armchair tube can be given as

$$\varepsilon_a = \frac{\delta\cos\left(\frac{\alpha}{2}\right) + \delta^{\rho}_{AB}\sin\left(\frac{\alpha}{2}\right)}{b\sin\left(\frac{\alpha}{2}\right)},$$

$$\varepsilon_h = \frac{\delta^{\rho}_{AB}\cos\left(\frac{\alpha}{2}\right) - \delta\sin\left(\frac{\alpha}{2}\right)}{b\left[1+\cos\left(\frac{\alpha}{2}\right)\right]}, \qquad (3)$$

where $\delta^{\rho}_{AB}$ is the elongation of $A$-$B$ bond, angle $\alpha$ is regarded as an almost unchanged constant when a planar graphene sheet is rolled into a nanotube.

The main characteristic of CNTs elastic properties is Young's modulus $E$. It is defined as the ratio of the uniaxial stress over the uniaxial strain in the range of stress in which Hooke's Law holds [8]:

$$E = \frac{4Dt}{D_{eff}}\left(\frac{\sigma}{\varepsilon_a}\right), \qquad (4)$$

where $\sigma$ is the tensile stress.

After taking into account the geometrical relations in tube's structure, putting $\alpha/2 = \pi/3$ [3] and substitution (2), (3) into (4) we obtained following expression for the Young's modulus of armchair and zigzag nanotubes

$$E = \frac{\lambda_i K^{\theta} K^{\rho}}{3b^2 K^{\rho} + 9\lambda K^{\theta}}\left(\frac{16\sqrt{3}D_i}{D^2_{eff_i}}\right), \qquad (5)$$

where parameters $\lambda_i$, $D_i$, $D_{eff\,i}$ ($i = 1, 2$) are taken by $\lambda_1$, $D_1$, $D_{eff\,1}$ for an armchair tube, and $\lambda_2$, $D_2$, $D_{eff\,2}$ for a zigzag tube; $K^{\rho}$, $K^{\theta}$ are force constants, which depend on the force field, $K^{\rho} = 97800$ kcal/mole/nm$^2$, $K^{\theta} = 126$ kcal/mole/rad$^2$ [4]; $\lambda_i$ is the elongation, equaled to the ratio of total nanotubes elongation $\Delta l$ to its length $l_0$ before deformation. For an armchair tube it is equal to

$$\lambda_1 = \frac{\mathrm{ctg}\left(\frac{\alpha}{2}\right)\sin\beta}{4\mathrm{ctg}\left(\frac{\alpha}{2}\right)\sin\beta - 2\cos\gamma\ \mathrm{ctg}\beta\sin\left(\frac{\alpha}{2}\right)}, \qquad (6)$$

where $\gamma = \pi/2n$ is the angle, related to the curvature effect (see Fig. 1 and Fig 2).

The ab initio calculations [3] show that angles $\alpha/2$ and $\beta$ is equal to

$$\frac{\alpha}{2} \approx \frac{\pi}{3}, \beta \approx \pi - \arccos\left[\frac{1}{2}\cos\gamma\right], \quad (7)$$

then from (6) we have

$$\lambda_1 = \frac{7 - \cos\left(\frac{\pi}{n}\right)}{34 + 2\cos\left(\frac{\pi}{n}\right)}. \quad (8)$$

For zigzag tube this parameter is given by

$$\lambda_2 = \frac{\cos^2\left(\frac{\beta}{2}\right)}{2\cos^2\left(\frac{\beta}{2}\right) + 2\left[1 + \cos\left(\frac{\pi}{n}\right)\right]\cos^2\alpha}. \quad (9)$$

It can be shown that

$$\frac{\alpha}{2} \approx \frac{\pi}{3}, \beta \approx \arccos\left[\left(\frac{1}{4}\right) - \frac{3}{4}\cos\left(\frac{\pi}{n}\right)\right], \quad (10)$$

so taking into account (10), expression (9) can be simplified to

$$\lambda_2 = \frac{5 - 2\cos\left(\frac{\pi}{n}\right)}{14 - 3\cos\left(\frac{\pi}{n}\right)}. \quad (11)$$

Poisson's ratio of SWNT is the ratio between the circumferential and the axial strains, so it can be defined as

$$\nu_i = -\frac{\varepsilon_h}{\varepsilon_a} = \frac{\frac{\lambda K_s b^2}{K_t} - 1}{\frac{\lambda K_s b^2}{K_t} + 3}, \quad (12)$$

where $K_s = 742$ nN/nm, $K_t = 1.42$ nN/nm [3].

