

First-Principles Molecular Dynamics Study on Helium- filled Carbon Nanotube

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Abstract. Investigation on carbon nanotube (CNT) filled by Helium (He) atoms is conducted using Density Functional Theory and Molecular Dynamics Simulation. It reveals that He atom is repelled by CNT's wall and find its stable position at the tube center. Vibrational analysis on modes correspond to radial inward and outward breathing movement of CNT shows that He filling tends to pull the CNT wall in inward direction. Furthermore, examination on C-C stretch mode reveals that the existence of He improve the stiffness of CNT's wall. Molecular dynamics calculations which are done on (3,3) and (5,5) nanotube with 0.25 gr/cm³ and 0.5 gr/cm³ He density at 300 K and 1500 K confirms the increase of stiffness of CNT wall by interaction with He atoms. Effects of variation of chirality, temperature and He density on CNT wall stiffness is also reported.

1. Introduction

There is a growing interest in these past few years on the effect of gas filling on carbon nanotubes (CNT) [1- 4]. The knowledge is relevant to various technological applications utilizing CNT such as heat transport on nano channel and sound absorption, to mention a few. These examples have a similarity that they can be explained by the movement of particles, either in form of vibration, diffusions or collisions.

It has been demonstrated that thermal gradient could drive nanometer size particles through CNT[5]. This is followed by computational studies that helps reveals the inherent relationship between heat and mass transport in CNT [6]. It would lead to further understanding on manipulation of nanoparticles by heat.

It was found that absorber material consisting of CNT and polymer composite shows some improvement on its sound absorbing performance [7]. This finding suggests some speculations with regard to the underlying mechanism. It has been speculated that CNT contributes by increasing the stiffness of the composite. However, another possibility for the mechanism is related to the trapping of gas particles from air inside the CNT. The situation is expected to alter the chemical and physical properties that lead to the improvement of acoustical characteristic of the system.



Some computational investigations have been conducted previously to study the behavior of gas particles inside nanotubes. Some works based classical molecular dynamics where effects of temperature and gas density on CNT mechanical properties were reported [6,8].

All of the aforementioned applications relies on phenomena that can be described by collective movements of atoms in CNT. Thus, it calls for a detail study in microscopic level related to particles interaction inside the nanotube, whether among themselves or with the CNT walls. In nano scale, additional effects related to quantum confinement as the gas particles trapped in such narrow space must also be considered. The wave function of gas atoms must feel the presence of the CNT's wall and vice versa. This feature is not available on previous classical simulation where quantum effect is not included. Therefore, a more detail investigation on atomic scale based on quantum simulation is needed.

In this paper, we present computational and simulation study on Helium (He) filled CNT based on first- principles density functional study (DFT) and Born-Oppenheimer Molecular Dynamics (BOMD). We aim to obtain an understanding on the behavior of He gas inside CNT and its effect on the surrounding wall.

2. Models and Methods

First-principles based calculations are done to study the system consisting of CNT filled with He atoms. Density Functional Theory (DFT) [9] is used in Kohn-Sham formulation [10] with plane-wave basis sets, implemented using Quantum Espresso package [11]. Perdew-Burke-Ernzerhoff(PBE) functional [12,13] is used to express the exchange -correlation functional within Generalized Gradient Approximation (GGA). Ion cores are represented by using Martin-Troullier norm-conserving pseudopotential [14]. Cut-off energy is taken at 40 Ry while brillouin-zone integration is done at $1 \times 1 \times 5$ Monkhorst-Pack grid [15]. In this simulation, armchair CNT of (3,3) and (5,5) chirality filled with He atoms are modeled. Periodic boundary condition is applied at the direction of CNT axis. Depending on the size and number of He atom, calculations done in this work can be categorized into three types:

Structural optimization is done using one unit cell of (3,3) CNT and one He atom. The purpose of this calculation is to find the equilibrium position for the He atom inside the CNT and its interaction with the CNT's wall. Dispersion correction is included to include weak Van der Waals force between CNT's wall and He atoms.

Vibrational frequency calculations are done using Perturbation Density Functional Theory (PDFT) [16] on the optimized structure to obtain vibration modes and their frequency. Vibrational calculation is calculated for gamma-point.

