The Study of Atomic Structure and Temperature Effects On Optimization of Carbon Nanotubes' Adhesion Force With Dynamic Molecular Simulation

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**The Study of Atomic Structure and Temperature Effects on Optimization of Carbon
Nanotubes' Adhesion Force with Dynamic Molecular Simulation**

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Abstract

Carbon Nanotubes (CNTs) and their application in biomedical engineering, space robotics, or material development are fast-paced revolutionary fields. The key parameter in defining the strength and failure mechanisms of any CNT is their adhesion force capacity to different substrates. Therefore, it is of high importance to find the optimum geometrical and environmental conditions that can optimize the adhesion force for different types of CNTs. This comprehensive work presents the study of the effects of CNTs' angle, length, diameter, temperature, chirality, and atomic defects on adhesion force. To systematically measure their effect on the adhesion force of CNTs, the single wall nanotube is simulated between two ideal graphene sheets. The simulation results show that the adhesion force increases as the angle, length, and diameter of various CNTs increase. Additionally, the temperature of the nanotubes plays a major role in the adhesion force. Adhesion force is maximized when the temperature is 300 K. Temperature can become a limiting factor on different applications of CNTs due to the atomic resonance and changes of the potential energies in their atoms. This study investigates the effect of chirality on different types of nanotubes. The results present that chirality has a higher effect on armchair-type nanotubes compared to other types. Moreover, the adhesion force of a nanotube with vacancies decreases by increasing the number of lost atoms. Thus, the adhesion force in an ideal nanotube with (11, 9) chirality is 6.14 nN. This is higher by 28%, 35%, 42%, and 53% compared to mono-vacancy, di-vacancy, tri-vacancy, and Stone-Wales defects if these defects are placed in the middle of nanotubes. Although there are extensive studies done in this field, the novelty of our work relies on the fact that different types of CNTs with different types of vacancies (with different locations) for different geometries are studied with the objective of enhancing adhesion force between CNT and graphene sheets.

Keywords:

Carbon nanotube, Graphene, Adhesion Force, Molecular Dynamic Simulation, Atomic Defect, Vacancy Defect, Stone-Wales Defect.

Nomenclature

F_{ij} , intermolecular force on molecule i by molecule j ;

F_{ext} , external applied force;

m , molecule mass;

r_c , cutoff distance;

r_{ij} , position between molecules i and j ;

t , time step;

T , temperature;

V_i , velocity of molecule i ;

N_{atom} , number of atoms;

Greek symbols

ε , energy parameter in Lennard-Jones (LJ) potential;

σ , length parameter of LJ potential;

ϕ , interaction potential;

δ , delta deviation;

1. Introduction

Many organisms in nature have a high adhesion force in their legs to enhance their ability to stick to different objects [1, 2]. Additionally, scientists have discovered that a carbon nanotube array has the adhesive capacity of gecko lizards' feet. One of the ultimate goals of CNT field is to develop bio-inspired systems such as robots based on what is learned from nature and biology. These phenomena in nature have motivated the CNT field to design and study nanotubes with high adhesion forces. The reason for focusing on improving adhesion forces in CNTs relies on the fact that at the tube level, the interface failure between adjacent CNTs is recognized as either peeling, shearing, or a combination of them which are directly related to the adhesion capacity between the nanotube and the substrate under-study. There are both computational and experimental studies that compare the high adhesion forces of CNTs with these organisms [3, 4]. CNTs are a class of nanomaterials that consist of a hexagonal lattice of carbon atoms, bent and bonded in one direction to form a nanotube [5, 6]. Due to their nanostructure and the strength of the bonds between carbon atoms, these nanotubes have exceptional mechanical properties. They also have good chemical stability, promising thermal conductivity, and high electrical conductivity [7, 8]. These properties are expected to be valuable in many areas of technology, such as electronics, optics, composite materials, nanotechnology, and other fields of material science. The previous theoretical and experimental studies are dedicated to the structurally dependent mechanical and thermal properties of CNTs [9-11]. The CNT angle, length, diameter, and chirality have some important effects on the mechanical and thermal properties of these nanotubes [12-15]. In these nanostructures, the reduction of nanotube diameters increased the effective cross-sectional area of CNT, thus improving CNT uniaxial strength [16]. Angle and diameter of nanotubes directly affect the mechanical properties of nanotubes. CNTs' strength, Young's modulus, and other mechanical