Shear modulus of SWNTs is given as

$$G_i = \frac{D_{eff_i}^4 - 16\left(\frac{D_{eff_i}}{2} - t\right)^4}{tD_{eff_i}^4}\left(\frac{\sqrt{3}}{3}\frac{\lambda_i K^\theta K^\rho}{b^2 K^\rho + \lambda K^\theta}\right). \quad (13)$$

Mathematical models of elastic properties of armchair and zigzag tubes have been obtained in the form of equations (2), (5), (8) and (11)-(13) with taken $i = 1$ for an armchair tube, and $i = 2$ for a zigzag tube. All of elastic characteristics can be evaluated based on those models.

## 3. RESULTS AND DISCUSSION

The elastic properties of two main types of CNT – armchair and zigzag – were investigated and discussed in this paper. We can say that calculated values of elastic properties largely depend on the assumption of the wall thickness $t$ of SWNT. There are other information about different wall thickness such as 0.69 nm, 0.57, 0.34 and 0.066 nm [4, 7]. In this investigation $t$ was taken as 0.066 nm.

It was build an application for estimation the elastic properties of SWNTs. Mathematical models were implemented as application using software Delphi 7. It makes possible to evaluate Young's modulus $E$, shear modulus $G$ and Poisson's ratio $\nu$ of armchair $(n, n)$ or zigzag $(n, 0)$ tubes with any specified chirality.

For example, it was investigated armchair tubes with chirality from (2, 2) to (40, 40) and zigzag tubes from (2, 0) to (40, 0). Those armchair tubes had diameter from 0.27 to 5.42 nm and zigzag tubes – from 0.16 to 3.13 Å. The values of Young's modulus ranged from 0.21 to 2.97 TPa for armchair and from 0.61 to 6.53 for zigzag nanotubes. The dependences of Young's modulus on diameter for both tube's configurations are shown in Fig. 3.

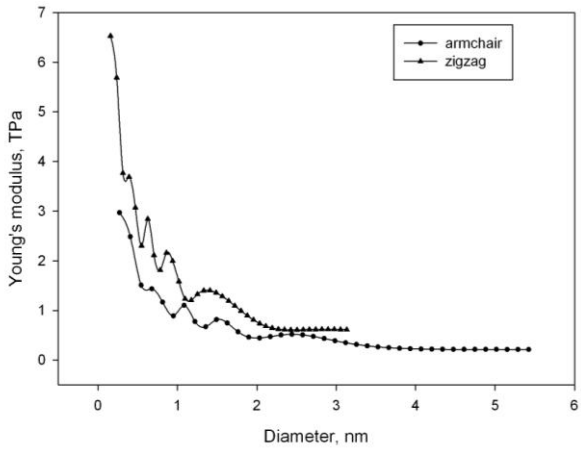


**Fig. 3** – The variation of Young's modulus with nanotube's diameter for armchair and zigzag tubes

The variation of Poisson's ratio with the diameter of the nanotube is shown in Fig. 4. It is seen that ratio of large tubes changes mostly independently on tube's diameter.

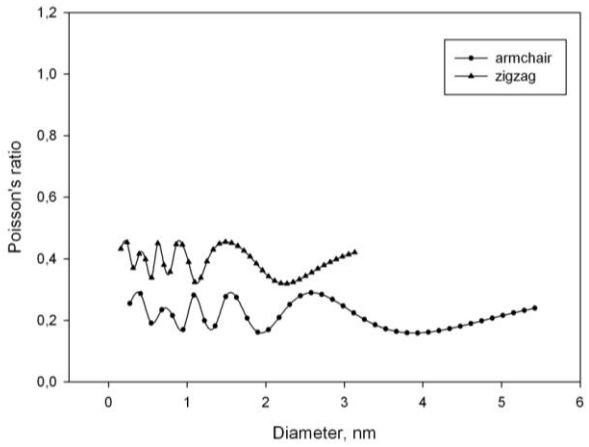


**Fig. 4** – The variation of Poisson's ratio with nanotube's diameter for armchair and zigzag tubes

We calculated that shear modulus was in the range of 0.11-1.05 TPa for armchair and was in the range of 0.31-1.99 TPa for zigzag nanotubes. Comparison of both results is shown in Fig. 5.