Dynamic calculations using Born-Oppenheimer Molecular Dynamics (BOMD) are done to study the dynamics of He filled CNT. (3,3) and (5,5) CNT are used filled with He atoms whose amount is chosen such as it simulate the desired density of 0.25 gr/cm^3 and 0.5 gr/cm^3 . The simulations are conducted at constant temperature NVT ensemble) at 300 K and 1500 K for each system. Temperatures are kept throughout the simulation by using Andersen thermostat. Simulations are run for 0.5 – 1 ps with 1 fs timestep.

3. Results and Discussions

Optimization calculation is needed to obtain the equilibrium position of He atom inside the (3,3) CNT. Initial structure prior to optimization is shown in figure 1a. It can be seen that we started by assuming the He atom to stick to the CNT's wall. This is important since we need to know whether some there is a chemical type of interaction between He and the CNT.

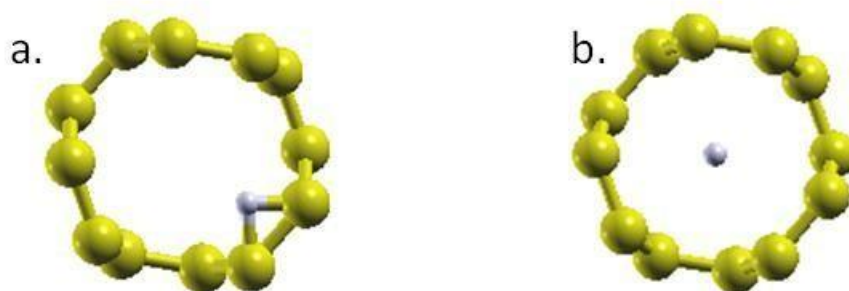


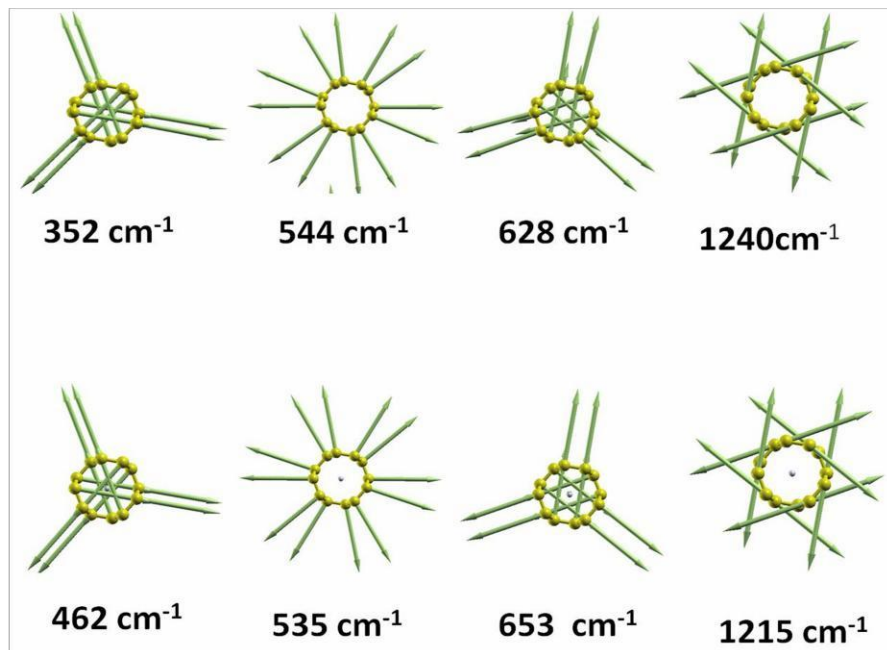
Figure 1. a) Initial configuration of (3,3) CNT with one He atom b) Final configuration of (3,3) CNT with one He atom

The final configuration after the optimization can be seen in figure 1b. It is clear that He atom tends to avoid the wall and prefers to stay in the middle of the tube. Therefore, there is no significant chemical bonding between He and the wall. Moreover, it was observed during the optimization course that the sticking of He tends to disrupt the C – C coordination at the walls which is clearly energetically unfavorable. This results in He atoms to be pushed against the nanotube wall. It must be noted that weak Van der Waals interaction has been included in the calculation. Therefore, it can be predicted that He atom interaction with CNT's wall is a long-range type and He preserves its noble gas characteristic. This long-range interaction means that CNT's wall is still able to sense the existence of the He atom as reflected by slight elongation of its C – C bond from 1.43 to 1.46 Å in average, prior and after of optimization respectively.

