Modeling of atomic interactions in carbon nanotubes

M Chwał¹ and A Muc¹

¹ Institute of Machine Design, Cracow University of Technology, Warszawska 24, 31-155 Cracow, Poland
E-mail: malgorzata.chwal@pk.edu.pl

Abstract: This work concerns atomic potentials applied in the description of carbon nanotubes mechanical behavior. The explicit relations of interatomic forces for different interatomic potentials have been derived. The fluctuations in the values of interatomic potential, interatomic force, elastic constant and Young’s modulus have been put forward to elucidate the similarities and differences between potentials. The present analysis may be helpful in the equivalent continuum modelling of carbon nanotubes and nanocomposites.

1. Introduction
The specific properties of nanoscale carbon structures, mainly carbon nanotubes, draw the attention of scientific and commercial world because of wide range of potential applications [1]. In the description of carbon nanotubes properties various instruments are applied in both the experimental and theoretical field [2-5]. The creation of interatomic interaction models is the key to understand the phenomena at the atomic level. In quantum mechanics the electron cloud notation is applied (atoms and bonds fill the space through the electronic clouds) in which location and momentum of particle can be predicted only to the Heisenberg’s constant – the uncertainty principle. In classical physics, the atomic orbitals definitions (the energetic levels) defined as the three-dimensional areas filled with electrons are applied. The interatomic bonds are being shown as lines and atoms as points to simplify the atomic structure models. The specific properties of carbon nanotubes are connected with the spatial arrangement of carbon atom bonds. Carbon has four valence electrons, which allows creating four bonds – two coming from s orbitals (spherical ones) and two coming from p orbitals (dumb-bells ones). Hybridization $sp^3$ creates a diamond structure. The graphite structure is created from partial hybridization $sp^2$. Hybridization $sp^2$ is known as the bond type $\sigma$ placed angularly on plane (every 120º). The bonds type $\sigma$ are strong covalent bonds that connect carbon atoms in plane. As a result, considering carbon nanotube as rolled-up graphite layers, a structure with high stiffness and strength is obtained. The remaining energetic level type $p$ is perpendicular to the plane and creates bonds between neighboring graphite layers called bonds type $\pi$. $\pi$-bonds, also called van der Waals interactions, are much weaker than bonds type $\sigma$. The description of nanostructure’s behavior starts from the consideration of interatomic interaction potential, i.e. special functions and physical constants based on overall rules of solid-state physics. Starting from the simplest description of interactions between two atoms, the interatomic potential may be really extended when very high accuracy in the atomic interactions is demanded. This paper is focused on the analysis of fluctuations in the values of interatomic potential, interatomic force, elastic constant and Young’s modulus in the function of interatomic distance in carbon nanotubes. The value of elastic constant applied in the current studies is also compared with literature data.

2. Modeling of atomic interactions
The nature of interactions depends on complicated quantum effects that occur on the level of elementary parts of atoms and control chemical properties such as valence and binding energy. The quantum effects also influence the interatomic bond topology, its formation and breakage. The potentials should explain the quantum effects even in the averaging sense to obtain reliable results in the numerical simulations basing on the solid-state physics. In general, an interatomic potential describes the outside force field energy, potential energy between atom pairs, potential energy between three atoms and so on. Often to make the numerical simulations shorter, the atomic interactions between other than neighboring ones are omitted.

The description of the behavior of a nanostructure starts with the consideration of interatomic interactions potential \( V(r_{ij}) \) and physical constants. Based on the potential theory, an interaction force vector is described as follows:

\[
\vec{F}(r_{ij}) = -\frac{\partial V}{\partial r_{ij}}
\]

where \( r_{ij} \) is the interatomic distance and \( n_{ij} \) is the unit vector between two atoms \( i \) and \( j \). In the present work an equilibrium static states of the nanostructure is defined as the equilibrium state without any external forces and moments which can be described for example through the minimum of potential energy for equilibrium distance \( R_{ij} \) between two carbon atoms. The atomic force is expressed in the equivalent form [6]:

\[
\vec{F}(r_{ij}) = k(r_{ij}) (r_{ij} - R_{ij}) n_{ij}
\]

where \( k(r_{ij}) \) is the elastic constant depending on an actual interatomic distance \( r_{ij} \). The variations of the elastic constant \( k(r_{ij}) \) and Young's modulus \( E(r_{ij}) \) are computed as:

\[
k(r_{ij}) = \frac{\partial V(r_{ij})}{\partial r_{ij}^2}, \quad E(r_{ij}) = \frac{k(r_{ij})R_{ij}}{S_{ij}}, \quad S_{ij} = \frac{4d_{ij}^3}{3}
\]

where \( d_{ij} \) and \( S_{ij} \) is the diameter and the cross-section area of the atomic bond, respectively. To analyze the behavior of atomic bonds in a carbon nanotube, the relations (2) and (3) have been applied.