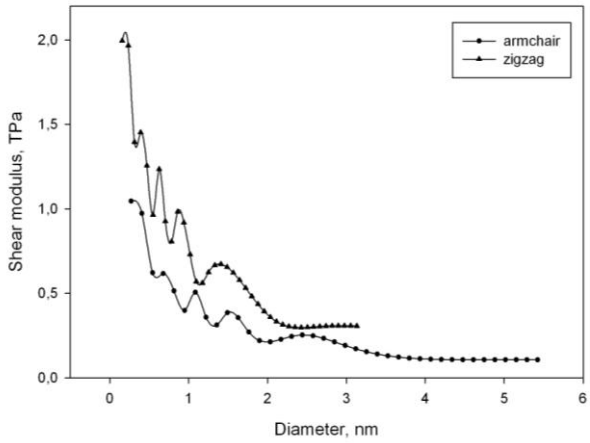


**Fig. 5** — The variation of shear modulus with nanotube's diameter for armchair and zigzag tubes

Some results of evaluation of Young's and shear modules, Poisson's ratio are shown in Table 1 for armchair tube.

**Table 1** – Results of evaluation of elastic characteristics of armchair SWNT

| (*n*, *n*) | *D*, nm | $D_{eff}$, nm | *E*, TPa | $\nu$ | *G*, TPa |
|---|---|---|---|---|---|
| (2, 2) | 0,27 | 0,34 | 2,97 | 0,26 | 1,05 |
| (3, 3) | 0,41 | 0,47 | 2,48 | 0,29 | 0,97 |
| (6, 6) | 0,81 | 0,88 | 1,17 | 0,22 | 0,51 |
| (7, 7) | 0,95 | 1,02 | 0,89 | 0,17 | 0,40 |
| (10, 10) | 1,36 | 1,42 | 0,67 | 0,18 | 0,31 |
| (11, 11) | 1,49 | 1,56 | 0,82 | 0,28 | 0,39 |
| (14, 14) | 1,90 | 1,96 | 0,46 | 0,16 | 0,22 |
| (15, 15) | 2,03 | 2,10 | 0,44 | 0,17 | 0,21 |
| (18, 18) | 2,44 | 2,51 | 0,52 | 0,28 | 0,25 |
| (19, 19) | 2,58 | 2,64 | 0,51 | 0,29 | 0,25 |
| (22, 22) | 2,98 | 3,05 | 0,39 | 0,25 | 0,19 |
| (23, 23) | 3,12 | 3,18 | 0,35 | 0,22 | 0,17 |
| (26, 26) | 3,53 | 3,59 | 0,27 | 0,17 | 0,13 |
| (27, 27) | 3,66 | 3,73 | 0,25 | 0,16 | 0,12 |
| (30, 30) | 4,07 | 4,13 | 0,22 | 0,16 | 0,11 |
| (31, 31) | 4,20 | 4,27 | 0,22 | 0,17 | 0,11 |
| (35, 35) | 4,75 | 4,81 | 0,22 | 0,20 | 0,11 |
| (40, 40) | 5,42 | 5,49 | 0,21 | 0,24 | 0,11 |

It is seen in Table 1 that Young's and shear modules have shown inverse diameter dependences. Modules are a quite sensitive to the nanotubes with small diameter and for large tubes from (30, 30) values of modules are getting equaled to constant.

**Table 2** – Results of evaluation of elastic characteristics of zigzag SWNT

| (n, 0) | D, nm | $D_{eff}$, nm | E, TPa | $\nu$ | G, TPa |
|---|---|---|---|---|---|
| (2, 0) | 0,16 | 0,22 | 6,53 | 0,43 | 1,99 |
| (3, 0) | 0,23 | 0,30 | 5,69 | 0,45 | 1,97 |
| (6, 0) | 0,47 | 0,54 | 3,07 | 0,40 | 1,26 |
| (7, 0) | 0,55 | 0,61 | 2,30 | 0,34 | 0,96 |
| (10, 0) | 0,78 | 0,85 | 1,81 | 0,36 | 0,81 |
| (11, 0) | 0,86 | 0,93 | 2,16 | 0,45 | 0,98 |
| (14, 0) | 1,10 | 1,16 | 1,23 | 0,32 | 0,57 |
| (15, 0) | 1,17 | 1,24 | 1,21 | 0,34 | 0,56 |
| (18, 0) | 1,41 | 1,48 | 1,40 | 0,45 | 0,67 |
| (19, 0) | 1,49 | 1,55 | 1,36 | 0,45 | 0,66 |
| (22, 0) | 1,72 | 1,79 | 1,09 | 0,43 | 0,53 |
| (23, 0) | 1,80 | 1,87 | 0,99 | 0,41 | 0,48 |
| (26, 0) | 2,04 | 2,10 | 0,74 | 0,34 | 0,36 |
| (27, 0) | 2,11 | 2,18 | 0,68 | 0,33 | 0,33 |
| (30, 0) | 2,35 | 2,41 | 0,61 | 0,32 | 0,30 |
| (31, 0) | 2,43 | 2,49 | 0,61 | 0,33 | 0,30 |
| (35, 0) | 2,74 | 2,81 | 0,62 | 0,38 | 0,31 |
| (40, 0) | 3,13 | 3,20 | 0,61 | 0,42 | 0,31 |