Effects of He on CNT's wall can be further examined by investigating the frequency of vibration modes. Out of obtained vibrational modes, we selected several vibration modes that correspond with the movement that represents the radial breathing and C – C stretch of the empty and He filled CNT. These vibrational modes are shown in figure 2

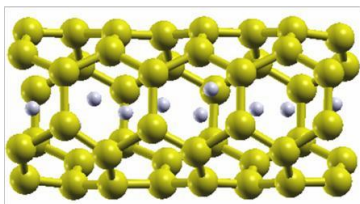
By comparing the magnitude of frequency of mode in empty CNT with the corresponding ones in He-filled CNT, certain tendencies can be identified. One can see that there is a tendency of frequency increment upon CNT filling for modes that corresponds to inward movement or CNT compression. An opposite tendency can be found for the outward radial movement. This result can be regarded as a sign that the existence of He atom inside the CNT tends to pull its surrounding structure inward, or in other words, He atoms tend to preserve the radial structure of the surrounding CNT walls.

Inward radial Outward radial Inward radial C-C stretch

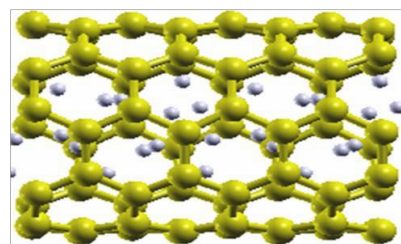
**Figure 2.** Selected vibrational modes of (3,3) CNT with one He atom.

Another similar conclusion can be drawn from the tangential movement of C atoms as can be seen on the mode with C – C stretch movement. In this case, the filling of He induces frequency decrement that can be taken as a sign of increment on stiffness of the C – C bond. Thus, it can be inferred that the effects of He atom is the preservation of CNT structure that may correspond to a stiffer CNT structure.

a.



b.

**Figure 3.** a) He filled (3,3) nanotube b) He filled (5,5) nanotube

To further understand the effect of He filling on CNT, we must extend our investigation by including more atom He and taking the system to higher temperature. To achieve this we employ Born-Oppenheimer Molecular Dynamics calculation (BOMD) on He-filled CNT with variation on chirality, He-atoms density and temperature. The systems are depicted in figure 3 for (3,3) and (5,5) CNT respectively.

figure 4a. shows the plot of the magnitude of forces on each of selected four C atoms of (3,3) CNT during BOMD running of around 400 timesteps or equal to 0.4 ps at 300 K. The He atoms filling is at

density of 0.25 gr/cm^3 . The fluctuation of the forces reflects the vibration of the C atoms about their equilibrium positions. If the density is increased to 0.5 gr/cm^3 , we could see that the force fluctuation is reduced (figure 4b). It appears that the increment of density at room temperature (300 K) tends to make CNT stiffer and becoming more difficult to vibrate. This is inline with previous conclusion from the vibrational analysis.