properties fluctuate with nanotube angle and diameter changes and do not follow a specific relationship. The type of nanotube is another important factor, especially from the application perspective. In terms of atomic structure, there are three types of nanotubes: armchair, zigzag, and chiral. From a practical point of view, the mechanical properties of each type of carbon nanotube are different [17].

Additionally, structural defects can change the mechanical properties of the CNTs [18-22]. In crystallography, a vacancy is a type of point defect in a crystal structure. A vacancy defect is when an atom is missing from one of the lattice sites. Due to the presence of temperature fluctuations in the environment, vacancy defects occur naturally in all crystalline structures. At any temperature, there is an equilibrium concentration of this defect [3, 23-25]. This type of defect can directly affect CNTs mechanical properties, such as adhesion force [3, 25]. A Stone–Wales defect is another crystallographic defect that involves the change of connectivity of two π -bonded carbon atoms, leading to their rotation by 90° with respect to the midpoint of their bond. From prior works, one can see this type of atomic defect can also affect the mechanical properties of different types of nanotubes. Although there have been extensive studies focused on analyzing these factors on the final quality of the CNTs, the effect of vacancy and Stone-Wales defects on the adhesion force on CNTs is still not fully understood in the field. Therefore, the novelty of this study is focused on investigating the effect of vacancy and Stone-Wales defects and their location on the adhesion force of simulated carbon nanotubes considering all of the above-mentioned parameters.

Adhesion force of ideal/defected CNTs has been scarcely explored by previous research[26-29]. Furthermore, in these studies, the effect of the CNTs' structural properties, such as diameter, chirality, and other atomic parameters of nanotubes on their adhesion force, has not

been completely investigated. In this work, theoretical calculations are performed to calculate the adhesion force of CNTs in various atomic properties and temperatures. The molecular dynamics (MD) method, which is based on Newton's Laws, is a powerful and convenient method for predicting mechanical behavior changes of atomic structures. In recent years, MD simulations have been utilized to study the thermal properties of various materials [30-32] as well as their mechanical and vibrational properties [33-35].

In our study, simulations are performed in two steps. In the first step, the effect of structure and temperature variation on the adhesion behavior of CNTs is investigated. Secondly, the effects of structural defects and their locations (defect location) in CNTs are examined on their adhesion behavior. To follow this procedure, the nanotubes with mono-vacancy, bi-vacancy, tri-vacancy, and Stone-Wales defects at 300 K are considered and then adhesion force for different locations of vacancies are calculated, and finally, the results are compared.

2. Computational Method

This work uses MD simulations to calculate the adhesion force of carbon nanotubes, given the initial conditions for the MD simulation settings (i.e., temperature, angle, dimensions). MD method is a commonly used computational method for tracing the physical translocation of atoms and molecules. In this method, atoms are allowed to interact for a fixed period, giving an insight into the mechanical evolution of the system. In the most common version, the trajectories of atoms are determined by numerically solving Newton's equations of motion for a system of atoms, where forces between the atomics and their potential energies are often computed employing interatomic potentials. The specific software used for this study is Large Scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) package [36-38]. This platform is developed by Sandia National Laboratories (SNL). The computational work for this study includes the following sequential steps:

Step A: Ideal CNTs adhesion force calculation: Ideal CNTs were simulated with various angles, lengths, diameters, chiralities, and temperatures. In this step, two graphene sheets were arranged in a horizontal way, sandwiching the CNT atoms placed in the middle of the box. Figure 1 represents the projection and perspective views of this assembly. In this simulation box, fixed boundary conditions are implemented in x, y, and z directions. Afterward, an external driving force (0.002 eV/angstrom) was exerted on the graphene sheets to push carbon atoms in the CNT structure to deform nanotubes. Finally, the simulation code is responsible for calculating the adhesion force for the given atomic structure. The magnitude of the external force applied to these simulations is set to 0.002 eV/angstrom. According to our MD simulations in this research, for this rate of external forces the carbon nanotube deformation occurs continuously. For this study, graphene wall temperatures are fixed at 298 K, 310 K, 320 K, and 340 K with 1 femtosecond time step and MD simulations run for 1 nano-second [5]. As the system reached equilibrium energy rate, computational running was intentionally kept on to observe deformation of CNT structure.

Step B: Defected CNTs adhesion force calculation: In the second step, atomic defects, such as vacancy and Stone-Wales defects, were introduced in the simulated nanotubes and variation of adhesion forces of these structures are calculated and compared with the ideal CNT represented in Step A.

Figure 1. Schematic of Simulated CNT and Graphene Sheets with LAMMPS: (a) Front, (b) Top, (c) Perspective, and (d) Left view.

The interatomic forces between carbon atoms in CNT or graphene structures (one structure) are accounted for by Tersoff potential. This potential is a three-body potential functional which explicitly includes an angular contribution of the force. The potential is widely used in various applications including silicon, carbon, and germanium. Tersoff potential is written in the following form [39]:

$$E = \sum_{ij} E_{ij} = \sum_i \sum_{j \neq i} V_{ij} \quad (1)$$

$$V_{ij} = f_C(r_{ij})[f_R(r_{ij}) + b_{ij}f_A(r_{ij})] \quad (2)$$

Where the potential energy is decomposed into a site energy E_{ij} and a bonding energy V_{ij} , r_{ij} is the distance between the atoms i and j , f_A and f_R are the attractive and repulsive pair potential respectively, and f_C is a smooth cutoff function.

$$\begin{aligned}
f_R(r_{ij}) &= Ae^{(-\lambda_1 r_{ij})} \\
f_A(r_{ij}) &= -Be^{(-\lambda_2 r_{ij})} \\
f_C(r_{ij}) &= \begin{cases} 1, & r_{ij} < R - D \\ \frac{1}{2} - \frac{1}{2} \sin \left[\frac{\pi}{2} (r_{ij} - R) / D \right], & R - D < r_{ij} < R + D \\ 0, & r_{ij} > R + D \end{cases}
\end{aligned} \tag{3}$$

The main feature of this potential is the presence of the b_{ij} term. The basic definition of this term is known as the strength of each bond which depends on the local environment and is lowered when the number of neighbors is relatively high. This dependence is expressed by b_{ij} , which can amplify or diminish the attractive force relative to the repulsive force, according to the environment, such that:

$$\begin{aligned}
b_{ij} &= \frac{1}{(1 + \beta^n \zeta_{ij}^n)^{2n}} \\
\zeta_{ij} &= \sum_{k \neq i, j} f_C(r_{ij}) g(\theta_{ijk}) e^{\lambda_3^3 (r_{ij} - r_{ik})^3} \\
g(\theta) &= 1 + \frac{c^2}{d^2} - \frac{c^2}{[d^2 + (h - \cos \theta)^2]}
\end{aligned} \tag{4}$$

The term ζ_{ij} defines the effective coordination number of atom i , i.e. the number of nearest neighbors, taking into account the relative distance of two neighbors $r_{ij} - r_{ik}$ and the bond-angle θ . The function $g(\theta)$ has a minimum for $h = \cos \theta$, the parameter d determines how sharp the dependence on the angle is, and c expresses the strength of the angular effect.

The following parameters in Table 1 are reported from previous research[40], which shows a model of interatomic potentials for multicomponent systems, taking $\lambda_3 = 0$.