3. Interatomic potentials

The interatomic interactions are described as attractive or repulsive behavior. A state in which the attractive force is balanced with the repulsive force (the sum of the reaction forces are equal zero) is called the atomistic equilibrium state. In this state the reaction forces between atoms have the same values, but opposite directions and it results in the minimum of potential energy. A decrease in the atomic distance causes an increase in the repulsive force whereas an increase in the atomic distance causes a decrease in the attractive force. In both situations changes in the potential energy are observed. The current analysis of carbon nanotube behavior involves Morse [7-8], Tersoff-Brenner [9-10] and Lennard-Jones [11-12] potentials.

Morse potential is written as:

\[
V^M(r_{ij}) = D^M e^{-2\beta^M(r_{ij}-r_0)} - 2e^{-\beta^M(r_{ij}-r_0)}, \quad V^M(R_{ij}) = -D^M
\]

where \( D^M \) is the minimum of potential and \( \beta^M \) is the constant correlated with energetic levels of atoms. Based on Eqs (1) and (4) the interatomic force for Morse potential is presented as:

\[
F^M = 2\beta^M D^M e^{-\beta^M(r_{ij}-r_0)} - e^{-\beta^M(r_{ij}-r_0)}
\]

For carbon atoms Tersoff-Brenner potential is as follow:

\[
V^TB(r_{ij}) = V^TB_2(r_{ij}) - B V^TB_1(r_{ij})
\]

\[
V^TB_2(r_{ij}) = f^{TB}(r_{ij}) \frac{D^{TB}}{S^{TB} - 1} e^{-\sqrt{S^{TB}}\beta^{TB}(r_{ij}-r_0)}, \quad V^TB_1(r_{ij}) = f^{TB}(r_{ij}) \frac{D^{TB}S^{TB}}{S^{TB} - 1} e^{-\sqrt{S^{TB}}\beta^{TB}(r_{ij}-r_0)}
\]
where $V_{sa}^r$ and $V_{sa}^a$ describe the repulsive and the attractive parts, respectively, $f^{TB}(r_{ij})$ is the cut-off function, $\overline{B}_s$ defines the "order" of atomic bonds, $S_{TB}^B$ and $\beta_{TB}$ are constants - see more details in [13].

The interatomic force in Tersoff-Brenner potential is written as:

$$F_{TB} = \frac{\beta_{TB} D_{TB}^r}{S_{TB}^r - 1} \left[ \sqrt{2 S_{TB}^r} \left( e^{-\beta_{TB} S_{TB}^r (r_{ij} - r_s)} - \overline{B}_{TB} S_{TB}^r \left( \frac{2}{S_{TB}^r} - \frac{1}{2} e^{-\beta_{TB} S_{TB}^r (r_{ij} - r_s)} \right) \right) \right]$$

(7)

In the current computations the following parameters for carbon have been used: $r_s=1.39$ (Å), $D_{TB}^r=9.613 \times 10^{-19}$ (Nm), $\beta_{TB}=2.1$ (Å$^{-1}$), $S_{TB}^B=1.22$ according to paper by Brenner [10].

Lennard-Jones potential applied to describe van der Waals forces in carbon nanotubes is written as:

$$V_{LJ}(r_{ij}) = \frac{A_{LJ}}{r_{ij}^{12}} - \frac{B_{LJ}}{r_{ij}^{6}}$$

(8)

where $A_{LJ}$ and $B_{LJ}$ are positive constants. The left-hand side component of "6-12" potential describes the repulsive forces whereas the right-hand one the attractive forces. The attractive behavior is observed for long interatomic distances while for short, a strong repulsive core appears. Starting from Eq. (8) and based on Eq. (1) van der Waals force between atoms can be computed in the following form:

$$F_{LJ} = \frac{12 B_{LJ}}{r_{ij}^2} \left( \frac{1}{r_{ij}^{12}} - \frac{1}{r_{ij}^{6}} \right), \quad A_{LJ} = \frac{2 B_{LJ}}{R_i^6}, \quad B_{LJ} = \frac{k_s}{72} R_i^{14}, \quad D_{LJ} = \frac{k_s}{72} R_i^8$$

(9)

The correlations between constants $A_{LJ}$ and $B_{LJ}$ were computed for equilibrium distance i.e. $r_{ij} = R_{ij}$, and $F(r_{ij}) = 0$.