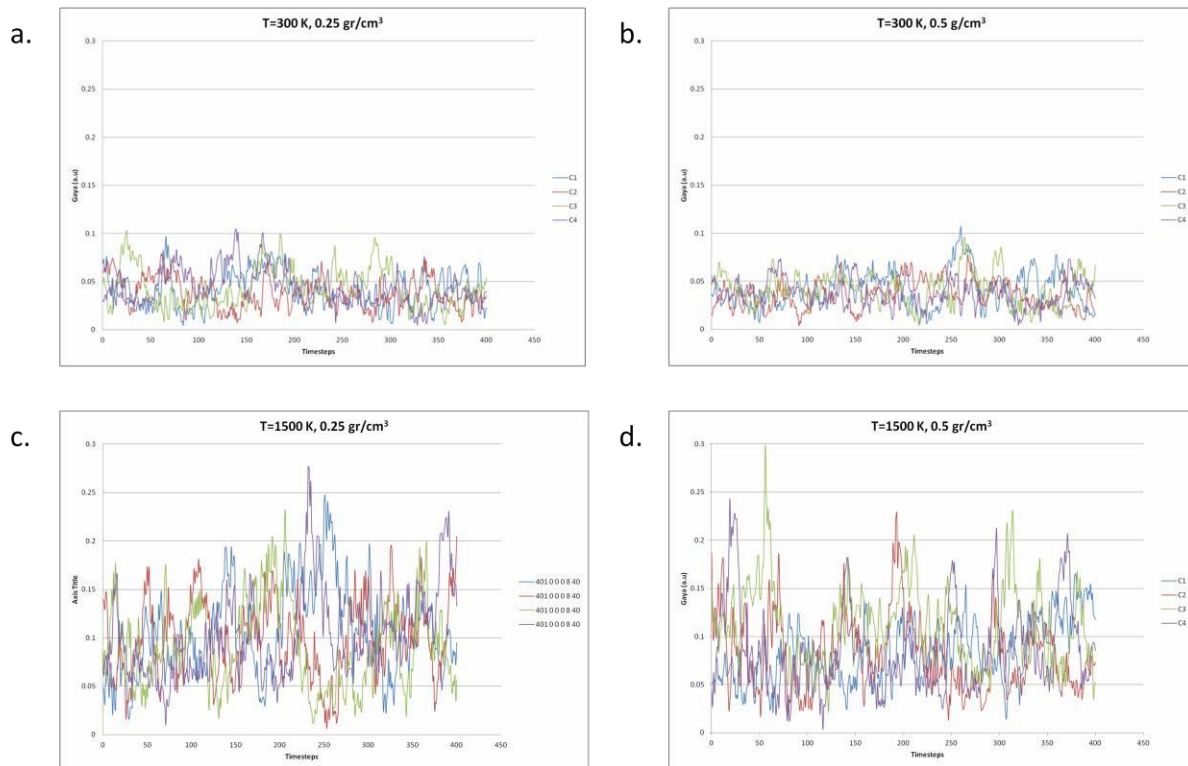


Figure 4. Plot of force magnitude versus time steps on selected four C atoms on He-filled (3,3) nanotube at a) 0.25 gr/cm^3 $T=300 \text{ K}$ b) 0.5 gr/cm^3 $T=300 \text{ K}$ c) 0.25 gr/cm^3 $T=1500 \text{ K}$ d) 0.5 gr/cm^3 $T=1500 \text{ K}$

However, at 1500 K, comparison between system with 0.25 gr/cm^3 (figure 4c) and 0.5 gr/cm^3 (figure 4d) shows no significant different on force fluctuation. It means that higher temperature could remove the effect of He on CNT.

The effect of CNT must also be taken into account. This is the main motivation to conduct BOMD simulation on (5,5) CNT. Fig 5a. shows plot of force fluctuation on four selected C atoms of (5,5) CNT at 0.25 gr/cm^3 and 300 K. By comparing it with force profile at 0.5 gr/cm^3 and at same temperature (figure 5b), we could immediately realize that unlike in (3,3) CNT, the increment of density seems to be has no effect on forces on C atoms. It may be caused by the lesser interaction between C and He atoms due to larger diameter of the (5,5) CNT.