Table 1. Numerical Values for Simulation Parameters

$A(eV)$	$B(eV)$	$\lambda(^{\circ}A^{-1})$	$\mu(^{\circ}A^{-1})$	β	n	c	d	h	$R(^{\circ}A)$	$S(^{\circ}A)$
1393.	346.7	3.4879	2.2119	1.5724	0.7275	3.8049	4.38	-	1.8	2.1
6				$\times 10^{-7}$	1	$\times 10^4$	4	0.57058		

Furthermore, we use Lennard-Jones (LJ) potential for interactions between graphene and CNT carbon atoms (two different structures). LJ potential function as following formula[41]:

$$\phi(r_{ij}) = 4\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right] \quad r_{ij} \leq r_c \quad (5)$$

Where ϵ is the depth of the potential well, σ is the finite distance at which the inter-particle potential is zero, and r is the distance between the particles. In this equation, *the* cutoff radius is shown with r_c to a maximum of 12 angstroms.

The total potential of the system is derived by adding Tersoff potential and Lennard-Jones (LJ) potential. The molecular dynamics simulation method is based on Newton's second law or the equation of motion, $F = ma$, where F is the force exerted on the particle as the gradient of the potential computed as above, m is its mass and a is its acceleration. From a knowledge of the force on each atom, it is possible to determine the acceleration of each atom in the system. Integration of the equations of motion then yields a trajectory that describes the positions, velocities, and accelerations of the particles as they vary with time. From this trajectory, the average values of properties can be determined. The method is deterministic; once the positions and velocities of each atom are known, the state of the system can be predicted at any time in the future or the past.

$$F_i = -\nabla_i V = m_i a_i = m_i \frac{dv_i}{dt} = m_i \frac{d^2 r_i}{dt^2} \quad (6)$$

Association of previous formulations is done by the velocity-verlet method to integrate Newton's Law as shown in the following equations:

$$\begin{aligned} v(t + \delta t) &= v(t) + a(t)\delta t \\ r(t + \delta t) &= r(t) + v(t)\delta t \end{aligned} \tag{7}$$

In these two equations, $r(t + \delta t)$ and $v(t + \delta t)$ are final position and velocity of atoms (respectively). Additionally, $r(t)$ and $v(t)$ are the initial rate of these mechanical parameters at each time step. The initial positions can be obtained from experimental structures, such as the X-ray crystal structure of the protein or the solution structure determined by Nuclear Magnetic Resonance (NMR) spectroscopy[42].

The initial distribution of velocities are usually determined from a random distribution with the magnitudes conforming to the required temperature and corrected so the net linear momentum (P) is zero:

$$P = \sum_{i=1}^N m_i v_i = 0 \tag{8}$$

The velocities, v_i , are often chosen randomly from a Maxwell-Boltzmann or Gaussian distribution at a given temperature which gives the probability that an atom i has a velocity v_x in the x direction at a temperature T .

$$P(v_{ix}) = \left(\frac{m_i}{2\pi k_B T}\right)^{\frac{1}{2}} \exp\left[-\frac{1}{2} \cdot \frac{m_i v_{ix}^2}{k_B T}\right] \tag{9}$$

The temperature can be calculated from the velocities using the following relationship:

$$T = \frac{1}{3N_{atom}} \sum_{i=1}^N \frac{|P_i|^2}{2m_i} \quad (10)$$

Despite equilibrium energy state at around 10^6 time steps, computational running was carried out until 1 nanosecond to exhibit the evolution of mechanical process and distribution of atoms. A CNT array consists of aligned CNTs, which are usually fabricated and used for practical applications. Thus, the adhesion force of a CNT array can be theoretically calculated as follows:

$$P = F \cdot N \cdot \rho \quad (11)$$

Where F is the adhesion force of the single wall CNT, ρ is the number density of the CNT array, which is 10^{10} cm^{-2} and N is the number of CNTs.