4. Results and discussion

Based on the interatomic potentials and information about the analyzed structure the elastic constant can be computed. This information allows for evaluating Young’s modulus values depending on the atom positions in the lattice. Considering three different interatomic potentials the carbon nanotube behavior was analyzed. In the equilibrium position, distance between carbon atoms $R_{ij} = 1.42$ (Å), atomic bond diameter $d_0 = 3.4$ (Å), and bond stiffness $E_0 = 1$ (TPa) were adopted from [14]. The elastic constant in the equilibrium position was obtained from Eq. (3) and was $k_0 = 639$ (N/m), which is close to the elastic constant values reported by Odegard et al. [15] – see Table1. For Morse and Tersoff-Brenner potential the constants were applied according to [16] and [10] respectively. Applied values are presented in Table 2. In the analysis of Tersoff-Brenner potential it was assumed that $f^{TB}(r_{ij}) = 1$ and $\overline{B}_s = 1$ - see Eq. (6).

| Reference                  | Elastic constant $k_0$ (N/m) | Equilibrium distance $R_{ij}$ (Å) |
|----------------------------|------------------------------|----------------------------------|
| Belytschko et al. [16]     | 831                          | 1.450                            |
| Brenner [10]               | 500                          | 1.550                            |
| Odegard et al. [15]        | 652                          | 1.421                            |
| Present value              | 639                          | 1.420                            |
Table 2. Values used in the computations of the interatomic potentials.

|                  | Lennard-Jones potential | Morse potential | Tersoff-Brenner potential |
|------------------|-------------------------|-----------------|---------------------------|
| \( D_{e}^{LJ} \) | \( 1.789 \times 10^{-19} \) (Nm) | \( D_{e}^{M} \) | \( 4.637 \times 10^{-19} \) (Nm) | \( D_{e}^{TB} \) | \( 7.245 \times 10^{-19} \) (Nm) |
| \( B_{e}^{LJ} \) | \( 1203 \times 10^{-140} \) (Nm\(^3\)) | \( \beta_{e}^{M} \) | \( 2.625 \) (Å\(^{-1}\)) | \( \beta_{e}^{TB} \) | \( 2.1 \) (Å\(^{-1}\)) |
| \( A_{e}^{LJ} \) | \( 293 \times 10^{-40} \) (Nm\(^7\)) | \( S_{e}^{TB} \) | \( 1.22 \) |

In literature, different values of the elastic constant in the equilibrium position may be found because of the modification in the assumed initial interatomic distance \( R_{0} \). It is discussed in [14]. The elastic constant was applied to find the minimum value of potentials and also some constants for Lennard–Jones potential. In the present analysis it was assumed that only the interactions with the closest neighbors are taken into account. Using the elastic constant in the equilibrium position and the values from Table 2 the changes of the potential, the interatomic force, the elastic constant and Young’s modulus were analyzed. The results are presented in Figs 1–4.

![Figure 1](image1.png)  
**Figure 1.** Interatomic potential \( V(r) \) vs interatomic distance.

![Figure 2](image2.png)  
**Figure 2.** Interatomic force \( F(r) \) vs interatomic distance.

For the equilibrium position of atoms, the potential has the minimum value. The highest value is observed for Tersoff-Brenner potential. An increase in the interatomic distance causes an increase in potential values. The potential value is close to zero when the interatomic distance is a few times greater than the equilibrium position. A decrease in the atomic distance causes an increase in the repulsive force. In the equilibrium position of atoms the interatomic force is equal zero. In this position the transition between the repulsive and attractive forces is observed, and an increase in atomic distance causes an increase in the attractive force. This tendency is mainly visible for Lennard-Jones potential. The changes in the elastic constant and Young’s modulus in the function of atomic distance are very similar. With an increase of the atomic distance a decrease of the elastic constant and Young’s modulus can be seen. These two values remain in the range of positive value. It is visible that presented curves for different potential types have a very similar nature but different values.
5. Conclusions
In the present work, various interatomic potentials used in the nanostructure characterization have been described. To analyze the behavior of carbon nanotubes Morse, Tersoff-Brenner and Lennard-Jones potentials have been chosen and the results for fluctuations of the interatomic potential, interatomic force, elastic constant, and Young’s modulus in the function of interatomic distance have been presented in diagrams. The diagrams have revealed similarities in the shapes of distribution and differences in the values of the analyzed properties. The present analysis may be helpful in the equivalent continuum modeling of carbon nanotubes [17-18] and nanocomposites [19-20].

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