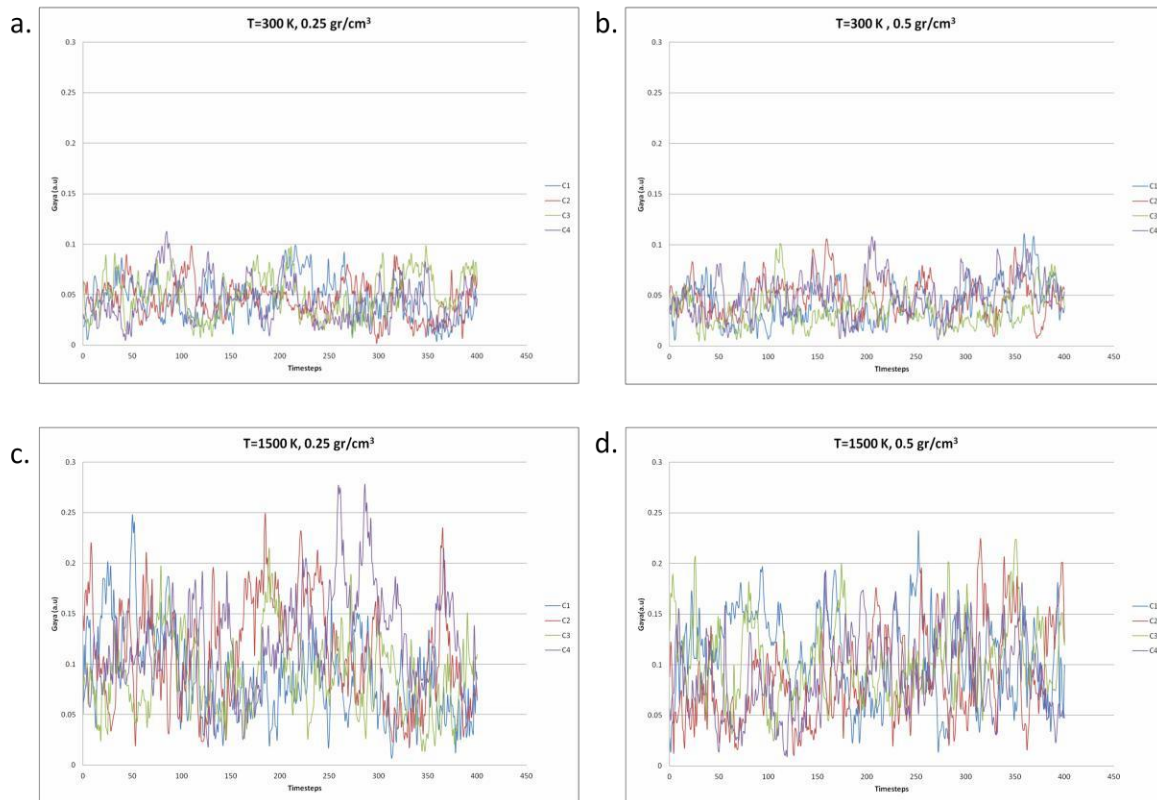


Figure 5. Plot of force magnitude versus timesteps on selected four C atoms on He-filled (5,5) nanotube at a) 0.25 gr/cm^3 $T=300 \text{ K}$ b) 0.5 gr/cm^3 $T=300 \text{ K}$ c) 0.25 gr/cm^3 $T=1500 \text{ K}$ d) 0.5 gr/cm^3 $T=1500 \text{ K}$

Interesting results are found at 1500 K, where the increment of density from 0.25 gr/cm^3 to 0.5 gr/cm^3 results in weaker force fluctuation. Thus, the effect of He on (5,5) CNT seems to work in opposite way than on (3,3) CNT. In this case, higher temperature may activate the interaction between C and He resulting in a stiffer CNT structure.

All these findings suggest that the performance of CNT as sound absorber may depends on the dimension of CNT, temperature and air density. However, depending on the mentioned parameters, the stiffness of CNT could be changing from one condition to others.

4. Conclusions

Investigations on He-filled CNT have been conducted using first-principles Density Functional Theory (DFT) and Born Oppenheimer Molecular Dynamics (BOMD). He atom is found to be repelled by CNT's wall and tend to find its equilibrium position at the center of CNT. Vibrational analysis reveals that He tends to preserve the CNT structural and improve its stiffness. This result is further confirmed by BOMD investigation that reveals the increment on CNT stiffness at higher He density. However, at higher temperature, the effect of He seems to be diminished.

Larger diameter of the CNT may put limit on the interaction of He with the CNT's walls. As a result, increasing the He density for this case does not change the CNT stiffness. Nevertheless, higher temperature could turn on the interaction and as in the case of smaller CNT, the increment of density backs to correlate with the increasing in CNT stiffness.

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