3. Results and Discussions

3.1. CNT Deformation Effect on Adhesion force

In our simulations, a sandwich structure model was implemented in order to calculate CNT adhesion force. Two single sheets of graphene were placed on the top and bottom parts of the simulation box. Both sheets were identical and only differed in their z coordinates. The graphene sheets were large enough to completely cover the simulated nanotube. In the middle of the sandwich model, a CNT lay along the y -axis. In simulations, a lower sheet could serve as the substrate and would be adhered to the CNT. The upper sheet was moved downward to compress the CNT as shown in Figure 2. Our calculations estimate the adhesion force as a function of the CNT deformation for (10,10), (12,0), and (11,9) CNTs with 100 nm length. In these simulations, the degree of deformation and adhesion forces have a direct relationship (shown in Table 2). As

depicted in Figure 3, after the CNT deformation degree exceeds 70%, by $\Delta = (1 - h/D) \times 100\%$ equation, the adhesion force of CNT has a higher rate of growth. This behavior was also reported in previous research done by Liu et al [3]. This research team reported an increase in the adhesion force of armchair CNT with increasing the deformation degree of CNT.

Figure 2. Schematic of CNT deformation as a function of time step: a) 1×10^5 , b) 2×10^5 and c) 3×10^5 time steps.

Figure 3. Adhesion force of CNTs versus deformation percent for (10,10) CNT with 100 nm length. Schematic of CNT and graphene at 20% and 60% deformation has been shown, as well.

Table 2. Adhesion force (nN) values for different CNT deformation degrees (%) for: armchair, zigzag, and chiral nanotubes with 100 nm length

CNT Deformation Degree (%)	Adhesion Force (nN) for Armchair Nanotube (10,10)	Adhesion Force (nN) for Zigzag Nanotube (12,0)	Adhesion Force (nN) for Chiral Nanotube (11,9)
20	0.13	0.08	0.10
40	0.15	0.09	0.11
60	0.31	0.17	0.23
80	10.83	6.47	8.84

3.2. CNT Angle Effect on Adhesion force

In this section, the adhesion force between CNT and the graphene sheets for different angles of CNTs was reported. To investigate the relationship between the adhesion force and the nanotube angles, five CNT samples are considered. These nanotubes chirality with 10 nm length and 2 nm diameter are (25,3), (23,6), (19,11), (17,13) and (15,15). From the following equation, the angle of CNTs can be found:

$$\theta = \sin^{-1} \frac{\sqrt{3}m}{2\sqrt{n^2+nm+m^2}} \quad (12)$$

These nanotubes angles are 6, 11, 21, 26, and 30 degrees, respectively. As shown in Figure 4 the adhesion force increases as the nanotube angle increases. When the distance between the CNT and the graphene substrate is slightly less than the cutoff distance, the C atoms on the bottom of the CNT are subject to a repulsive force generated by the graphene sheet. Furthermore, by increasing the angle of the nanotube, the side area of the atomic structure increases so there will be more

carbon atoms in the nanotube which will cause more adhesion force. As the number of carbon atoms in the nanotube increases, the amount of potential energy increases with a negative sign (based on Equations 1 and 2). Finally, improving this physical quantity will increase the adhesion force of CNTs as reported in Table 3.

Figure 4. Adhesion force versus CNTs angles

Table 3. adhesion force values for different CNTs angles with 10 nm length and 2 nm diameter

CNT Chirality(m,n)	(25,3)	(23,6)	(19,11)	(17,13)	(15,15)
Diameter (nm)	2.085	2.075	2.057	2.04	2.034
Length (nm)	10	10	10	10	10
CNT angle (degree)	6	11	21	26	30

Adhesion force (Nn)	4.33	5.54	6.35	7.72	8.91

3.3. CNT Chirality, Diameter and Length Effects on Adhesion Forces

The types of CNTs are characterized by chirality numbers (n,m). A zigzag carbon nanotube is of the form (n,0) and an armchair nanotube is one of the forms (n, n). All other carbon nanotubes are called chiral nanotubes. Moreover, for the chiral vector (n, m) the diameter of a CNT can be determined using the following formula:

$$d = (n^2 + m^2 + nm)^{0.5} \times 0.0783 \text{ nm} \quad (13)$$

In this simulation, twenty one (21) nanotubes with 10 nm length and different chirality were simulated. The diameter of these nanotubes was defined based on equation (13).