Table 2 shows some results of calculations of elastic characteristics of zigzag SWNT. Young's and shear modules. Values of Young and shear modulus decrease with diameter increase. But for large tubes they getting equaled constant as for armchair tubes. Comparing the values at Table 1 with Table 2 it can be notice that they have the same decreasing of elastic modules, but values of zigzag SWNT are larger then of armchair.

## 4. CONCLUSIONS

In this paper we present the approach for investigation the elastic properties of SWNTs, based on molecular mechanics. The mathematical models for simulation Young's modulus, shear modulus and Poisson's ratio of armchair and zigzag tubes were built. Those parameters were investigated as functions of the nanotube size and structure.

Results of evaluations show that values of Young's and shear modulus for zigzag tube are larger than for armchair tube, especially for smaller tubes, but they both decrease rapidly while the diameter increases. With diameter increasing Young and shear modulus of the both type of tubes begin to have the constant value. As for Poisson's ratio, we can say that zigzag tube is more sensitive to the diameter than that of the armchair tube. It should be pointed out that the elastic properties simulated in the present work agree reasonably with the reported results in literature [3, 4].

## Пружні властивості одношарових вуглецевих нанотрубок

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В даній роботі виконано моделювання пружних властивостей двох основних типів одношарових вуглецевих нанотрубок: armchair та zigzag за допомогою аналітичної моделі молекулярної механіки. Мета даної роботи полягає у дослідженні і порівнянні модуля Юнга, модуля зсуву та коефіцієнта Пуассона різних типів трубок як функцій від діаметра. Ми отримали ряд спрощених виразів для розмірно-залежних пружних властивостей трубок armchair ($n$, $n$) та zigzag ($n$, 0), які є базовими для побудови математичних моделей. З використанням цих моделей були оцінені еластичні властивості одношарових вуглецевих нанотрубок. Було передбачено, що трубка zigzag більш чутлива до хіральності ніж armchair. Модулі Юнга та зсуву обох типів трубок зменшувались з ростом діаметра. Коефіцієнт Пуассона варіювався від 0.16 до 0.29 та від 0.32 до 0.42 для трубок armchair та zigzag відповідно, але він був незалежний від хіральності. Помітно, що передбачені значення еластичних характеристик трубки zigzag більші ніж для armchair, особливо для малих трубок. Результати дослідження можуть бути використані для дизайну, аналізу та оцінки функціонування і створення нових матеріалів на основі вуглецевих нанотрубок.

**Ключові слова:** вуглецева нанотрубка, хіральність, armchair, zigzag, модуль Юнга, модуль зсуву, коефіцієнт Пуассона.

## Упругие свойства однослойных углеродных нанотрубок

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В данной работе выполнено моделирование упругих свойств двух основных типов однослойных углеродных нанотрубок: armchair и zigzag с помощью аналитической модели молекулярной механики. Цель данной работы заключается в исследовании и сравнении модуля Юнга, модуля сдвига и коэффициента Пуассона различных типов трубок как функций от диаметра. Мы получили ряд упрощенных выражений для размерно-зависимых упругих свойств трубок armchair ($n$, $n$) и zigzag ($n$, 0), которые являются базовыми для построения математических моделей. С использованием этих моделей были оценены эластичные свойства однослойных углеродных нанотрубок. Было предсказано, что трубка zigzag более чувствительна к хиральности чем armchair. Модули Юнга и сдвига обоих типов трубок уменьшались с ростом диаметра. Коэффициент Пуассона варьировался от 0.16 до 0.29 и от 0.32 до 0.42 для трубок armchair и zigzag соответственно, но он был независимым от хиральности. Заметно, что предсказанные значения эластичных характеристик трубки zigzag больше чем для armchair, особенно для малых трубок. Результаты исследования могут быть использованы для дизайна, анализа и оценки функционирования и создания новых материалов на основе углеродных нанотрубок.

**Ключевые слова:** углеродная нанотрубка, хиральность, armchair, zigzag, модуль Юнга, модуль сдвига, коэффициент Пуассона.

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