Table 4. Adhesion force as a function of CNT diameter for various type of CNT (chirality).

CNT TYPE	CNT Chirality	Diameter (nm)	Length(nm)	Adhesion Force (nN)
Armchair	(4,4)	0.5426	10	3.51
	(5,5)	0.6783	10	3.94
	(6,6)	0.814	10	4.86
	(7,7)	0.9496	10	5.16
	(8,8)	1.085	10	5.50

	(9,9)	1.221	10	6.02
	(10,10)	1.3566	10	6.33
Zigzag	(7,0)	0.5481	10	3.03
	(8,0)	0.6264	10	3.47
	(9,0)	0.7047	10	3.88
	(10,0)	0.783	10	4.01
	(11,0)	0.8616	10	4.24
	(12,0)	0.9399	10	4.76
	(13,0)	1.0179	10	5.02
Chiral	(4,3)	0.476	10	3.21
	(5,4)	0.6117	10	3.82
	(6,5)	0.7472	10	4.04
	(7,6)	0.8827	10	4.16
	(8,7)	1.018	10	5.23
	(9,8)	1.1538	10	5.61
	(10,9)	1.2894	10	5.98

Figure 5. Adhesion force versus diameters for different types of CNT (Armchair, Zigzag, and Chiral) with 10 nm length.

As depicted in Figure. 5, the adhesion force of the CNTs in each category increases with a larger nanotube diameter. This behavior of the nanotubes is due to the increase in the number of carbon atoms, so that as the number of atoms increases, the simulated system energy increases, and the number of atoms interacting with graphene sheets increase (due to increasing in the nanotube's diameter) hence; higher adhesion force measured. Additionally, Figure 5 shows that the maximum adhesion force is observed for armchair and then chiral and the minimum is related to zigzag type. Finally, Figure 5 also represents that the armchair type has a higher slope; therefore, the diameter of CNT has a higher effect on this type compared to chiral and zigzag types.

In the longitudinal direction of nanotubes, such behavior is also expected. By increasing the length of CNTs the adhesion force in the simulated atomic structure will be enhanced. To investigate this issue, we simulated various nanotubes with different lengths ranging from 2 nm to 10 nm (by 2 nm interval). Table 5 and Figure 6 show that the maximum adhesion force belongs to CNT with a 10 nm length and the minimum adhesion force belongs to a nanotube with 2 nm, respectively. In this figure, the maximum adhesion force is related to armchair and then chiral and the minimum is related to zigzag as the behavior that CNTs show for different diameters.

Table 5. Adhesion force as a function of CNT length for various type of CNT (chirality).

CNT TYPE and Chirality	Diameter (nm)	Length(nm)	Adhesion Force (nN)
Armchair (7,7)	0.9496	2	2.31
		4	3.55
		6	3.98
		8	4.34
		10	5.16
Zigzag(12,0)	0.9399	2	1.98
		4	3.01
		6	3.34
		8	3.95

		10	4.76
Chiral(8,6)	0.9529	2	3.21
		4	3.82
		6	4.04
		8	4.16
		10	5.23

Figure 6. Adhesion force versus length for different types of CNT (Armchair, Zigzag, Chiral) with 0.9 nm diameter.

3.4. Temperature effect on Adhesion force

In the next step, the adhesion force of CNT with 10 nm length and diameter ranging from 1.33 to 1.35 nm, temperature range from 100 K to 500 K was studied. Figure 7 clearly shows that the adhesion force of CNTs fluctuates with increasing temperature and reaches its maximum value at 300 K. This adhesion feature makes CNTs suitable for use at room temperature and unsuitable for some application such as high-temperature rubber. Nevertheless, the adhesion force rapidly drops while the temperature continues to increase from 300 K to 500 K. In our simulated nanotubes, as the temperature increases from 100 K, carbon atoms come close to the graphene sheet and so the adhesion force increases. Furthermore, by increasing the temperature from 300 K to 500 K, carbon atoms on the bottom of the CNT tend to vibrate by a significant amplitude and so the distance between CNT atoms and graphene sheet is farther than that at 300 K, to keep their energy at the minimum. Therefore the distance becomes larger and the adhesion force decreases, respectively. This CNT configuration has been reported in previous studies and can be considered as a criterion of the correctness of the interatomic potential used in simulations and the path traversed during the study [3]. In Liu et al.'s work, the temperature of nanotubes increases from 100 K to 400 K (by 20 K temperature interval). The adhesion force of the armchair nanotube increases as the temperature changes from 100 K to 300 K and then decreases from 300 K to 400 K. In our research, three different types of CNTs (Armchair, Zigzag, and Chiral) have been considered, and as Figure 7 shows, adhesion forces reach the peak at 300 K and then decrease from 300 K to 500 K in all of them. Furthermore, as we can see again the adhesion forces for armchair are higher than chiral and zigzag.

Table 6. Adhesion force as a function of Temperature for various type of CNT (chirality).

CNT TYPE and Chirality	Diameter (nm)	Temperature (K)	Adhesion Force (nN)
Armchair(10,10)	1.35	100	2.31
		200	3.55
		300	3.98
		400	4.34
		500	5.16
Zigzag(17,0)	1.35	100	5.06
		200	5.37
		300	5.98
		400	4.87
		500	4.19
Chiral(11,9)	1.33	100	5.58
		200	5.66
		300	6.14
		400	5.04

		500	4.99

Figure 7. Adhesion force versus Temperature for different types of CNT (Armchair, Zigzag, and Chiral) with 1.35 nm diameter and length 10 nm.

3.5. CNT Atomic Defect

In atomic structures, defects such as vacancy and Stone-Wales defects are common phenomena[19, 20]. In this work, the effect of mono-vacancies, di-vacancies, tri-vacancies, and Stone-Wales defects on the adhesion force of CNTs is studied. Figure 8 represents mono-vacancies, di-vacancies, and tri-vacancies results from the removal of one, two, and three atoms from the initial atomic structure (Zigzag nanotube (11,9)) with 10 nm length at 300 K. A Stone–Wales defect is a crystallographic defect that involves the change of connectivity of two π -bonded carbon atoms, leading to their rotation by 90° with respect to the midpoint of their bond (Figure 8d). In CNT structure, Stone-Wales defect will lead to the formation of two heptagons and two pentagons, which replaces the original four hexagons surrounding them[21]. Table 7 shows that the adhesion force decreases as the number of lost atoms increases from 1 to 3 atoms (mono-vacancies, di-vacancies, tri-vacancies). Between different nanotubes, the ideal nanotube has

maximum adhesion force (6.14 nN) and CNTs with Stone-Wales defect have the minimum adhesion force. CNT with

Figure 8. Schematic cross-section of CNTs with different defects. (a), (b), (c), and (d) correspond to mono-vacancy, di-vacancy, tri-vacancy, and Stone-Wales defects, respectively.

mono-vacancy defects have the maximum rate of adhesion force between defected nanotubes. This phenomenon occurs due to a change in the atomic positions and bond orientation which causes a decrease in the amount of atomic potential energy. Furthermore, we implemented the atomic defects on different coordinates of nanotubes and calculate the effect of defect position on the adhesive force of CNTs. For this purpose, the location of the atomic defects applied to the five positions of nanotubes is shown in Figure 9. The molecular dynamics results show that, the minimum rate of adhesion force occurs when the atomic defect is implemented in the middle of the nanotube. Additionally, when the defect positions in CNT are symmetrical, the amount of

adhesion force also is approximately equal. This behavior occurs because of the symmetry in the arrangement of atoms. The energy of the simulated system is proportional to the position of carbon atoms which results in the non-uniformity of the adhesion force in studied structures.

Figure 9. Various permitted positions for different atomic defects (vacancy and Stone-Wales defects) in carbon nanotubes.

Table 7. Effect of vacancy location on adhesion force for zigzag CNT at 300K

CNT TYPE and Chirality	Defect type	$x = 0$	$x = 1/4$	$x = 1/2$	$x = 3/4$	$x = 1$
Zigzag nanotube (11,9) with 10 nm length and diameter 1.33 nm at 300 K	Mono-vacancy	4.57	5.02	4.41	5.01	4.55
	Di-vacancy	4.05	4.34	3.98	4.35	4.01
	Tri-vacancy	3.57	3.61	3.54	3.60	3.57
	Stone-Walls	2.92	2.99	2.87	3.01	2.94

	Ideal Nanotube-No defect	6.14

Conclusion:

Carbon Nanotubes (CNTs) field is a fast-growing one that can enhance scientific and industrial capabilities in designing and fabrication complex systems. Due to the advantages of CNTs, many studies have focused on optimizing adhesion force for different geometries of certain types of CNTs. However, there is no study that has considered all different combinations of parameters and studied their effect on adhesion force. This comprehensive study is focused on studying the effect of diameter, length, temperature, chirality, different types of CNTs, and different types of vacancies at different locations are studied. In this study, the dynamic molecular simulation was implemented to investigate different configurations for sandwiched carbon nanotubes by graphene sheets. All the simulations were performed at a temperature of 300 K as an initial condition.

In this work, it is shown that by increasing the CNT's angle, the interaction between the carbon atoms located in the nanotube and the graphene sheet increases. Therefore, higher CNT angles can provide higher adhesion forces between the two atomic structures calculated at room temperature. The second parameter under study was the diameter of the carbon nanotubes. It is found that there is a direct correlation between the diameter of CNT and their adhesion forces. As the diameter increases, the adhesion force increase and vice versa. This atomic behavior is due to the increased

cross-sectional area between the CNTs and the graphene sheets. Based on this assumption, the higher number of carbon atoms from the CNT interact with the sheets, hence, the higher adhesion force is observed. The third factor under study is the length of CNT. By increasing the length of the nanotube, the amount of potential energy and adhesion force is increased. Therefore, it is found that the angle, diameter, and length of CNT all have a direct correlation with the adhesion force. As above mentioned, all the simulation was done at room temperature (300 K). The temperature factor was also studied. It is found that by increasing temperature based on Boltzman's theory, the vibrations of atoms increase. It is found for values of temperature lower than 300K, the adhesion force is decreasing. For temperatures above 300 K, the adhesion force also decreases. Therefore, the highest (optimum) adhesion force was observed at 300 K. This can be a useful insight in designing systems that have environmentally abnormal conditions. It should be mentioned that all the above studies were done with ideally perfect CNTs. However, it is known that CNTs are prone to defects. An additional set of simulations are done by introducing systematic vacancy defects in CNTs. It is found that the minimum adhesion force is related to Stone-Wales defects. The location of vacancy is also studied and found that a vacancy at the middle of CNT can lower adhesion forces drastically.

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Availability of data and material: Derived data supporting the findings of this study are available from the corresponding author on request.

Code availability: N/A

Authors' contributions: Vahid Molaei: Conceptualization, Data collection, Software, Data analysis, and interpretation.

Dr. Mehrnoosh Damircheli as the corresponding author: Conception or design of the work, Supervision; Validation; Visualization; Roles/Writing - original draft; Writing – review, Critical revision of the article,& final approval of the version to be published.

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